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DEPARTMENT OF MATERIALS ENGINEERIG

EFFECT OF ORE TYPE ON THE LEACHING AND BIOSORPTION CHARACTERISTICS OF LEAD FROM WASTE CUPELS USING SPENT TEA LEAVES (CAMELLIA SINENSIS)

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CERTIFICATION

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

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DEDICATION

Dedicated to my beloved mum (Beatrice Nyumutsu), Mr. Daniel Wenyah, Mr. Marvin Korli, and the entire family not forgetting Dr. Kofi Abban, and Dr. Kwadwo Nyantakyi Adu-Darko as well as all friends for their inspirations and support.

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ABSTRACT

Waste cupel samples from two commercial gold fire assay laboratories in Ghana were sampled and characterized. The selection of the fire assay laboratories was based on the type of ore being processed. Comparative study of the effect of ore type (oxide and sulphide) on the leaching and biosorption characteristics of lead from waste cupels using spent tea leaves (*Camellia sinensis*) was investigated. Both laboratories use magnesia (MgO) cupels. Waste cupel samples were collected, pulverised and characterized prior to acid digestion. The mineralogical and chemical compositions were determined using X-ray Diffraction and Inductively Coupled Plasma Optical Emission Spectroscopy / Mass Spectroscopy, respectively. Leachates from the waste cupels were contacted with spent tea leaves and the biosorption efficiency and specific metal uptake determined. Results show that lead concentrations in waste cupels from oxide ore (CWO) increased as particle sizes increased whilst lead concentration from sulphide ore (CWS) decreased with increased particle sizes. The biosorption efficiency of lead was higher in CWO leachate (> 99 %) than in CWS leachate (< 98 %). For a given biomass concentration, CWO recorded a higher specific metal uptake as compared to CWS. The specific metal uptake in both samples were affected by the volume of leachate and lead concentration in leachate. In both samples, the adsorption isotherms fitted well in Langmuir model. The results from this study indicate that spent tea leaves can be used as an adsorbent to render waste cupels non-toxic before disposal.

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CHAPTER ONE

INTRODUCTION

1.1 Background

Mining companies process high tonnages of mixed ores from different sections of the concession daily. In order to account for the total amount of precious minerals processed, various methods are used to determine the grade of ores obtained. Pb-fire assay method (in which the main reagent is lead in flux) is the most widely used method for gold analysis in geological materials due to its accuracy and precision (Cerceau et al., 2016). This method allows accurate determination of gold contents in ores, even when the gold content is in very minute concentrations. The first stage of this process is crucible fusion which involves mixing the ore sample with assay reagents such as fluxes, oxidizing and reducing agents and firing at elevated temperature (~1100 ^{o}C) to produce lead button and slag. This stage is followed by cupellation in which lead button is placed in a cupel, heated to about 950 ^{o}C to oxidize the lead and subsequently absorbed into the pores of the cupel. This leaves a metallic gold with a small amount of silver as a tiny bead at the bottom of the receptacle. The silver-gold alloy is then digested in an acid and the gold concentration determined using Atomic Absorption Spectrometer.

Cupellation leads to the cupel becoming highly contaminated with lead. It is estimated that 135 tonnes of lead waste resulting from Pb-FA are generated annually in Brazil. (Cerceau et al., 2016). This is because the used cupel is replaced after each cycle to prevent contamination and also for effective absorption of lead. Thus the lead contaminated cupels, which have the potential to pose serious risk to humans and the environment, cannot be disposed indiscriminately into the environment.

1.2 Problem Statement

It has been reported that tonnes of wastes containing lead are generated annually from fire assay analysis. In Brazil, 1.5 million Pb-FA tests are performed every year which produces about 330 tonnes of lead-contaminated waste (Magalhães et al., 2012).

The amount of waste cupels generated annually in Ghana has not been reported. However, it is estimated that about 32,000 waste cupels are produced monthly in eight known commercial fire assay laboratories in Ghana upon personal communication with one assay laboratory manager. This translates to about 384,000 waste cupels being generated annually. A study conducted by Martin-Torres et al. in 2008 showed that 56 wt % of some used cupels contain lead oxide and 0.7 wt % contains copper oxide.

Thus averagely 13.4 metric tonnes of lead oxide are generated from cupellation process annually in Ghana and it is unclear how the waste cupels are managed and treated. A study by Magalhães et al. (2012) revealed that lead in waste cupel leachates far exceed maximum allowable limits and thus can be classified as highly toxic.Waste cupels therefore, have the potential to pose serious risk to humans and the environment, and hence cannot be disposed indiscriminately into the environment. For instance, improper disposal of lead based paint has been linked to diseases such as brain and nervous damage, high blood pressure and reproductive problems (Wadanambi et al., 2008). That notwithstanding, lead has many uses which include radiation shielding in medical analysis, video display equipment, as additive in gasoline, paint and other protective coatings, in the formulation of lead based flux for lead-fire assay analysis among others (Cerceau et al., 2016; Magalhães et al., 2012). Therefore, successful extraction of the lead would be beneficial for industrial use.

Efforts have been made to render cupels contaminated with lead non-hazardous by leaching with different solvents followed by chemical precipitation. For instance, the leaching characteristics of lead in waste crucibles using hydrochloric and nitric acids followed by chemical precipitation has been reported (Magalhães et al., 2012). The hazardous waste cupels were rendered non-toxic by the removal of lead through extraction. In another work, a method of leaching lead from cupel waste which allowed removal of about 96 % of PbO by weight was reported (Cerceau et al., 2016). The cupel residue consisted of periclase (MgO), litharge (PbO) and massicot (PbO). It is envisaged that the mineralogical associations could affect the leaching characteristics of lead from waste cupels.

Recently, search on the use of low-cost adsorbents for the removal of heavy metal ions including lead have been reported (Zuorro and Lavecchia, 2010; Yang and Cui 2013; Gisi et al., 2016). One of such adsorbents is spent tea leaves (*Camellia sinensis*). Tea leaves are used widely due to its beneficial effects on health, such as antioxidant, anticarcinogenic, antimicrobial activities (Khan and Mukhtar, 2008). After usage, the spent tea leaves are usually disposed of as waste. Spent tea leaves are composed of cellulose, hemicelluloses, lignin, condensed tannins and structural proteins (Yang and Cui, 2013). The characteristics of the compositions are such that, spent tea leaves have high affinity for metals since they contain active functional groups for adsorption of metal ions (Brown et al., 2000). The use of spent tea leaves as adsorbent for lead (II) in waste water has been reported (Ahluwalia and Goyal, 2005). Additionally, comparative study of the use of spent leaves of green and black tea has been investigated (Zuorro and Lavecchia, 2010). Both green and black tea proved to be very good adsorbent for the removal of lead. In another study, spent tea leave was alkali treated and used as adsorbent for the removal of lead (II) from aqueous solution (Yang and Cui, 2013). The treated spent tea leaves improved the adsorption of lead as compared to green and yellow tea.

Gold deposits in Ghana can be classified mainly into two; oxide and sulphide ores. There is limited information, if any, on the comparative study of the effect of ore type on the leaching and biosorption characteristics of lead from waste cupels. Effect of Ore Type on the Leaching and Biosorption Characteristics of Lead from Waste Cupels Using Spent Tea Leaves (Camellia sinensis), therefore seeks to characterise waste cupels from two fire assay laboratories in Ghana handling two different ore types and compare their leaching and biosorption properties using spent tea leaves as an adsorbent.

1.3 Aim and Objectives

The aim of the study is to characterise and compare two different waste cupel streams from two commercial fire assay laboratories in Ghana and assess their leaching and biosorption behaviour using spent tea leaves as an adsorbent.

The specific objectives include;

1. Determination of the chemical and mineralogical characterisation of waste cupels.
2. Granulochemical analysis of the waste cupels.
3. Determination of the biosorption efficiency of lead leachates using spent tea bags.

1.4 Justification

Lead is a heavy metal which is very toxic and poses health problems to living things especially man. To render the waste less toxic to humans and the environment, there is the need to reduce the lead concentration in the waste to tolerable limits. This could be achieved through leaching and subsequent precipitation of the lead oxide. The leaching characteristics also depend on the mineralogical associations of lead oxide in the waste cupels. Therefore, the project seeks to determine the chemical and mineralogical compositions of waste cupels from two different laboratories handling two different ore types – oxide and sulphide ores, respectively. Assay laboratories use different reagents to assay different types of ores and in various quantities. This will give an insight into the chemistry of the compounds formed and methods of treatment before disposal. Thus it is important that different ores are selected and their leaching and biosorption efficiencies determined. Conclusion(s) drawn from the study will assist in the proper disposal methods for the waste from the two ore streams.

1.5 Scope of the Study

This study was limited to waste cupels that were used in cupellation of free milling gold ore and sulphide gold ores. Thus, waste cupels were collected from two different assay laboratories in Ghana that analyse oxide ores and sulphide ores, respectively. The study also used spent yellow label tea bags to adsorb lead from cupel waste leachates. Leaching and biosorption efficiencies for the two waste streams were determined, and the results analysed and discussed.

1.6 Structure of thesis

The thesis consists of five (5) chapters.

Chapter one discusses the Introduction and Background of the study carried out, Chapter two touches on the Literature Review, Chapter three dwells on Methodology, the fourth chapter discusses the Results obtained from the study and the final chapter, Chapter five provides Conclusions and Recommendations of the study.

CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

This chapter reviews the various laboratory processes that lead to the generation of waste cupels. Specifically, fire assay processes, types of cupels, manufacturing of cupels, possible contaminants in cupel, as well as its effects on the environment are reviewed. Finally, available disposal methods of waste cupels and possible recovery techniques are assessed.

2.2 Assaying

Assaying is a branch of analytical chemistry that deals with the quantitative estimation of metals in ores, furnace products, coins etc. This is accomplished by fire and reagents in most cases. Assaying is chiefly employed in mining and metallurgical operations. Metals that can be quantified by assaying includes gold, lead, copper, zinc, tin etc. (Lodge, 1915). Herein assaying of ores containing gold is reviewed.

2.3 Assay of Different Types of Gold Ores

Metallurgists classify gold ores into two main categories: free milling and refractory ores. Free milling ores are those which produce 90 % gold upon leaching with cyanide. Refractory ores are those that produce low recovery of gold or acceptable gold recovery upon complex pre-treatment or addition of more reagents (Zhou et al., 2004). Gold ores can also be classified into 11 types based on the mineral processing techniques required and mineralogical characteristics as follows (Zhou et al., 2004):

Table 2.1 Classes of Gold Ores

(a) Placers	e.g. Witwatersrand (South Africa), Jacobina (Brazil)
(b) Quartz vein-lode ores	e.g. Timmins Camp Hollinger – McIntryre (Canada)
(c) Oxidized ores	e.g. Pierina (Peru), Yanacocha (Peru), Yilgarn region (Australia), Prestea-Bogoso (Ghana) (Dzigbodi-Adjimah and Asamoah, 2010)
(d) Silver-rich ores	e.g. Rochester, Candelaria and Tombstone (USA), La Coipa (Chile)
(e) Copper sulphide ores	e.g. Grasberg and Batu Hijau (all in Indonesia), Bulyanhulu (Tanzania)
(f) Iron sulphide ores	e.g. Many sulphide ores, including Carlin-type gold ores
g) Arsenic sulphide ores	e.g. Giant Yellowknife, Campbell Mine (Canada), Tarkwa (Ghana)
(h) Antimony sulphide ores	e.g. Big Bell (Australia), Hechi (China), Manhattan (USA)
(i) Bismuth sulphide ores	e.g. Maldon (Australia)
(j) Telluride ores Gold	e.g. Cripple Creek (USA), Emperor (Fiji), Kalgoorlie (Australia), Kumtor (Kyrgyzstan)
(k) Carbonaceous – sulfidic ores Gold occurs mainly as fine-grained gold particles	e.g. Carlin, Cortez, Getchell, Betze and Meikle (all in the USA).

The characteristics of some gold ores changes with time from free-milling to refractory and double refractory ores during exploitation leading to a reduction in profitability of mineral during extraction (Adam et al., 2004).

2.3.1 Assay of Oxidized Ores

Oxidized ores are found in the Prestea-Bogoso area in South-Western Ghana (Dzigbodi-Adjimah and Asamoah, 2010). The assay of this type of ore is quite simple and requires using the right type of flux. Oxidized ore basically does not require the use of extra reagents. A standard/known quantity of the pulverized oxide sample is fluxed with pre-mix flux and the fire assay method carried out. 3 g -5 g of flour could be added to the flux to increase the lead button weight in the case of very high oxide content.

2.3.2 Assay of Complex Ores

Sulphide gold ores occur in Prestea mines in Ghana (Hammond, 1997). In the case of complex (sulphide) ores, some reagents such as nitre, soda ash, litharge in small varying quantities are added to the sample before fluxing with a pre-mixed flux. The sulphide ores are reducing and acidic in nature. These contain metal ions that will be collected in the button with the lead and silver. Some of these ions in excess will affect the formation of the button, while others will affect the cupellation process and the digestion stage.

2.4 Methods for Gold Ore Assaying

Due to variations of elements and the complex nature of ore deposits, the need to analyse ores to ascertain its economic value is imperative. Several methods are currently being employed by assay lab to estimate quantitatively the amount of gold in a specific ore. Some of the methods can be used alone whiles other methods are partial and must be combined with other methods to ensure total recovery. The methods include Instrumental Neutron Activation (INA), aqua regia digestion/ Atomic Absorption (AA), Graphite Furnace Atomic Analysis (GFAA), Inductively Coupled Plasma Emission Mass Spectrometry (ICP/MS), combination of Cyanidation with AA, GFAA or ICP/MS methods and fire assaying. Among these methods, fire assay has been the most utilised and preferred method (Creswell, 2017).

Instrumental Neutron Activation Analysis (INAA) is an isotope analytical technique which is used in the quantitative estimation of gold in ores (Bode et al., 2009). This technique can also be used for determination of elements in other substances other than ores, for example metallic materials (Moreira et al., 2005). It involves the use of neutron irradiation to convert stable atomic nuclei into radioactive nuclei, followed by subsequent detection of gamma radiation as the radioactive nuclei decays (Bode et al., 2009).

Aqua regia is also an analytical method and it always precedes solvent extraction and flame absorption spectroscopy processes and has been extensively employed as an assay method for the analysis of gold ores (Blyth et al., 2004). This process involves the dissolution of 5 grams of the sample in aqua regia (a mixture of hydrochloric acid and nitric acid in the ratio of 3:1), followed by solvent extraction and flame absorption spectroscopy processes as analytical finishing technique. It is a low cost technique and produces rapid results in some few hours (Creswell, 2017).

Graphite Furnace Absorption Analysis (GFAA) is one of the techniques employed in gold analysis and belongs to the family of atomic adsorption technique. GFAA is widely adopted as a result of its versatility and sensitivity (Gaecia-Olalla and Aller, 1991). In conducting a gold assay using GFAA, the procedure usually proceeds in two stages. The first stage being the separation of the gold and silver from non-precious content of the ore using fire assay methods, followed by determination of the content of the separated silver and gold using GFAA (Petrovic et al., 2000). Apart from gold and silver, other elements such as tellurium and arsenic in ores have been determined using GFAA (Donaldson, 1998; Donaldson and Leaver, 1990).

Cyanidation also known as the Bulk Leachable Extractable Gold (BLEG) is a method that has been extensively used in Australia where it was developed and to lesser extent in Africa and the Nevada. BLEG method is highly employed because large samples can be analysed at low cost (Creswell, 2017). BLEG is a partial method, because it is combined with fire assay or AAS methods to ensure total recovery of gold (Tawiah et al., 2008). BLEG involves the weighing of 1 kg of ore sample to 5 kg of ore sample in a polyethene bottle and the addition of cyanide solution followed by agitation by bottle rolling for a period of time ranging from few hours to several days depending on the laboratory (Creswell, 2017). The disadvantages associated with BLEG include excessive cyanide consumption (presence of carbonates or sulphide), loss of gold by absorption onto carbonaceous materials and contamination of samples as a result of reuse of bottles (Abzalov, 2016).

2.5 The Fire Assay Process

2.5.1 History of Fire Assaying

The genesis of fire assaying can be traced to the finds in Troy II (about 2600 B.C.) and in the Cappadocia Tablets (2250-1950 B.C.). In the findings, it was proved that very pure silver was made in the twenty-fifth century B.C. Base on this evidence it can be concluded that fire assaying was invented in Asia Minor in the first half of the third millennium B.C. shortly after the discovery of the manufacture of lead from galena. Wertime (1973) provided the first convincing evidence of the production of silver from lead ores from cupel buttons found at Mahmatlar in the late third millennium B.C. and that are now in the Hittite Museum in Ankara, Turkey.

The Romans also successfully desilvered lead down to 0.01 percent or even to 0.002 percent in some cases and marked their cupelled desilvered lead "EX ARG." From this work, Roman lead pipe was found to be desilvered almost completely. In addition to the employment of fire-assay techniques for refining lead and silver, the fall of the Roman Empire by the invasions and conquests of the barbarian hordes resulted in the stagnation of intellectual life for about 500 years. During this stagnation period no significant advancement in the art of fire assaying took place. After this period vigorous works in the art of fire assaying begun which was as a result of renewal of learning in the latter centuries of the Middle Ages. Prominent among the men who were involved in the vigorous works was Agricola (1494 -1555). In about 1529, he started writing "De Re Metallica" (1556), which he completed in 1550 but was unable to send to the publishers until 1553. This was primarily due to the delay of the wood cuts for publication. A year after his death his work was successfully published. In this book, Agricola, who was the first author to attempt to cover the subject of fire assaying in its entirety, arranged his material systematically. In his book he described the tools and equipment to be used in assaying, laid emphasis on the quantitative aspects of each step, and for the first time gave instructions for assaying. "De Re Metallica" was definitely the first and foremost textbook on fire assaying, and it served as a guide to miners and metallurgists for the following 180 years. Several publications on fire assaying and metallurgy although appeared in the sixteenth and seventeenth centuries following Agricola's "Be Re Metallica," it was not until the first half of the eighteenth century that creditable works (for instance, C. A. Schluter's "Hutte-Werken, Braunshweig," published in 1738, cited by Hoover and Hoover in their translation of Agricola, 1556) began to supersede Agricola's book. Numerous publications on fire assaying, mining, and metallurgy followed in the 19th and 20th centuries. With continuing worldwide use and interest in the noble metals, one can confidently predict that fire-assay techniques will still be used in the future for the determination of the noble metals (Lodge, 1915).

2.5.2 Lead Fire Assay

Lead fire assay process, which has been used for many centuries, is a quantitative chemical analysis. The metal of interest in a sample is separated from gangue (materials of non-realizable interest) by heating the sample in a fusion process at high temperatures approximately 1100 ^{0}C. This is followed by cupellation process at about 950 ^{o}C, where the valuable metal is recovered from lead button (Battaini et al., 2014). The objective of the fire assay process is to make possible or give a figure which is representative of precious/noble metal in any given quantity of material. Traditional fire assaying process involves several stages. A detailed description of the processes involved is presented below.

2.5.3 Sample Preparation and Weighing of Samples

Samples for assay analysis are crushed, pulverized and a representative sample taken. Part of the representative sample is weighed (usually 30 g) on a balance into disposable cups. The measured sample is then mixed with a fluxing agent.

2.5.4 Assaying Fluxes

Fluxes for fire assaying contain chemicals that are naturally intrinsic or commercially added. These chemicals or reagents may play multiple roles during fire assaying depending on the matrix of the sample. Traditional composition for fire assaying fluxes include Sodium Carbonate (Na_2CO_3), Sodium Tetraborate ($Na_2B_4O_7$), Silica (SiO_2), Litharge (PbO_2) and a reductant (flour, maize and charcoal). The role of each reagent is summarised in Table 2.2.

Table 2.2: Fire assay reagents and their roles

Reagent	Role
Litharge	A source of lead to collect the precious metals. It is also a strong basic flux and reacts with metallic oxides and silica to form a slag. By far the most expensive component of a fire assay flux.
Sodium carbonate	A powerful basic flux that is usually the principal component of fire assay flux. It reacts with silicates to form a slag.
Sodium tetraborate	An acidic flux that lowers the fusing point of all slags. It forms fusible complexes with limestone and magnesite.
Silica	An acidic flux that forms the principal component of many samples. Small amounts are present in the flux to prevent attack on the fire assay crucibles when assaying samples deficient in silica.
Reductant	A source of carbon used to reduce the litharge to lead.

Source: ALS Minerals Fire Assay Technical Note, 2012

2.5.5 Fusion Stage of Fire Assaying

Theory of Fusion in Fire Assay

The main theory behind fusion in fire assay process is to render infusible ore fusible. This is because most ores are by themselves infusible, but if pulverized and mixed in proper proportion with suitable dry reagents (flux components) in a fireclay crucible, the mixture will fuse at an easily attained temperature (Haffty et al., 1997). In this sense the ore and flux components are assumed to be so intimately mixed that each particle of ore is in contact with particles of the flux components. As the temperature of the mass is gradually raised, the carbon (in the flour) or the sulphides of the charge reduces part of the PbO (litharge) to lead (commencing at 500 °C -550 °C). The mist of lead droplets produced collects or alloys with the noble metals released from the surrounding particles of decomposed ore. Slag miscible compounds such as lead silicates formed from part of the PbO are also absorbed by the slag. For a successful reduction and absorption, the conditions should be such that the slag remains viscous until the ore particles are thoroughly decomposed and every particle of the noble metals has been taken up by the adjacent suspended droplets of lead. After this point has been reached, the temperature is to ensure that the slag is thoroughly fluid. This allows the lead droplets to accumulate and fall like fine raindrops through the slag to form the lead button in which the noble metals are concentrated (Haffty et al., 1997).

Crucible Fusion

Crucible fusion is a separation process in which the precious metals are separated from impurities by collection in a metallic phase, whereas the adulterated components are absorbed into a slag phase using a high heat resistant crucible. To achieve this, a suitable portion of the sample is weighed (usually 30 g), mixed homogenously with the appropriate flux and melted in a refractory crucible at approximately 1100 °C. A crucible fire assay fusion process is an example of oxidation- reduction (Redox) reaction. During the fusion process, the adulterated components are transformed to their oxide states which are imbibed by the slag due to the fact that metallic oxides are quite soluble in slag phase as compared to metallic phase. Thus preventing them from entering the metallic phase and forming basis of separations made in fire assay (Bugbee, 1981; Cerceau et al., 2016).

After fusion, two main products are formed – slag and metallic phase. On one hand, the slag phase must have the following characteristics: (1) be pasty at formation temperature, (2) low capacity for metallic metal, (3) able to decompose the sample by the fluxes, (4) low specific gravity, and (5) should be able to contain all the impurities. On the other, the metallic phase must have the following characteristics: (1) minimum amount of impurities, (2) bright, soft and malleable, (3) button close to its desired weight, and (4) complete recovery of the noble metal (Bugbee, 1981).

Once the fusion process is complete, the crucible is taken out from the furnace and its melted glowing red-hot contents are poured into a mould using tongs. After the melted glowing red-hot content has cooled and solidified, it is separated from the slag by knocking off. The lead button is shaped into a square or rectangular piece, put into a cupel and sent for cupellation in a muffle furnace.

2.5.6 Scorification

Scorification is another type of fusion process in fire assay. It bores its name from the vessel used for the fusion process as the vessel is called a scorifer and a typical one is shown in Figure 2.1. Scorification can be a substitute to crucible fusion. It is extensively used for certain gold and silver assays. The process involves mixing ore samples with lead and covered with borax. Generally, scorification is not mainly recommended for noble metal determination but is mainly for reduction of button size and the cleaning of badly contaminated button. In this instance the badly contaminated lead button or the button to be reduced in size is transferred to the scorifer and covered with borax and heated to a temperature of 1050 °C -1100 °C. At this required temperature the lead oxidizes and slag forms containing the oxidized base metal contaminants (Beamish, 1966).

Figure 2.1: A scorifier (www.hswalsh.com)

2.5.7 Re-fusion

Repeat fusion is a special method that is conducted (usually with a different flux) when an undesirable fusion was obtained and sufficient sample is available. Slag from the first fusion can be reprocessed when the sample is insufficient. Indications of an unsuccessful fusion are (a) the slag contains shot (globules of lead); (b) the melt is viscous and gives a sloppy pour; (c) the charge is too siliceous as is indicated by glassy streamers, or too basic which gives a muddy pour and a stony appearance. A slag is said to be too basic when it is high in litharge from which an insufficient amount of lead was reduced. This is recognized by its higher-than - average specific gravity and crystalline character. Unsuccessful fusion can also happen when the sample has not even decomposed. Unsuccessful fusions usually fall into one or more of the categories just listed based on their pour and the nature of their slag. Considerable thought and experimentation is expedient in determining which flux component to alter and the right amount to use to obtain successful fusion. In some instances, generalities may be stated, but in others the problem is unique. No specific set of conditions can unequivocally be stated for the cause of shot in the slag. Consequently, no generalities can be stated to avoid the production of shot. However, some hypotheses or observations may be or have been suggested. For instance, if the melt is viscous it may cause the globules of lead, which is as a result of particles of PbO produced from the reduction which remained in suspension and prevented them from combining to form the lead button. In another instance the globules of lead may become coated and thus prevented from combining. Melt which is more fluid in the former instance may aid in the combining and collection of the lead globules. In the latter instance, more investigation is needed to ascertain the causes for coating of the lead globules. However, the addition of a considerable amount of $Na_2B_4O_7$, (30 g -35 g), as in fusing chromite ores, seems to prevent coating of the globules in many cases. When there is the onset of a viscous pour, fluidity must be increased by increasing one or more flux components, frequently Na_2CO_3 or PbO or $Na_2B_4O_7$, but sometimes SiO_2 or CaF_2. When the pour is highly siliceous the usual treatment is to increase the Na_2CO_3 by 5 g -10 g, and when the pour is too basic, increase the SiO_2 and $Na_2B_4O_7$. Both pours need additional PbO (about 20 g). If, during the pour and after cooling, material similar to the sample appears on the side of the fireclay crucible and in the slag, the sample obviously has not decomposed. This condition suggests that the proper flux may not have been selected. Further study and experimentation to select the proper flux will usually solve this problem. However, in a few instances, such as when fusing chromite concentrates, it may be necessary to decrease the size of the sample from the routine 15 g to 3 g to obtain an acceptable fusion (Bugbee, 1981).

2.5.8 Cupellation

The second major stage in fire assaying is the cupellation stage. Cupellation is a process in which the lead is oxidized and subsequently absorbed into the small shallow porous cup called the cupel, leaving silver and gold as a bead in the cupel. Proper temperature for cupellation ensures about 98.5 % of lead oxide being absorbed by the cupel and volatilization of the remaining 1.5 % (Bugbee, 1981). A successful cupellation involves preheating the cupel to get rid of any moisture, carbon dioxide or organic matter. The cupel is a small cup-like vessel or receptacle that has the ability or tendency to absorb lead and is made of bone-ash or magnesia which is able to absorb lead from sample placed in. The lead buttons are placed in the cupels arranged on a cupel fork, sent to the cupellation furnace and the furnace door closed at a temperature of about 950 ^{0}C for about 45 minutes.

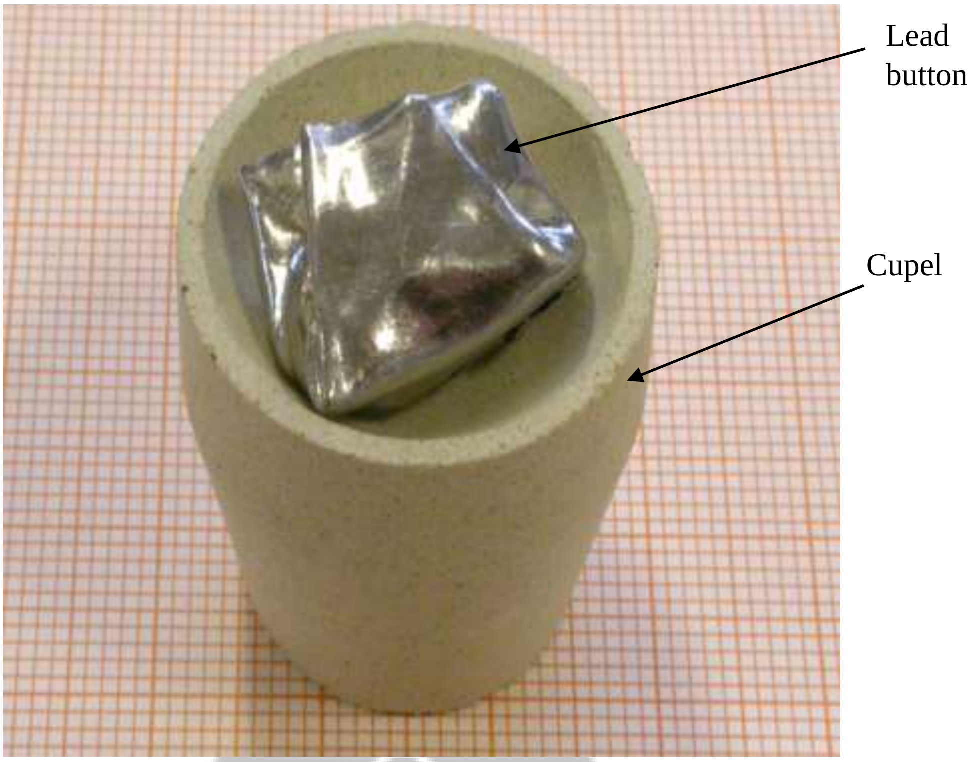

Figure 2.2: Lead button in cupel prior to cupellation (Battaini et al., 2014)

Figure 2.3: Cupels which have absorbed litharge during the cupellation (Battaini et al., 2014)

As the temperature of the button rises, the lead button melts and is covered with a dark scum composed mostly of litharge. After a while the scum will fuse, exposing the melted alloy. This phenomenon is known as the “opening” or “uncovering” (Bugbee, 1981; Zysk, 1981). After the button has “opened” and the lead is being oxidized, it is observed that molten litharge slides off the surface of the lead and is absorbed by the cupel (McGuire, 1978). When cupellation is complete, the cupel is taken out of the furnace, allowed to cool for about 15 minutes to 30 minutes and the gold-silver bead sent for acid digestion. The used or contaminated cupels, referred in this thesis as waste cupels, are then discarded.

Lead button undergoes several transformational stages before the end of cupellation. The transformation stages help assayers in the control of cupellation temperature and when to close or open the furnace door as the temperature and amount of air available for oxidation greatly affects the cupellation process. The ability of an assayer to control these two processes plays an integral role in ensuring the success of cupellation (Bugbee, 1981). When the cupels with the beads are ready, the furnace door is closed. Once the cupels have been sufficiently heated, the lead button melts at once and is covered by a dark scum. If the temperature is right the dark scum disappears and the molten lead becomes bright. At this stage the lead button is said to have opened up or uncovered. This transformation informs assayers of the onset of a rapid oxidation of lead which considerably raises the temperature of the molten alloy above that of the surrounding.

After the uncovering stage, the molten lead assumes a convex shape and allows patches of molten litharge to pass down the surface giving it a lustrous experience. At this point the lead button is said to drive. Following this, the furnace door is opened to admit more air to facilitate the oxidation process which is ongoing and the temperature subsequently reduced by the assayer. When the temperature is high enough from the oxidation the cupel absorbs the litharge. Greater part of the litharge is absorbed and a small part is volatilized.

After cupellation has proceeded for few minutes, a ring of absorbed litharge can be noticed around the cupel, and its colour is an indicator to the assayer whether the cupellation temperature is right or not. If the temperature is right the colour is red and dull. As cupellation proceeds further, temperature must be monitored. If the temperature becomes low the absorption of litharge by cupel becomes difficult. When this stage is reached the temperature must be raised to prevent the occurrence of a phenomenon called freezing. This occurs when litharge, instead of being absorbed by the cupels forms a pool which forms between the annular space between the lead and the cupel which subsequently increases in size, covers the lead and then solidifies. At this stage the lead button is said to have frozen.

Toward the end of the cupellation process the temperature is raised and the molten alloy becomes rounded in shape and rich in silver. Lustrous drops of Litharge appear and move about the surface. When the last of the lead goes off the drops disappear and the fused litharge covering causes the bead to emit succession of rainbow colour by an interference effect. This phenomenon is called play of colour. Shortly after this, the colours disappear the beads become bright and silvery. This stage is called brightening (Bugbee, 1981).

Losses during cupellation

Noble metal losses during cupellation occur as a result of their absorption into the cupel and volatilization. It has been found that adsorption of noble metals into cupels account for 90 % of the loss of noble metals (Shvetsov and Adel'shina, 2004).

Noble metals that can be lost during cupellation are Gold, Silver, Iridium, Osmium and Ruthenium. Gold losses during cupellation are considered negligible. This is because silver is said to have a shielding effect on gold during cupellation (Bugbee, 1981).

During cupellation silver can be lost through absorption of silver by cupel. The amount that can be lost through this process varies with temperature, draft and the type, shape and density of the cupel (Zysk, 1981). Silver can also be lost by a phenomenon called spitting. This occurs as a result of the violent release of oxygen that dissolved into the silver during the cupellation. When this happens it leads to the throwing off of silver particle. Silver is also lost when the bead develops rootlets that extend into cracks in the cupel (Bugbee, 1981). Osmium is also lost during cupellation. For Osmium almost all is lost by volatilization. Cupels absorb approximately 50 % and 20 % of partially oxidised ruthenium and of iridium (Potts, 2012).

2.5.9 Parting and Acid Digestion

For parting to be complete/successful, the ratio of silver to gold must be at least one is to three, else the silver will not dissolve completely. This issue could be resolved by adding silver to the fusion, if the approximate silver-gold ratio is known, or by recupelling the doré bead with three times its weight in silver. A third solution to the problem is to run a preliminary assay. The addition of this silver during the assay is known as inquartation (McGuire, 1978). Prior to acid treatment, the bead must be flattened with a hammer or anvil to make easier a rapid and complete parting of the silver-gold alloy as it provides a large surface area for reaction to occur.

Nitric acid is mostly used in the parting process to separate the silver from the gold in the bead. Precautionary measures must be taken to ensure that the-acid and wash water used are free from any form of chlorides. This could lead to precipitation of the dissolved silver or possible combination of the nitric acid to dissolve gold leading to an adverse effect in the outcome of the assay (Bugbee, 1981).

Furthermore, a secondary parting is necessary to ensure complete separation of the silver-gold alloy using a stronger acid such as hydrochloric acid. To check for the completion of the parting process, the evolution of nitrogen oxide gas ceases. It is topped up with some quantity of water, corked, shaken very well, the precipitates allowed to settle and sent for instrumental analysis (Creswell, 2017). Parting is usually followed by annealing process and weighing of the gold. Annealing is important stage of the process as it prevents weighing unwanted materials left in the gold, destroy the porosities in the bead, and prevents adsorption of water and moisture.

2.5.10 Instrumental Analysis of Gold

Some fire assay laboratories complete the assay process by digesting the prill (dore bead) and the concentration of gold in solution determined using analytical instrument. In this case, parting, annealing and weighing is not carried out. Instrumental analysis of gold is achieved by using a Flame Atomic Absorption Spectrometer (AAS) or Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). These analytical instruments are usually calibrated with standard solutions which would be compared to the concentration of gold in the digested sample. The sample is aspirated in an acetylene flame. A beam of light from a gold lamp at a wavelength corresponding to that of gold is passed through the flame and the gold in the sample absorbs light proportionally to the concentration of gold in the sample (Creswell, 2017).

2.6 Cupels

Cupels are small shallow circular receptacles, cup-like in nature and used for assaying gold or silver with lead. It consists of a solid cylinder with a shallow hole/depression in the upper most part. Cupel has a diameter of 33 mm and a shape of an inverted truncated cone about 13mm thick in the centre, with a typical shallow concavity at the top, surrounded by a low rim (see Figure 2.4). A macroscopic look reveals a grey colouration with white inclusions as well as several black marks at the bottom, on the outside surface and the sides (Martinón-Torres and Rehren, 2005). Cupels are made to be thick and porous.

Figure 2.4: Cupel used for cupellation (www.lmine.com)

Lead button containing precious metals from a sample is placed into a cupel, and during the assaying process the cupel is durable and able to provide good lead absorption. The precious metal is not imbibed into the cupel because it has a high surface tension, thus failure to be oxidized when cupelled. The height of the cupel must be such that it can absorb about 98.5 % of litharge from the lead button (Shepard and Dietrich, 1940).

Little information is given on the origin and use of cupellation but as far back as the 12th century, written reference was made on the use of cupels by Theophilus Divers Arc. Since then there was a change in the process till the 16th century. Chemical analyses of cupels used between 13th to 18th century for mineral assaying suggest that the cupels were composed mainly of calcium oxide (CaO) with minor fractions of P_2O_5, SiO_2, MgO, Al_2O_3 and FeO respectively (Martinón-Torres and Rehren, 2005).

2.6.1 Types of Cupels

The various names of cupels produced are based on the materials used in their making. These include magnesia (made from magnesia) cupels, bone ash from animal bones and cement and bone-ash composite cupels. Magnesia cupels are commonly used today.

Bone Ash Cupel

This type of cupel is produced from heating of animal bones to drive off water and to decompose carbonates into oxides and leaving calcium phosphate. Properly burned sheep bones contain approximately 90 % tricalcium phosphate, 5 % calcium oxide, 1 % magnesium oxide, and 3 % calcium fluoride (Shepard and Dietrich, 1940).

It is worthy to note that, during the calcination process, there may be some undesirable components such as organic matter, carbonates and nitrates as well as other salts that decompose at cupellation temperature (850 °C to 900 °C) or lower. The evolution of the gases during cupellation causes loss by the spitting of the lead. “Spitting” can be controlled by allowing cupel to cool naturally in the muffle with door partially open and then withdrawing cupel gradually towards the door of the muffle and hold till button solidifies (Shepard and Dietrich, 1940).

Magnesia Cupel

Purchased as a finished product and produced from calcining magnesite, cupels are produced under high pressure and temperature conditions and the most common type of cupel used. They come with different trade names such as Mabor, Calmix, and Morganite among others. They are formed under high pressure and use special bonds to increase their strength. Due to the processing route, magnesia cupels have better heat capacity and thermal conductivity than bone-ash or Cement cupels, and hence the heat of oxidation of the cupelling lead is abstracted more rapidly. The alloy is therefore maintained at a lower temperature than with bone-ash or cement cupels, but higher muffle temperatures must be maintained throughout the cupellation cycle. Largely on account of lower alloy temperature near the finish of cupellation the loss of silver by cupel absorption is greatly decreased and is usually less than half of the loss obtained with bone-ash cupels, under analogous cupellation conditions. The gold loss with magnesia cupels as compared with bone-ash cupels is same (Lewis et al., 2007).

Cement or Composite Bone-Ash-Cement Cupels

More commonly used with various percentages of bone ash is Portland cement. Cement contains approximately 62 % CaO, 22 % SiO_2, 10 % Al_2O_3 + Fe_2O_3 and minor amounts of MgO, SO_3 and other impurities. Water serves as a moistening agent. When allowed to dry, various aluminates and silicates are formed, which cause the cement to harden or "set”. The internal bonding of cement gives cement cupels greater strength than pure bone ash. When cement is used as part of the cupel composition, the amount of mixing water should be approximately 8 % to 12 %. With moisture content outside the range of 5 % to 15 % , cement cupels become susceptible to cracking during drying and mostly crack or check on heating (Shepard and Dietrich, 1940).

Cupellation losses in pure cement cupels are relatively higher than bone ash cupel. However, cement and bone ash mixtures, with 75 % or less cement drastically reduce percentage of losses as those of pure bone ash cupels. A cupel containing 70 % cement and 30 % bone ash costs about one-third as much for materials as a pure bone-ash cupel; also, it has much greater strength and hence is less prone to fracture in handling. However, it is virtually impossible to recover materials from damaged unused cupels with high cement content. This is due to the fact that the setting reactions are irreversible, whereas damaged bone ash cupels can be easily pulverized easily and recycled to make new cupels (Shepard and Dietrich, 1940).

2.6.2 Manufacturing of Cupels

Ring and Plunger

Various types of cupel-making machines are on the market. The simplest and least expensive is a ring and plunger (see Figure 2.5). The ring is set upon an anvil and filled with the cupel mixture. Then the plunger or die is inserted, and the head of the plunger is struck sharply several times with a wooden mallet or a hammer, slightly turning the plunger within the ring after each blow. Considerable experience is needed to make cupels efficiently with this device. Aside limited production capacity, the biggest problem with the hand mould is the difficulty in applying uniform pressure, which results in uneven cupel density. Eventually, this causes variations in silver absorption (Lewis et al., 2007).

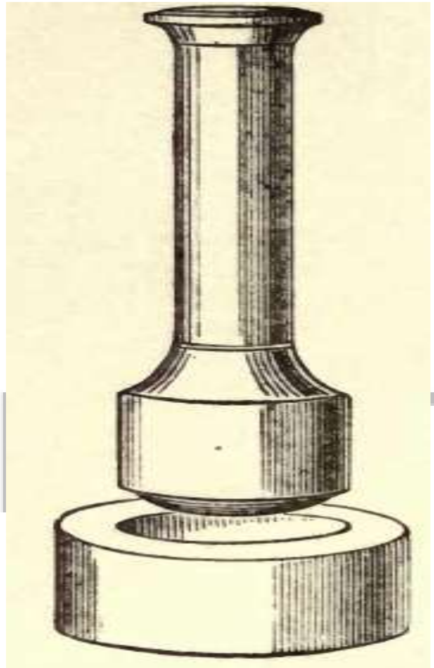

Figure 2.5: A ring and plunger cupel making machine (www.911metallurgist.com)

Lever-type Cupel Machine

For greater capacity and uniformity, a lever-type cupel machine is used. A foot-lever machine is preferred to a hand-lever machine, as it has greater potential capacity and requires less physical exertion. In addition to moulding time, allowance must be made for the preparation of the batch. Figure 2.6 shows schematic diagram of a lever-type machine.

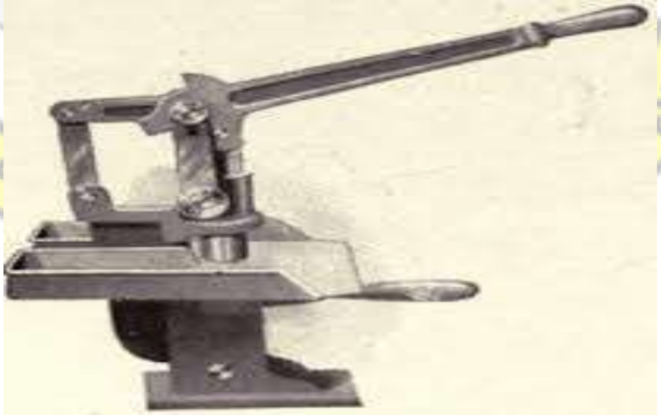

Figure 2.6: Hand level cupel machine (www.911metallurgist.com)

If desired, uniformity of pressure can be attained in making cupels in foot- or hand-lever machines, by providing an extension of the operating lever that may be weighted with a known weight, such as a bar of lead or a bucket of shot.

The amount of water used in mixing cupel materials should be just sufficient so that the mixture will cohere when firmly pressed in the hands. The optimum amount of water for any of the bone-ash or cement cupel mixtures, or of either alone, is from 10 % to 12 %, but a slightly larger, amount may be preferred for pure bone ash. Cement will set better if the water content is approximately 8 %.

If bone-ash-cement cupels are to be made, the dry ingredients are mixed thoroughly on a mixing cloth, or in a mixing box or barrel, and then sifted through a 10-mesh or finer screen. To avoid puddling, water is added to the dry cupel batch in small increments, and the batch is kneaded slightly after each water addition. After all the water has been added, the entire batch is thoroughly kneaded with the hands and passed through a 10-mesh or other suitable screen to break up lumps and obtain more uniform diffusion of the water. The batch should then be covered with a damp cloth to prevent loss of moisture before being used, and mixtures containing cement should be used as soon as possible after adding water, in order to prevent premature setting of the cement.

Finished cupels are placed in an air drying rack and are ready for use whenever the free moisture has evaporated. Accelerated drying, as with hot air, should be avoided, as this may cause checking or cracking. Whatever free moisture may be present in an air-dried cupel is expelled when the cupels are preheated in the muffle just before using, a practice which is necessary in all cases in order to remove combined water, CO_2, and other volatile matter that would cause spitting and to avoid delayed opening of the but if placed in cold cupel (Bugbee, 1981).

2.7 Lead

Lead as the 82nd element on the periodic table is a naturally occurring, bluish-grey metal that is found in the earth's crust, in lead ore. It belongs to group 14 together with elements such as Carbon, Tin and Silicon. It is the element which has the most metallic characteristics in the group. It has the symbol Pb. Lead has four stable isotopes and two oxidation states. The oxidation states are divalent and tetravalent with the divalent state as the common state. Lead compounds usually have high melting points and low solubility in water. Lead dissolves well in Nitric acid, hot concentrated Sulphuric acid, but slowly in weak acid water (Bugbee, 1981; Fonger, 1995). Lead has a poor electrical conductivity but a good sound and vibrational absorptivity. Lead is the end-product of the radiometric decay of three radioactive minerals: uranium, thorium and actinium (Lewis-Sr, 2008). Lead, specifically existing as lead-sulphide in galena ore, forms an estimated amount of 10 to 17 milligrams per kilogram (mg/kg) or 0.001 % to 0.002 % of the earth's crust. A study revealed that deteriorating paint is a major cause of the increasing levels of lead in soils except in the immediate surroundings of roads. (Tarrago & Brown, 2017)

Another prevailing source of lead in soils especially around busy roads is gasoline combustion. A study at sites close to four busy roads in the U.S. recorded approximately lead concentrations of 150 mg/kg to 540 mg/kg of dry soil in the top 5 cm of soil at a distance of 8 m from the road. The highest lead concentrations were recorded at the top 3 cm to 5 cm of soil. A similar observation was made at the river bottom sediments. The study also revealed that concentration of lead in soil decreased with the distance from the roadway. At 32 m away from the road, lead concentration decreased to 55 mg/kg from 164 mg /kg of dry soil (Haar, 1975).

Table 2.3: Lead chemistry and compounds

Molecular Formula & Substance Name	**CAS Registry Number**	**Synonyms**	**Colour**	**Molecular Weight**	**Specific Gravity**	**Melting Point °C**	**Water Solubility g/100 ml (0-25 °C)**
$C_4H_6O_4Pb$ Lead Acetate	301-04-2	Sugar of lead	Colourless crystals or white granules	325.3	3.25	280	44.3
$PbBr_2$ Lead Bromide	10031-22-8	---	White powder	367	6.66	373	0.8441
Cl_2Pb Lead Chloride	7758-95-4	Lead dichloride	White crystals	278.1	5.85	501	0.99
$PbCrO_4$ Lead Chromate	7758-97-6	Chrome yellow	Yellow crystals	323.2	6.12	844	6×10^{-6}
O_2Pb Lead Dioxide	1309-60-0	Brown, plumbic acid; lead oxide brown	Brown crystals	239.2	9.37	290	Insoluble
PbN_2O_6 Lead Nitrate	10099-74-8	lead dinitrate	white crystals	331.2	4.53	470	37.65
$Pb_3P_2O_8$ Lead Phosphate	7446-27-7	Normal lead orthophosphate	white powder	811.5	7	1014	1.4×10^{-5}
$C_4H_{10}O_8Pb_3$ Lead Subacetate	1335-32-6	Lead monosubacetate	white powder	807.7	-	-	-
$PbSO_4$ Lead Sulphate	7446-14-2	Lead bottoms	white rhombic crystals	303.3	6.2	1170	0.0042
PbS lead sulphide	1314-87-0	Plumbous sulphide	silvery, metallic crystals or black powder	239.2	7.5	1114	Insoluble

Source: (Report on Carcinogens Background Document for Lead and Lead Compounds, May 2003)

2.7.1 Effects of Lead

It has been estimated that the massive processing of lead ores across the globe has released about 300 million tonnes of lead into the environment within the past five centuries (Haar, 1975). Several attempts have been made in some countries to control lead. However, considerable of lead is reserved in soil, dust, and house paints. These major sources have perpetually affected humans over the years. It has also been predicted as a potential problem in many developing countries. The studies have been reported from Africa, Asia and South America (Tong et al., 2000). Essentially, lead is not required in the human body. There enough evidence to prove that accumulated lead is metabolic poison which affects the hematopoietic, cardiovascular, nervous, renal, and reproductive systems in humans negatively. Also, lead exposure has been linked with the obstruction of mental growth (Tong et al., 2000; David and Hoffman, 1977). Generally, the main source (70 %) of lead in the human body is diet. However, other sources like cigarettes, dust, or house paints, must considered in specific cases. For instance, in occupational exposure, absorption through respiration is the main intake route for victims (David and Hoffman, 1977).

David and Hoffman (1977), reported that in a typical urban environment with lead concentration of 1 pg/ m^3 to 2 pg/ m^3 in air, a normal person will absorb an average of 16 *ng* Pb per day which is approximately 35 % of the total lead absorbed in a day. Workers who are involved in lead production encounter lead exposure in various forms. These include motor vehicle assembly, battery manufacture and recovery, lead mining and smelting, lead alloy production, glass, paint, ceramics and printing industries. In developed countries, stringent measures are employed in industry to reduce lead poisoning; however, this is not the case in developing countries (Alessio et al., 1976; Schirnding, 1999). EPA has determined that lead is a probable human carcinogen. Lead can affect every organ and system in the body. Long-term exposure of adults can result in decreased performance in some tests that measure functions of the nervous system; weakness in fingers, wrists, or ankles; small increases in blood pressure; and anaemia (Schirnding, 1999). Exposure to high lead levels can severely damage the brain and kidneys and ultimately cause death. In pregnant women, high levels of exposure to lead may cause miscarriage. High level exposure in men can damage the organs responsible for sperm production (Martin and Griswold, 2009).

Studies have shown that about 35 % of the inhaled lead by man is deposited in the lungs whilst 10 % of lead from diet is absorbed. However, several data sources show that, the dietary contribution to Pb-B is approximately 6-18 μg of lead per 100 ml of blood per 100 μg of dietary lead intake (Waldron, 1978). Studies on both animals and humans reveal that the general characteristics of lead distribution and excretion are fairly lucidly defined. The body burden of lead can be subdivided into a large, slow-turnover compartment and a smaller more rapidly-exchanging compartment. The larger compartments are only found in bones. The level of lead in the large compartment surges throughout individual's life. The smaller compartment comprises soft tissues including blood. The amount of lead in soft tissues and in blood increase incessantly till early adulthood and then change little. The blood-brain barrier in adults is impermeable to inorganic lead. However, the blood-brain in children is not well developed and thus allows inorganic lead to penetrate it. Eventually, the high gastrointestinal uptake and the permeable blood–brain barrier makes children especially vulnerable to lead exposure and subsequent brain damage. Organic lead compounds penetrate body and cell membranes. Tetramethyl lead and tetraethyl lead penetrate the skin easily. These compounds may also cross the blood–brain barrier in adults, and thus adults may suffer from lead encephalopathy related to acute poisoning by organic lead compounds.

2.7.2 Non-Cancer Effects

Lead Exposure leads several diseases, among which are mental retardation, a consequence of loss of IQ points, as well as increased blood pressure. Studies on humans and laboratory animal have revealed that Lead affects the blood tissues, kidneys, and nervous, immune, and cardiovascular systems negatively. Dietary intake of large amount of lead can cause gastrointestinal effects like colic, constipation, abdominal pain, anexoria and vomiting (Prüss-Ustün et al., 2004). The definition of an elevated concentration of lead in the blood is 10 mg/dl. However, a recent investigation revealed that health effects of lead may become conspicuous at concentrations of < 5 mg/dl (Lanphear et al., 2000). Approximately, 120 million people across the globe had blood lead concentrations of between 5 mg/ dl - 10 mg/ dl in the year 2000, and almost the same population had elevated concentrations of > 10 mg/ dl. Forty per cent of all children in the study had blood-lead concentrations of > 5mg /dl and half of these children had blood-lead concentrations of >10mg /dl; of these children, 97 % were living in developing countries. The burden of disease caused by mild mental retardation as a consequence of Lead exposure caused 9.8 million disability-adjusted life years (DALYs), and the burden from cardiovascular diseases caused by elevated blood pressure resulted in 229 000 pre mature deaths and 3.1 million DALYs. In total, these two outcomes alone account for about 0.9 % of the global burden of disease. Several health outcomes resulting from exposure to lead could not be quantified in this analysis, in particular, increased delinquent behaviour and its impact on injuries (Lanphear et al., 2000).

The toxicity of lead absorption by the body primarily affects the nervous systems. Thus the nervous systems are main targets for lead toxicity in the body (Lanphear et al., 2000; Sjögren et al., 1990). Proposed mechanisms of toxicity are focused on the Lead's ability to imitate calcium actions and interactions with proteins in neurons (Jones et al., 2009).Voltage-regulated calcium channels are obstructed by Lead. This prevents the inflow of calcium and release of neurotransmitters and eventually preventing synaptic transmission. Encephalopathy is the most dangerous neurological effect of lead exposure (Prüss-Ustün et al., 2004). Encephalopathy occurs at blood lead concentrations ≤ 90 mg/dl and, ≤ 140 mg/dl for children and adults respectively. However, neurotoxic effects occur at much lower blood-lead concentrations than those that cause encephalopathy. A study investigated occupational exposure to lead and revealed that persons with blood-lead concentration of 40-120 mg/dl have symptoms such as loss of appetite, malaise, lethargy, headache, fatigue, forgetfulness and dizziness. Prüss-Ustün et al. (2004), gave an account on children who were victims of lead poisoning were mentally retarded and showed some behavioural disorders.

Schwartz (1995), carried out an investigation to examine relationship between blood-lead concentration and systolic blood pressure in adult males. The study showed that there is a significant relationship. It was observed that a reduction in blood-lead concentration from 10 mg/dl – 5 mg/dl correlated with a drop in blood pressure of 1.25 mmHg (95 % CI 0.87–1.63). It has been proposed that lead influences calcium activity, which correlates to modulation of blood pressure through vascular tone. *In vitro* studies have reported increased blood pressure in isolated tail arteries and increased responsiveness to alpha-adrenergic stimulation in response to exposure to lead. High blood pressure has been linked with upsurge in vulnerabilities to cardiovascular and cerebrovascular disease.

Absorbed lead restrains the metabolism of some enzymes involved in haem biosynthesis. Several researches have proved that the breakdown of ALAD (d-aminolevulinic acid dehydratase) is affected even at very low blood-lead levels with no known threshold. Lead-induced anaemia emerges from a combination of reduced haemoglobin formation (caused either by impaired haem synthesis or globin chain formation) and reduction in erythrocyte survival because of haemolysis (Schwartz et al., 1990).

2.7.3 Cancer Effects

Lead is not genotoxic in vitro, but increases the mutagenicity of other mutagens, possibly acting via inhibition of DNA repair (Hartwig, 1994). Animal studies showed that lead does cause cancer in animal studies, principally kidney cancer in two; rats and mice exposed to lead via the oral means of administration. EPA has considered lead to be a probable human carcinogen, and, under more recent assessment guidelines, it would likely be classified as likely to be carcinogenic to humans. Lead acetate and lead oxide acted synergistically to increase kidney and lung tumors, respectively, after administration of known carcinogens (nitrosamines, benzo[a]pyrene).

2.7.4 Effects of Lead on the Environment

Approximately, 300 million tonnes of lead have been released into the environment within the last five centuries through the extensive extraction of lead from its ores (Tong et al., 2000). Though several steps have been taken in some advanced countries to control lead, it has been discovered that huge reserves of the metal still exist in soil, dust and house paint. Over the years, these sources have continuously affected many people across the globe. Lead has also been listed as a potential problem in most advancing countries. The studies have been reported from Africa, Asia and South America. Despite, the existence of lead in most plants and some beneficial applications of lead, it is not listed as an extremely important mineral for plants (Tong et al., 2000). Compared to other metallic elements, the adsorption of lead by plants depends on many factors. Essentially among these factors are; species, soil pH, ion exchange capacity, soil composition and metal concentration. In addition, the degree of precipitation, light and temperature are also essential factors (Demayo et al., 1982).

Plant Lead uptake is enhanced at lower pH values and in soils with low organic composition. The accessibility of lead to plants can be minimized by transforming lead to hydroxide, carbonate or phosphate compounds with very low solubility. This can be achieved by adding lime or phosphates. Generally, lead has an inclination to accumulate in the topsoil. Eventually, shallow rooted plants are prone to relatively higher lead concentrations than the deeply rooted plants (Demayo et al., 1982). The study analysed oats, red clover, beans (shallow rooted) and peanuts (deep rooted) grown in soil containing 820 mg Pb / kg (dry weight). It was observed that shallow rooted plants exhibited poor growth and spotty discoloration whereas deep rooted plants (peanuts plants) remained unaffected under same conditions (Walker et al., 1977).

2.8 Waste Cupel Handling

Cupellation refers to the process of treating lead button in order to extract the precious metals from the lead (Bugbee, 1981). During cupellation, Lead is oxidized into molten litharge (PbO) and absorbed into the cupel. The precious metals have high surface tension and resist oxidizations under the cupellation conditions, eventually they are not absorbed by the cupels (Mpofu et al., 2016). The disposal of waste cupels containing lead into the environment is now a cause for major concern. For some years now, there has been an upsurge in the volume of Lead-bearing waste generated by industries. Lead bearing waste comes in the form of cupels, slag and fusion crucibles. Several companies bury the lead contaminated cupels in concrete lined pits and are fraught with the perpetual upsurge in the volume of the buried cupels over time (Mpofu et al., 2016).There’s not much information available on how cupel waste is disposed in Ghana. Some mining companies with on-site laboratories employ the recycling method whiles most commercial laboratories outsource the waste management to waste management companies. To reduce cost of waste treatment most mines in Ghana with on-site laboratories use the recycling method to dispose of cupel waste.

In this method, cupel waste is milled with the ore and ends up mixed with the metallurgical samples sent back to the lab for analysis. Some of the waste also ends up in the tailings dam lined with geo-material and is impermeable. This produces some amount of lead waste since the cupel waste contains lead which when not handled well could contaminate the environment.

Effort was made to recover lead from the waste cupels through lead electrodeposition. Enhancement of operation parameters for the electrodeposition of lead metal from acetic acid leachant was carried out. Acetic acid (10 %) was chosen as a leachant over EDTA (0.1 M) due to its higher leaching and electrode position efficiencies (73.3 % vs 68.1 %) and (95 % vs 90.8 %) respectively. However, EDTA (0.1 M) proved less corrosive to the carbon electrodes than acetic acid (Mpofu et al., 2016). Also acid leaching was used to extract lead from the hazardous Lead-bearing waste by contacting it with hydrochloric and nitric acids and subsequently precipitated in sodium metasilicate solution (Magalhães et al., 2012).

2.9 Adsorption

Adsorption is a sorption process which involves the buildup of particles (solid, liquid or gas) at the interface between solid surface and bulk solution (Sparks, 2003). In other words, it refers to process in which particles of matter cling to the surface of a solid or liquid by forming layer or film. The solid substance which attracts particles onto its surface is termed adsorbent whereas the liquid or gas particles bound to the surface are called the adsorbents. However, adsorbent is referred to as adsorptive prior to adsorption (Webb, 2003). Adsorption has been characterized as one of the few most cost effective methods in removing heavy metals from solutions (Özacar et al., 2008; Wasewar, 2010). It is also one of the most widely used technological methods in protecting the environment globally (Chen, 2015). Adsorption process is applied in the treatment of wastewater, removal of contaminants in industrial processes, drying of process air among a host of other applications.

2.9.1 Types of adsorption

Solid materials usually display non- uniform distribution of surface energy. As a result, they molecules may get bound to the surfaces when they are very close to interact (Webb, 2003). Based on the strength of the solid surface-molecule bond, adsorption processes can be grouped into two classes, namely physical and chemical adsorptions.

Physical adsorption

Physical adsorption is a mere physical attraction of molecules by the heterogeneous surface of solid materials. It is a consequence of non-specific, very weak Van der Waal forces and weak solid-gas interactions. Due to the low adsorption energies ($\leq$ 80 kJ/mol) in physical adsorption, adsorbate molecules are usually not bound to any specific location on the surface of the adsorbent and hence are able to disperse freely along the adsorption surface. Unlike chemisorption, physical adsorption is easily reversible due to its low adsorption energy (Webb, 2003).

Chemical adsorption

Chemical adsorption involves the sharing of electrons between adsorbate and adsorbent which usually leads to the formation of complexes or compounds at adsorption surface. In chemical adsorption, bond strength are usually very high. Conventionally, the energetic threshold separating the binding energy of physisorption from that of chemisorption is about 0.5eV per adsorbed species. Consequently, the process is almost irreversible. Unlike physical adsorption, chemical adsorption only occurs when there is direct contact between adsorptive and adsorbent. Thus, chemisorption is typically monolayer.

2.9.2 Adsorption isotherms

According to IUPAC, adsorption isotherm refers to the relationship between the quantity of adsorbent and adsorptive in the bulk phase under equilibrium conditions. The study of adsorption or equilibrium isotherms is very important in the development of perfect model equations for design purposes (Wasewar, 2010). Modeling of equilibrium or isotherm data is crucial in forecasting adsorption behavior (Chen, 2015). Özacar et al. (2008) asserted that, adsorption isotherms are critical in the description of adsorbate particles and adsorbent interactions, optimization of adsorbent efficiencies, and interpretation and prediction of degree of adsorption. Adsorption isotherm can be depicted from a plot of concentration of solid phase against liquid phase. Many adsorption isotherm models have been developed over the years with regards to various parameters. Notable among the numerous adsorption isotherm theories with regards to heavy metal adsorption are; Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich et al. (Chen, 2015). Generally, adsorption model isotherms have been characterized by non-linear curves depicting adsorption process at constant parameters, pH and temperature (Foo and Hameed, 2010). However, researchers have utilized linear approaches in analyzing adsorption isotherm data. Despite the tendency of linear approach to cause discrepancy between predictions and experimental data, linear analysis of isotherm data has been described by current researchers as an alternative and easier approach (Chen, 2015).

Langmuir Isotherm model

This adsorption isotherm assumes that all adsorption sites are similar and active sites do not depend on activities of adjacent sites (Özacar et al., 2008). It also assumes that adsorption occurs at some specific homogeneous surface within the adsorbent (Wasewar, 2010). It also assumes the formation of monolayer adsorbate on the surface of the adsorbent during adsorption (Foo and Hameed, 2010). Hence, once a site is occupied by adsorbate molecule, no further adsorption will occur at that site (Allen et al., 2004). The Langmuir Isotherm has been used by several researchers for the adsorption of metal onto tea factory waste adsorbents (Wasewar, 2010).

The Langmuir equations are;

$$q_e = \frac{K_L\, C_e}{1 + a_L\, C_e} \qquad (2.1)$$

The linearized form of the Langmuir Isotherm is expressed as;

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad (2.2)$$

C_e = equilibrium concentration

K_L = Langmuir constant related to energy of adsorption

q_e =adsorption capacity at equilibrium

Langmuir constants can be evaluated from the linearized equation by plotting $\frac{C_e}{q_e}$ against C_e. The value of K_L which can be obtained from the intercept of the plot and is $\frac{1}{K_L}$, and also a_L from the slope as $\frac{a_L}{K_L}$.

Freundlich Isotherm

This isotherm is also a two parameter isotherm model and the oldest module which describes non ideal and reversible adsorption process. Unlike the Langmuir Isotherm model, the Freundlich model is not restricted the formation monolayer adsorbate on the surface of adsorbent (Foo and Hameed, 2010). This model also assumes surface heterogeneity and as such can be applied in multilayer adsorption (Chen, 2015). It also assumes that adsorbate concentration increases with increase in concentration of adsorbate on the surface of adsorbent. The non-linearized form of the Freundlich equation is;

$$q_e = K_F \, C_e^{b_F} \tag{2.3}$$

Where K_F and b_F are Freundlich constants. b_F = heterogeneity factor and K_F = adsorption capacity.

The linearized form of the Freundlich Isotherm model is expressed as;

$$\ln q_e = \ln K_F + b_F \ln C_e \tag{2.4}$$

It is worthy to mention that both Langmuir and Freundlich equilibrium data do not fit well into single set of constants over wide range of concentration.

Three parameter isotherms

These are isotherms usually developed to feature both Langmuir and Freundlich isotherms by incorporating three parameters. These three parameter isotherms have applicability in both heterogeneous and homogeneous system over wide range concentrations. Notable among them are; The Redlich–Peterson isotherm, the Tempkins, the Toth Isotherm among others.

The Redlich–Peterson isotherm

This isotherm model theory has postulated an equation which incorporates three parameters and may be used to express adsorption equilibria over wide range of concentration (Allen et al., 2004). The empirical equation is expressed as;

$$q_e = \frac{K_R C_e}{1+a_R C_e^{\beta}} \tag{2.5}$$

where $\beta \leq 1$

This empirical equation is linearised at low surface coverage and transformed to Freundlich and Langmuir at high adsorbate concentration and when $\beta=1$ respectively. The linearised form of the equation is expressed as;

$$\ln\left[\frac{K_R C_e}{q_e} - 1\right] = \ln a_R + \beta \ln Ce. \tag{2.6}$$

Hence, a plot of $\ln[\frac{K_R C_e}{q_e} - 1]$against ln Ce gives a straight line with slope β and intercept a_R (Allen et al., 2004).

The Tempkins model isotherm

This isotherm assumes that adsorbate – adsorbent interactions reduce the heat of adsorption of all molecules in the film linearly with coverage (Allen, Mckayb, & Porter, 2004). The non-linear form of Tempkin isotherm is expressed as;

$$q_e = \frac{RT}{b}(\ln A C_e) \tag{2.7}$$

The expression can be linearized as;

$$q_e = \frac{RT}{b}\ln A + \frac{RT}{b}\ln C_e$$

where $B = \frac{RT}{b}B$ is related to heat of adsorption of molecules. (2.8)

2.10 Adsorbent

Adsorption is the sticking of molecules of gas, liquid, or dissolved solids to a surface. The solid, liquid or gas in the process of adsorption on which the adsorbate (substance which has been adsorbed) accumulates is termed an adsorbent.

2.10.1 Types of Adsorbents

The main types of adsorbents used are: activated alumina, activated carbon, molecular sieve carbon, molecular sieve zeolites, silica gel and polymeric adsorbents. Some bio materials such as tea leaves and coffee could also serve as adsorbents. Adsorbents could occur naturally e.g. some zeolites or could be manufactured (such as activated carbons). An adsorbent material has specific characteristic that include porosity, pore structure and nature of adsorbing surfaces. Distribution of pore sizes in adsorbents is throughout the solid. Classification of pore sizes include 3 ranges:(a) macropores–these have "diameters" in excess of 50-nm, (b) mesopores (also known as transitional pores) –with "diameters" in the range 2 – 50nm, and (c) micropores–these have "diameters" which are smaller than 2nm.

Adsorbents such as carbon, silica gels and alumina, are in the non-crystalline solid state of a typically crystalline solid, have no definite form or clear shape and contain complex networks of inter-connected micropores, mesopores and macropores. In contrast, pores in zeolite adsorbents have precise dimensions. Some typical requirements for commercial adsorbents are (Buekens and Zyaykina, 2009):

- Must be highly porous and have high internal surface.
- Should have a high adsorption efficiency in a wide range of adsorbate concentrations.

- A good balance between macro-pores (for fast internal transport) and micro-pores (for large internal surfaces).
- Chemical structure unable to be adsorbed by water (for treatment of moist gases) unless the adsorbent is to be used as a desiccant.
- Heat resistant stability unaffected by a cyclic regeneration.
- Mechanical integrity during handling.
- Low pressure drop over the adsorbed bed.
- Inexpensive (and – eventually – disposal) of adsorbents.

2.10.2 Tea Leaves as Adsorbents

Sharmila and Muthusamy (2013) investigated the removal of heavy metal from industrial effluent using bio adsorbents (*Camellia sinesis*) and concluded that spent tea leaves adsorbed lead more than cadmium. Also, Zuorro and Lavecchia (2010) studied the removal of lead ions from aqueous solutions using spent tea leaves. The conclusion of the investigation proved the feasibility of the use of spent leaves on the removal of lead ions from aqueous solutions. These show that spent tea leaves could also act as adsorbents. The study also proved that certain mechanisms such as surface adsorption, chemisorption, complexation, ion exchange, micro precipitation and metal hydroxide condensation greatly influence waste substances sticking to heavy metals (especially lead) (Demirbas, 2008).

To understand this phenomenon, it is important to establish the functional groups involved in the process of adsorption. It is postulated that charges on functional groups found in proteins or cellulose, hemicellulose, pectin and lignin play a role in heavy metal removal (Basso et al., 2002; Pagnanelli et al., 2003). Reactions occur to substitute hydrogen ions or give out an electron pair that form metal complexes with the metal-binding sites (Ofomaja and Ho, 2007; Demirbas, 2008). Lead is a metal known to bind strongly with proteins and this association forms the fundamentals of lead-induced cytotoxicity. Electrostatic and covalent bonds are known to effect the lead protein interaction. Electrostatic bonds exist between the positive charges on the lead ions and the negative charges on the protein surface. Additionally, covalent bonds bind the lead ions and the N-, O- or C- on the protein group (Ghering et al., 2005; Srinivas et al., 2007).

CHAPTER THREE

METHODOLOGY

3.1 Introduction

This section presents the methods used for the analysis of waste cupel samples obtained from selected assay laboratories. The main objective was to render lead contaminated cupels less toxic. The methodology has been grouped into three stages including mineralogical and chemical characterization of the waste cupels, granulochemical analysis, acid lead leaching and biosorption behaviour of lead from leachates.

3.2 Sampling and Sample Preparation

Waste cupels were obtained from two commercial assay laboratories in Ghana. The two laboratories treat different ores – oxide and sulphide ores, respectively. Waste cupels generated from the treatment of oxide ores labelled “CWO” whilst waste cupels generated from the treatment of sulphide ores labelled “CWS”. Both samples were crushed using laboratory mortar and pestle before grinding with a pulveriser. The powders were thoroughly mixed and jones riffle sampler was used to divide the powders before storing in sample bags for further analysis.

3.3 Chemical Analysis

The chemical compositions were determined using Inductively Coupled Plasma Mass Spectrometer (ICP MS Agilent 7900). Five (5) grams of the waste cupel samples were weighed into 50 mL digestion tube. 2.5 mL nitric acid and 2.5 mL hydrochloric acid was added and the mixture placed on a hot block which has been pre-heated to 105 ^{o}C for 40 minutes. 10 mL of deionize water was added and returned to the hot block for 80 minutes. The mixture was allowed to cool, and diluted with deionize water to the 50 mL mark. Metal concentrations in the sample were read against appropriate blanks and standard solution. Measurements were conducted in triplicates.

Additionally, over sizes of 100 µm, 600 µm, and 2360 µm from the two waste cupel streams were sampled, digested and lead concentration determined using Flame Atomic Absorption Spectrometer (AAS), Model-Nov AA 400p. 1 gram of the waste cupel powder was weighed into 50 mL digestion tube. 1 mL distilled water was added and shaken well for effective mixing. 4 mL of nitric acid and perchloric acid was added using ratio of 1:1, followed by 5 mL sulphuric acid and thoroughly mixed. The tubes were put into a digestion block and heated at 200 ^{0}C for 30 minutes and cooled to room temperature. The mixture was topped up with distilled water to the 50 mL mark. The digest was transferred into pre-acid washed PET bottles and stored below 4 ^{0}C before analysis. A reagent blank was also prepared using the fresh uncontaminated cupel. A minimum lamp warm up time of 15 minutes was required. Stability was greatly improved by having the flame burning for at least 10 minutes before use. Once warmed up and very stable, the 238.3 nm line was employed since the 217.0 nm line may require non atomic absorption corrections to be made. Certified lead nitrate standards used include 1 mg/L, 2 mg/L and 3 mg/L.

3.4 Mineralogical Analysis

PAN analytical Empyrean Series 2 X-Ray Diffraction (XRD) was used to identify the crystalline phases present in the waste cupels. The XRD analysis was carried out with Cu K-alpha radiations wavelength of 1.54060, K-Alpha2 wavelength of 1.54443 and K-Beta wavelength of 1.39225. Generator settings were set at 45 kV and 40 mA. Measurements were conducted at ambient temperature (~25 ^{0}C). Samples were scanned from 10 ^{0} to 90 ^{0} at a scan rate of 0.04 ^{0} per minutes.

3.5 Granulochemical Test

500 g each of dry powdered waste cupels were passed through 100, 150, 425, 600, 1180, and 2360 µm sieves assembly (see Figure 3.1) and agitated for 15 minutes. The masses of powder retained on each sieve were obtained and the percent retained on each sieve was calculated. Lead concentrations were determined for the following particle size ranges: -100 µm, +100 µm to -600 µm and +600 µm to -2360 µm for the waste cupel samples using Atomic Absorption Spectrometer (AAS).

Figure 3.1 A set of stacked sieves for analysis

3.6 Acid Leaching of Lead from Waste Cupel

It has been reported that HCl and HNO_3 can leach about 42 % and 82 % of lead respectively from printed circuit board (Ranitović et al., 2016). However, the process is usually obstructed by leaching of other reactive metals that might be present. Also Magalhães et al. (2012) established that nitric and hydrochloric acids are the most economically and technically suitable leachants for the extraction of lead from waste crucibles. As such, acid leaching was employed in dissolving lead from waste cupels.

1 gram each of sample CWO and CWS were weighed into separate beakers. A mixture of 2.5 mL of 65 wt % HNO_3 and 10 mL of 37 wt % HCl was added to each sample and heated at 95 ^{0}C for 15 minutes. The clear filtrates were collected into a 100 mL volumetric flask. The residues and filter papers were washed with 5 mL hot HCl and 5 mL hot deionized water in their respective volumetric flasks. Residues were digested with 5 mL HCl and the digestate added to the filtrate in their respective volumetric flask. The filtrates were topped up to the 100 mL mark and lead concentrations determined using AAS.

3.7 Biosorption of Spent Tea Leaves (*Camellia sinensis*)

Spent tea leaves were used as adsorbent. Spent tea bags were collected, washed with distilled water and dried in an oven at 70 ^{0}C for 24 hours before storing in polythene bags for the metal uptake experiment. 8 grams of the dried tea leaves was contacted with 200 mL of the lead leachate in a 500 mL Erlenmeyer flask. The flask content was conditioned to a pH of 5 with addition of 1 M NaOH whiles stirring was maintained at 100 rpm. Adsorption was conducted at room temperature (~25 ^{0}C). Samples were collected at pre-determined intervals from 30 to 300 min at 30 minutes intervals and the residual metal determined using an AAS. The metal uptake which shows the rate of the adsorption by the spent tea leaves was calculated using the equation

$$Q = \frac{(C_i - C_f)V}{1000M} \quad (3.1)$$

Where Q denotes the specific metal uptake (mg/g), V is the volume of the metal solution, C_i and C_f are the initial and final concentrations of lead ion in solution (mg/L), and M is the weight of the dry tea leaves used for the adsorption. The biosorption efficiency (R %) was calculated as follows:

$$R\ \% = \frac{100(C_i - C_f)}{C_i} \qquad (3.2)$$

All experiments were conducted in triplicates and a repeatability tolerance of ± 5 % used for calculation of results.

Analysis of Spent Tea Bags using Fourier Transform Infrared Spectroscopy (FTIR)

Tea bags (both spent and impregnated with lead after adsorption) were analysed with FTIR to assess the functional groups. Serial number of FTIR used was 102669 and model BRUKER Platinum ATR FTIR 1003271/06. Blank tea bags were washed severally with distilled water and dried in an oven overnight at 70^0C. Spent tea bags used for adsorption were also allowed to dry and both samples sent for ATR FTIR analysis. The Attenuated Total Reflectance technique avoids further preparations of sample. Thus, the samples were used for the analysis without any further preparation. Samples were ground and pressed onto the ATR Element surface using a mechanical clamp. This was done to ensure good contact between the sample and the surface of the ATR element. Results were obtained in spectrum graphs.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, results obtained from the waste cupel characterization, acid leaching and biosorption behaviour of spent tea leaves are presented. Two different cupel waste samples were investigated in this work. The samples were labelled as CWO and CWS, respectively. CWO samples were obtained from cupels used to analyse oxide ores whereas CWS samples were obtained from cupels used to analyse complex/sulphide ores. Oxide or free milling ores are gold ores that do not contain sulphide minerals whereas complex ores are ores with gold occluded in sulphides like pyrites. Unused cupels were also characterized for comparison.

4.2 Chemical Characterization

Table 4.1 shows the chemical composition of fresh and waste cupels investigated. Both laboratories used MgO cupels as indicated by the relatively high concentrations of Mg (105.3 mg/kg) in both samples. The concentration of Mg decreased from 105.3 mg/kg to 18.4 mg/kg and 18.5 mg/kg in CWO and CWS samples, respectively, with associated significant increase in lead concentrations. The concentration of lead was slightly higher in CWS (113,931.9 mg/kg) than in CWO (108,552.7 mg/kg). Other variations in chemical compositions in the two waste cupel samples included Cr, Co, Cu, Zn, and Ag. These elements were not present in the fresh cupels. However, they are usually associated with the ore and subsequently the lead button. It is also interesting to know that the concentration of Ag was 7.1 mg/kg in CWO sample but was absent in CWS sample. Loss of Ag into cupels has been attributed to insufficient Pb/Cu ratio (Martinón-Torres and Rehren, 2005, Hammond, 1997). Insufficient lead present in the charge results in part of the oxidised copper present as Cu_2O rather than as $PbO.Cu_2O$ (Bayley and Eckstein, 2006). In effect, pure lead oxide or $PbO.Cu_2O$, a significant amount of silver (Ag) could be dissolved in Cu_2O. Thus, a low Pb/Cu ratio results in the formation of Cu_2O which transports the silver into the cupel structure.

Furthermore, from Table 4.1, CWS sample showed lower concentrations of minor elements as compared with CWO sample. These differences could be attributed to chemical composition differences in ore type.

Table 4.1: Chemical composition (mg/kg) of fresh and waste cupels samples determined using ICP-MS/ICP-OES analysis

Element	CWO	CWS	Fresh Cupel
Mg	18.4	18.5	105.3
Cr	10.9	4.6	-
Co	0.7	0.4	-
Cu	20.8	9.2	-
Zn	4.0	2.7	-
Ag	7.1	-	-
Pb	108552.7	113931.9	-

4.3 Mineralogical Characterization

Figures 4.1 to 4.3 show the XRD analyses of fresh and waste cupels (CWO and CWS). Fresh cupels were made from magnesite which corroborates the chemical composition results shown in Table 4.1. Magnesia cupels are commonly used due to its excellent properties including higher heat capacity, higher thermal conductivity, and higher strength as compared to bone-ash or cement cupels. They are also stronger than bone-ash cupels. Magnesia cupels decrease loss of silver by cupel absorption during cupellation(Shepard and Dietrich, 1940, Martinón-Torres and Rehren, 2005).

From Figures 4.2 and 4.3, it is evident that the waste cupel samples (CWO and CWS) were contaminated with lead oxide after the cupellation process. These results confirm the chemical analysis results presented in Table 4.1. Furthermore, no evidence of PbO - Cu_2O reaction was observed even though Cu was detected in both samples. Thus either the Cu_2O existed in amorphous state or the concentration was below detectable limit of the XRD used. It is also evident that CWO sample exhibited sharper peaks compared with CWS sample. Furthermore, the relative intensities of the peaks were lower in CWO compared to CWS sample. This is due to the relatively higher concentrations of minor elements found in CWO sample. Thus variation in the mineralogical composition affected the crystallinity and peak intensities of the phases present in the waste cupels.

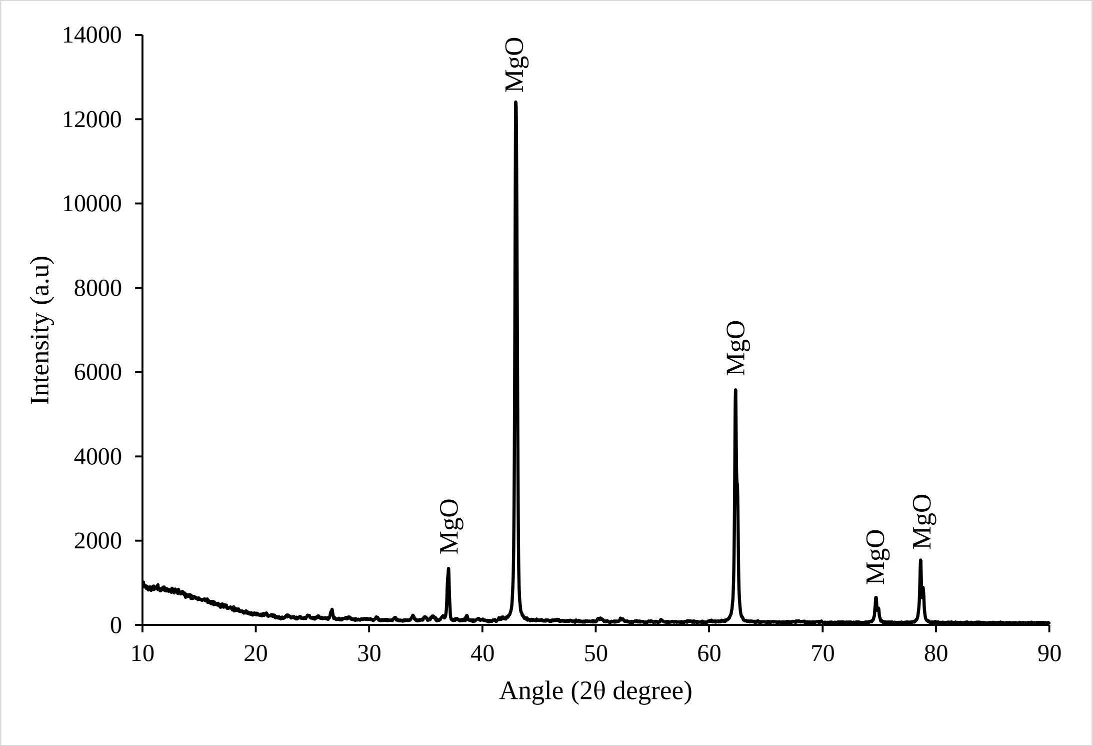

Figure 4.1: XRD pattern of fresh cupel showing MgO as major crystalline phase

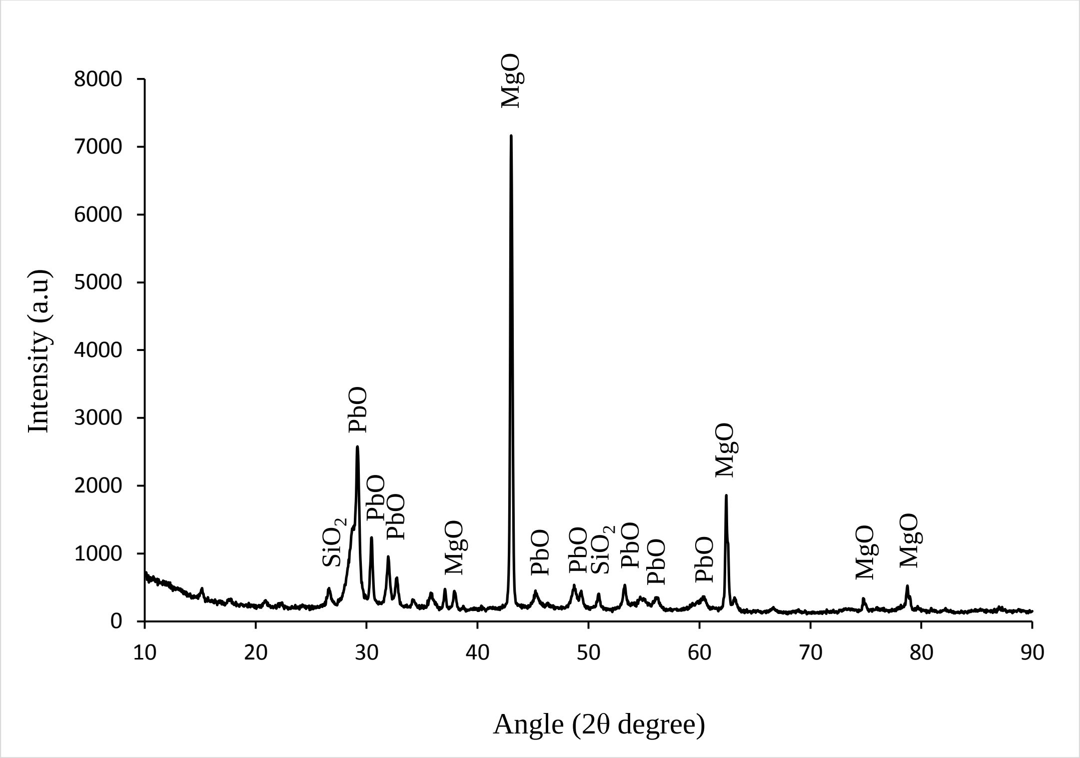

Figure 4.2: XRD pattern of CWS sample of waste cupels showing PbO, MgO and SiO_2 as the major crystalline phases

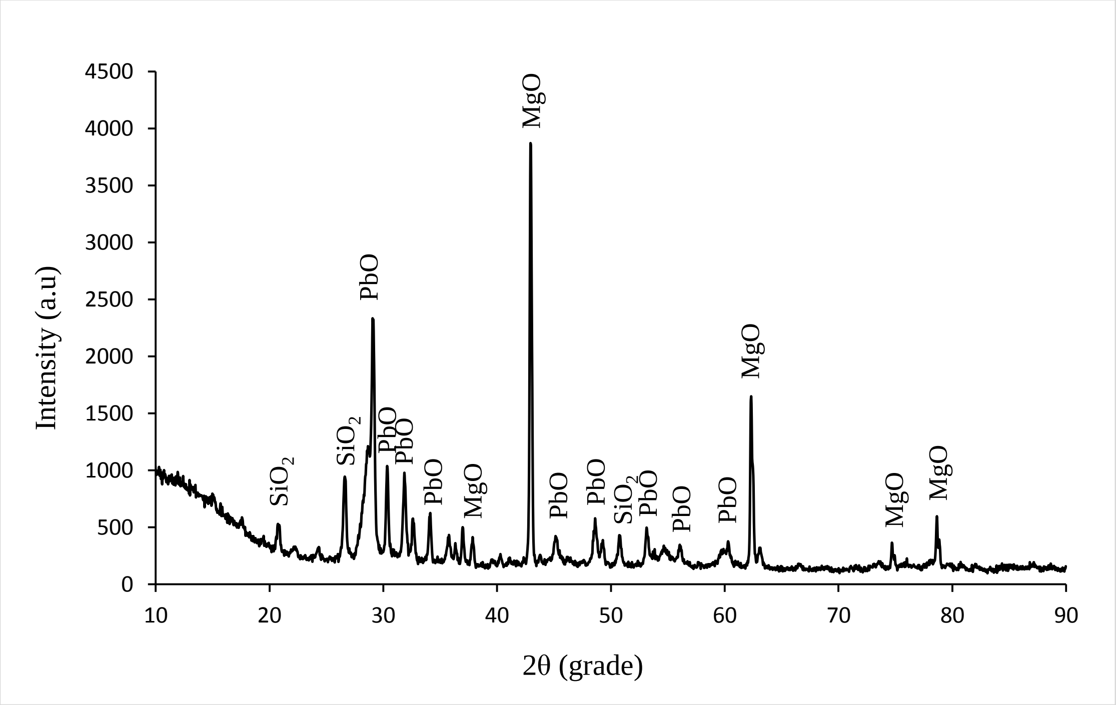

Figure 4.3: XRD pattern of CWO sample showing PbO, MgO and SiO_2 as the major crystalline phases

Figure 4.5 shows the results of particle size distribution as a function of lead concentration. It was observed that the lead concentration in CWS decreased with increasing particle size whilst in CWO, lead concentration increased with increasing particle size. As mentioned earlier, the crystallinity of CWO is higher than in CWS. Crystalline particles are harder and more difficult to reduce their particle sizes due to the existence of strong bonds in the crystal structure. Thus the lead could have been trapped in the larger crystallite sizes of CWO samples and therefore unable to report to the finer particle size range. To prove this, Scherer's equation was used to calculate the crystallite sizes of CWO and CWS samples using the following equation:

$$D_p = \frac{K\lambda}{B\cos\theta} \tag{4.1}$$

where D_p is the average crystallite size (µm), K is the Scherer constant (0.94 for spherical crystallite with cubic symmetry, λ is the X-ray wavelength (1.54178Å), B is FWHM of XRD peak, and Θ is the XRD peak position.

It was observed that MgO crystallite size in waste cupel samples were 62.53 µm and 45.76 µm for CWO and CWS, respectively. Thus, the MgO mean crystallite size in CWO sample was higher than that of CWS samples. The larger MgO crystallite sizes in CWO have the tendency to trap smaller lead oxide crystallite sizes (39.43 µm) and therefore prevented PbO particles from reporting to the finer particle size range. The average crystallite size of PbO in CWS sample was 42.81 µm which is close to the crystallite size of MgO in CWS. Thus, it will be easier for the PbO to be entrapped in the larger MgO crystallite in CWO sample than in CWS. The results suggest that, depending on the ore type, there is the tendency to have differences in lead concentration in various size fractions. Thus there is the need to handle these two waste streams differently, especially during crushing and milling stages.

4.4 Granulochemical Analysis

Figure 4.4 shows the particle size distribution of waste cupel powders. Sample CWS had finer particle size distribution than sample CWO. About 23 % of CWO particles were above 2360 µm sieve size. Furthermore, about 26 % of CWO and 31 % of CWS powders had particle sizes less than 100 µm. Thus samples investigated were mainly coarse. The difference in the size distribution could be attributed to the difference in samples crystallinities. As shown in Figures 4.2 and 4.3, CWO is more crystalline than CWS and therefore size reduction was more difficult compared to CWS. It has been reported that, smaller particle sizes have higher concentration of lead (Magalhães et al., 2012). Thus the effect of particle sizes on lead distribution was investigated.

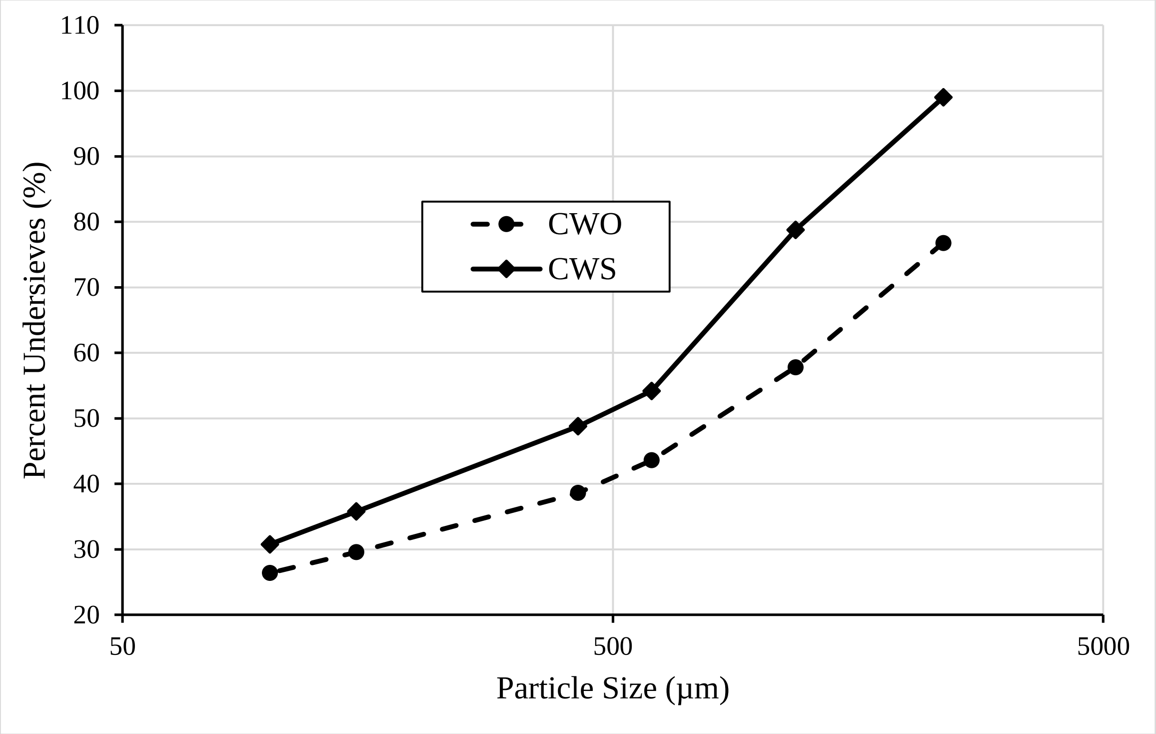

Figure 4.4: Particle size distribution of CWS and CWO samples

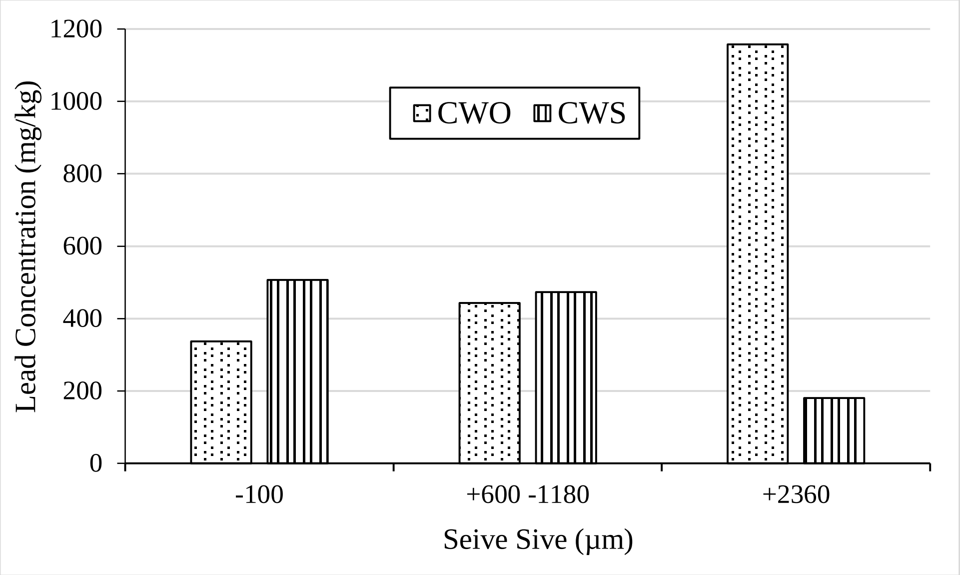

Figure 4.5: Lead concentrations as a function of size fractions in investigated samples

4.5 Acid Leaching of Lead

Lead was leached from waste cupel samples and the leachate contacted with spent tea leaves at varying contact time. A study by Ranitovic et al., (2016) showed that HNO_3 could be used to leach 82 % of lead from waste printed circuit boards independently whereas HCl dissolved about 42 % Pb from the same sample. However, the process is usually hindered by counter reactions and the dissolution of other reactive metals that might be present in the sample. Furthermore, Magalhães et al. (2012) established that HNO_3 and HCl acids are the most economically and technically suitable leachants for the extraction of lead from waste crucibles. Therefore, the sequential use of the different leachants was adopted in this work to establish the optimization of Pb dissolution.

HNO_3 and HCl were used as lixiviates. The two samples (CWS and CWO) were digested and analysed using an Atomic Absorption Spectrometer (AAS). In order to determine the biosorption efficiency, the initial average lead concentrations in both samples were determined and found to be 55640 mg/kg and 46300 mg/kg for CWO and CWS, respectively. The higher concentration of lead in CWO sample corroborate the results shown in Figure 4.5.

4.6 Biosorption Efficiency of Lead (II) using Spent Tea Leaves

Figure 4.6 shows lead adsorption using spent tea leaves as a function of time whilst Figure 4.7 shows the corresponding biosorption efficiency. It could be observed that the concentration of lead decreased drastically within the first 180 minutes of contact time for sample CWS after which the lead concentration in the leachate increased slightly. For CWO sample, lead concentration decreased significantly within the first 30 minutes. Thereafter, a slight decrease in lead concentration was observed up to 180 minutes of contact time after which lead concentration increased slightly. Furthermore, lead concentration in CWS leachate remained higher than that of CWO after adsorption at all contact times. Thus, adsorption was more efficient in CWO leachate which had higher initial lead concentration (55,640 mg/kg) than in CWS leachate (46,300 mg/kg).

The biosorption efficiency was above 99 % in CWO leachate and less than 98 % in CWS (see Figure 4.7). It has been reported that biosorption of lead increases with increasing lead concentration (Ahluwalia and Goyal, 2005). As the tea leaves became saturated with lead and the lead concentration in the leachate decreased, the biosorption efficiency decreased in both samples. Figure 4.8, illustrates lead ions binding to the amide groups. The lead ions bind strongly and faster to the amide groups on the protein component of the tea bag due to the fact that there are more negatively charged amide functional groups in the tea bag thereby providing more binding sites for lead (positively charged ions). In addition to this fact, lead has a strong affinity for protein. This further increases the rate of adsorption of the tea bags thus a drastic decrease in the concentration of lead upon contact with the tea bags within a period of time.

It is however interesting to note an increase in the concentration of both CWS and CWO after adsorption time of 210 minutes. With this unusual increase, further studies would have to be conducted to establish the trend.

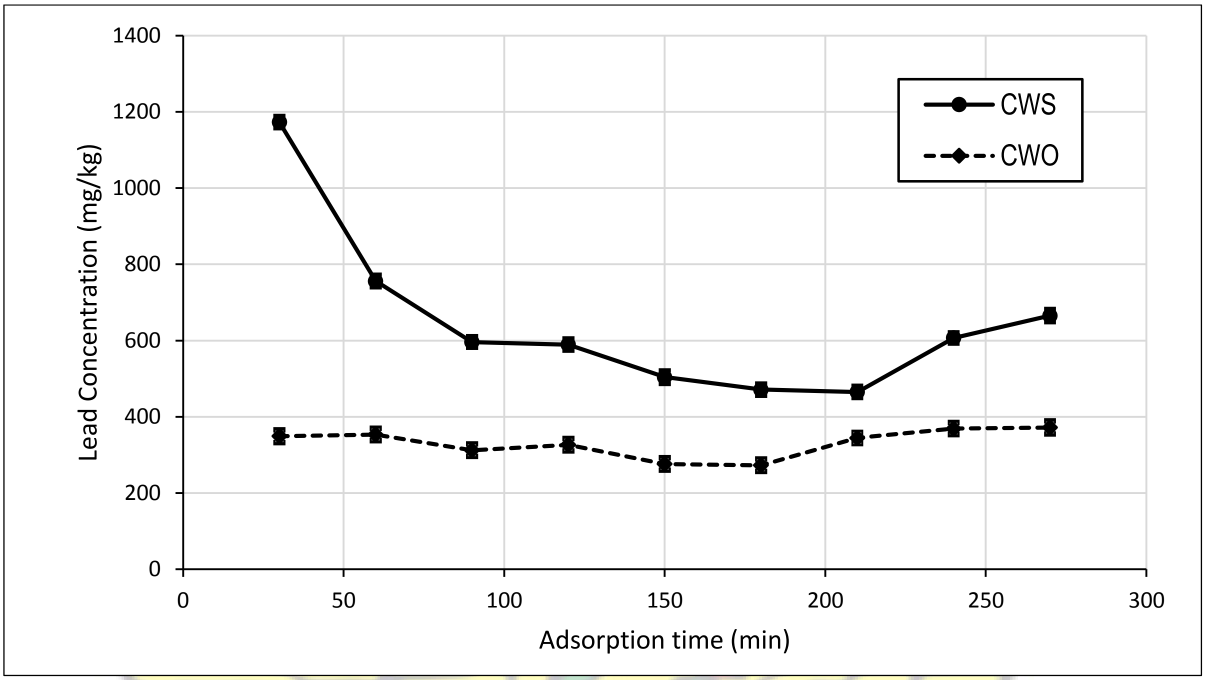

Figure 4.6: Concentrations of CWS and CWO after adsorption with used tea bags

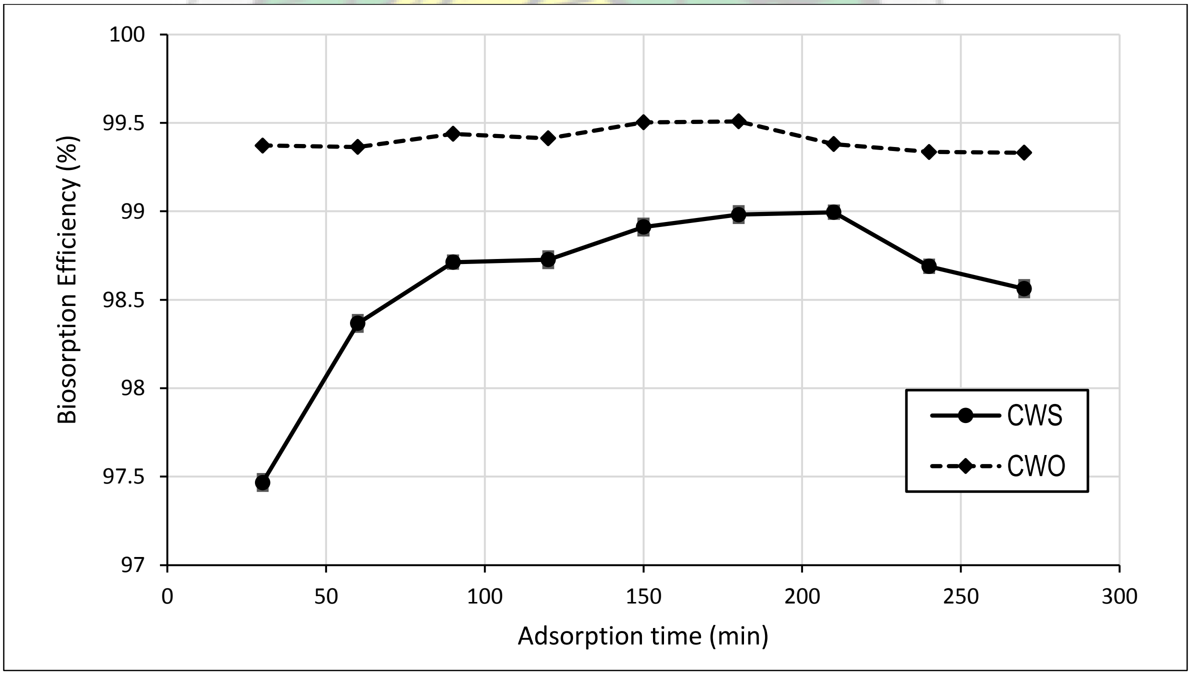

Figure 4.7: Biosorption efficiency of spent tea leaves for CWS and CWO

Lead adsorption from solution by waste tea leaves is a physicochemical process which utilizes ion exchange, adsorption and complexation, and precipitation mechanisms to remove or extract organic and inorganic substances from solution (Fomina and Gadd, 2014). It has been reported that dried biomass of waste tea leaves can remove up to 96 % lead from a 20 mg/L of solution (Ahluwalia and Goyal, 2005).

Tea leaves have some functional groups such as hydroxide, amide and amine, which have strong affinity for metal ions. The functional groups therefore serve as binding sites for lead during adsorption (Ahluwalia and Goyal, 2005). Figure 4.8 shows the Fourier Transform Infrared Spectrum (FTIR) analysis of spent tea bag before and after adsorption of lead. Appendix A4 shows the wavenumbers and the various functional groups before and after adsorption process.

Spectral analysis of pre and post adsorption indicated changes in peaks of functional groups. This is an indication that the functional groups were responsible for the biosorption. The spectral analysis reveals that the bonded hydroxyl functional groups and secondary amine functional groups were the key functional groups involved in the biosorption of lead with waste tea bags (Malkoc & Nuhoglu, 2006). The shifts in band and peak intensities after adsorption signifies binding of by functional groups with lead during the adsorption process (Ahluwalia & Goya, 2005).

A slight shift in peak from 3334.01 cm^{-1} before adsorption to 3327.73 cm^{-1} shows that the OH^{-} group has sites for adsorption hence the trend noticed. Also a noticeable shift from 1518.46 cm^{-1} to 1542.30 cm^{-1} for the secondary amines NH^{-} shows there were more bonding sites for adsorption by the secondary amines. The OH^{-} group and the NH^{-} group are primarily responsible for adsorption due to the affinity for the positively charged Pb ions in solution.

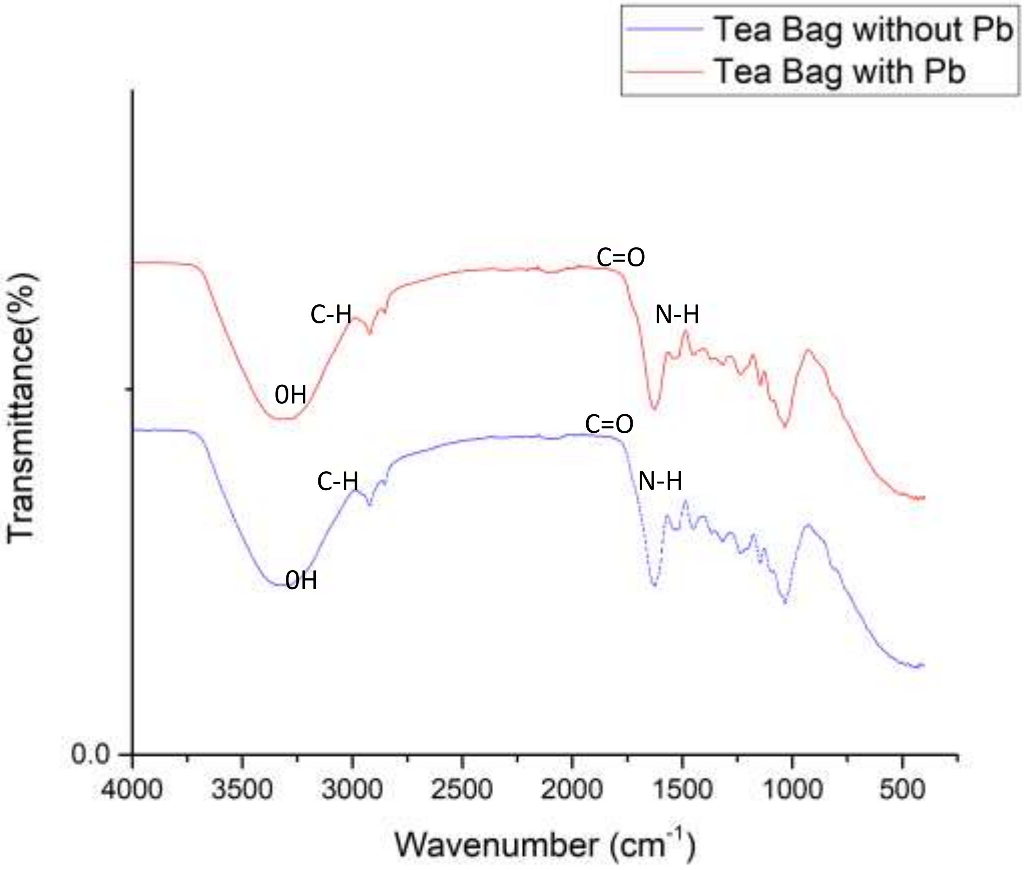

Figure 4.8 FTIR Scan of Spent Tea Bags with Lead (Pb) and without Lead (Pb)

Adsorption of lead using tea leaves is relatively cost effective method that utilizes dead or living biological material including microorganisms, agricultural wastes and natural residues (Fomina and Gadd, 2014). The adsorption process is natural, economical and relatively in abundance as waste from cafeterias. Figure 4.9 shows the chemsketch of complex structures depicting waste tea leaves impregnated with lead using ACD. The figure illustrates adsorption of lead ions onto the amide functional group.

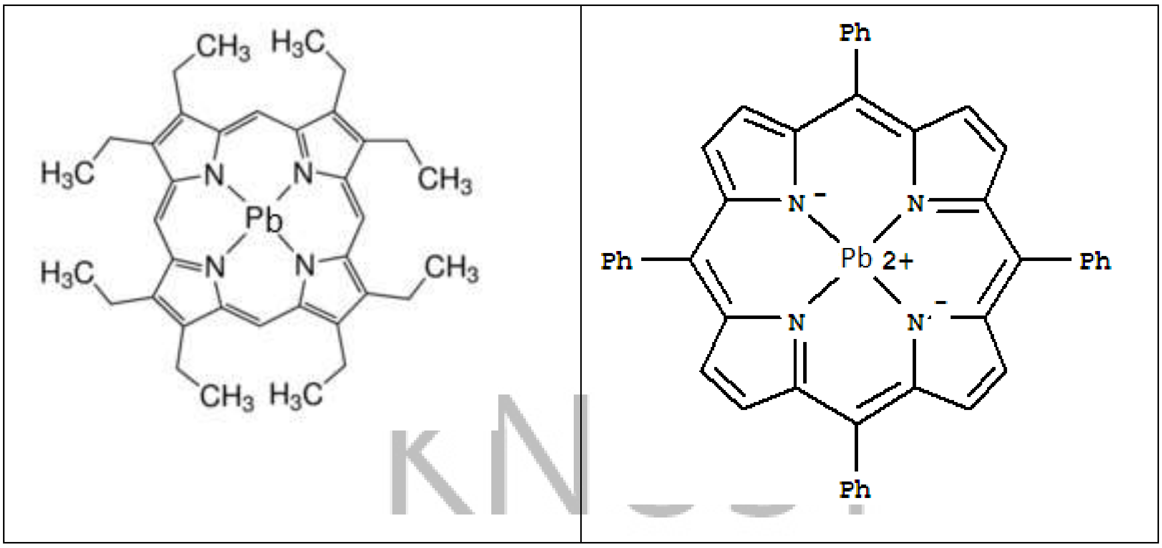

Figure 4.9: Adsorption of lead ions onto the amide functional group (source: chemsketch, ACD)

The specific metal uptake was calculated and the results are shown in Table 4.2. The specific metal uptake for CWO remained constant at 1.39 mg/g within contact time of 240 minutes using 10 mL of solution. The specific metal uptake decreased to 0.83 mg/g when 6 mL of solution was used. Thus specific metal uptake is a function of volume of lead leachate for a given biomass of adsorbent. Similar observations were made for CWS where the specific metal uptake was 1.15 mg/g within contact time of 240 minutes using 10 mL of solution and decreased to 0.69 mg/g when the volume of solution was 6 mL. From the observations above, biosorption efficiencies and specific metal uptake were affected by the initial lead concentration and volume of leachate. The mechanisms of adsorption were tested by fitting the specific metal uptake values in the Langmuir and Freundlich adsorption models.

Table 4.2: Specific metal uptake (mg/kg) for CWO and CWS

Time (min)	**CWO**	**CWS**
30	1.39	1.14
60	1.39	1.15
90	1.39	1.15
120	1.39	1.15
150	1.39	1.15
180	1.39	1.15
210	1.39	1.15

4.7 Biosorption Mechanism

Adsorption isotherms were used to elucidate the adsorption mechanism. Lead uptake capacity of spent tea leaves was investigated using varying lead concentrations on a fixed biomass. Experimental data obtained were fitted into the Langmuir and Freundlich adsorption models and the best fitted model was used to explain the biosorption mechanism. These two models have been used extensively to investigate adsorption mechanisms (Crittenden et al., 2012).

The Langmuir model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites and can be represented linearly by the equation:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \qquad (4.1)$$

Where C_e is the concentration of lead after adsorption (mg/L), q_e is the specific metal uptake (mg/g), b and q_{max} are constants relating to energy of adsorption and maximum adsorption capacity, respectively. The Freundlich model assumes a heterogeneous, non-uniform surface and can be represented linearly by the equation

$$\ln q_e = \ln K_f - \frac{1}{n} \ln C_e \qquad (4.2)$$

Where K_f and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity, respectively.

Figure 4.10 shows the results of the Langmuir isotherm model whilst Figure 4.11 shows the results for the Freundlich isotherm model for CWO and CWS samples, respectively. Langmuir isotherm parameters for adsorption of lead onto spent tea leaves for both CWO and CWS were determined from the slopes and intercepts of their plots. Results revealed that Langmuir adsorption isotherm was the best model for the lead ion adsorption onto spent tea leaves. Both had R^2 of 1. The maximum adsorption capacity (q_{max}), however, was higher in CWO (1.390 mg/g) than in CWS (1.134 mg/g). Thus, the binding sites for lead adsorption on spent tea leaves are uniform and have similar adsorption energies leading to a mono layer adsorption process (Chung et al., 2015).

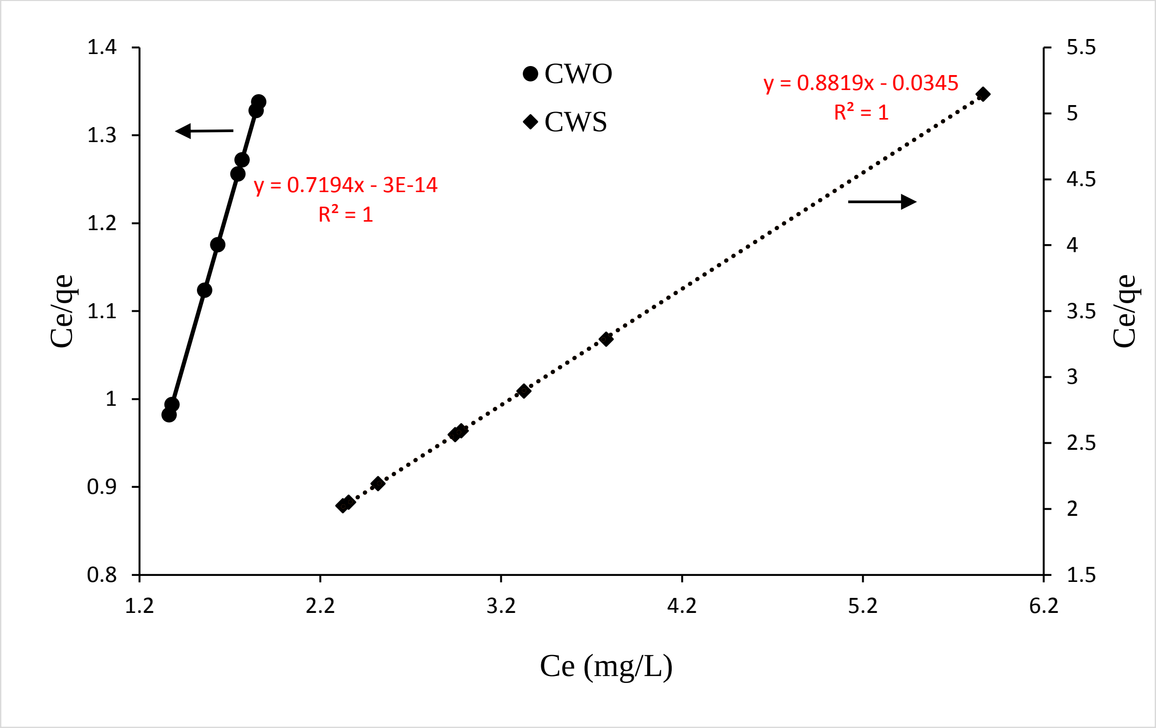

Figure 4.10: Experimental data of spent tea leaves fitted to linearized forms of Langmuir isotherm model

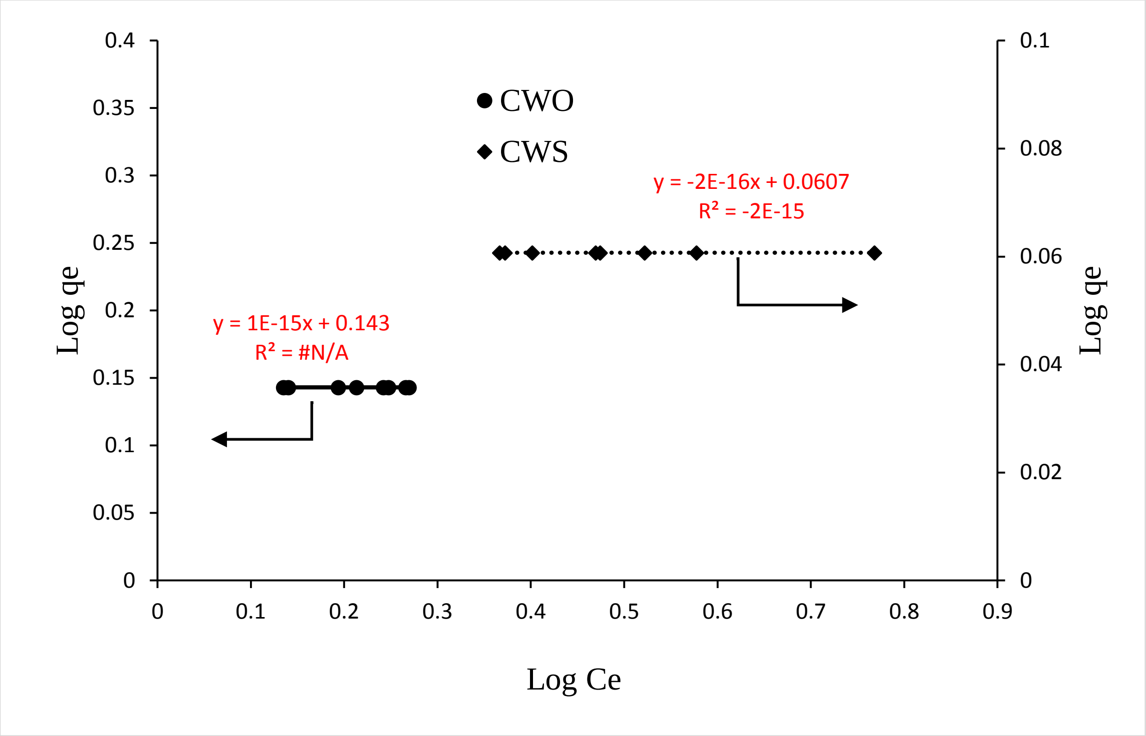

Figure 4.11: Experimental data of spent tea leaves fitted to linearized forms Freundlich isotherm model

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

A study of the characterization of cupel waste from two commercial fire assay laboratories in Ghana has been successfully conducted. The effect of oxide and sulphide ores on the leaching and biosorption characteristics of lead from waste cupels using spent tea leaves (*Camellia sinensis*) has been investigated. Results show that cupel wastes are highly contaminated with lead (in excess of 10000 mg/kg or 10000 ppm) which is above the Ghana EPA maximum permissible level of 0.10 ppm for Mining and Minerals Processing discharges into Natural Water Bodies and therefore can be classified as toxic waste. Lead concentrations in CWO sample increased as particle sizes increased whilst in CWS sample, lead concentration decreased as particle sizes increased.

The efficiency of biosorption of lead onto spent tea leaves initially increased and thereafter remained almost constant. The efficiency was higher in CWO than in CWS due to higher lead leachate concentration in the former sample. The decrease in the rate of adsorption was due to the available active sites occupied by the lead ions and hence no further adsorption was possible. Adsorption in both samples fitted well with Langmuir isotherm model, with CWO sample having its adsorption capacity than CWS sample. It can be concluded that, in the treatment of cupel wastes, the ore type affects the lead distribution in the particle size ranges, leaching behaviour and biosorption mechanism of spent tea leaves. The results show that spent tea leaves can be used to reduce the lead concentration in waste cupels to tolerable limits before disposal to landfill sites.

5.2 Recommendation

From the viewpoint of sustainability, it is recommended that, further experiment is conducted on green and yellow tea to compare efficiency with black tea (e.g. Lipton Yellow Label Tea). Also, a research conducted into cupels used to treat other ore types apart from the oxides and sulphide ores can be investigated. It is also recommended that lead should be recovered from pregnant tea bags for industrial use. Further studies should be conducted to validate concentration of lead trend observed in over sieves of CWO sample as well as that noticed in the biosorption efficiency.

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APPENDIX A

Appendix A1

Equilibrium isotherm data values for CWO sample

q_e	**Ce**	**Ce/q_e**
1.39	1.746	1.256115
1.39	1.768	1.271942
1.39	1.562	1.123741
1.39	1.634	1.17554
1.39	1.381	0.993525
1.39	1.365	0.982014
1.39	1.86	1.338129
1.39	1.846	1.328058
0.83	1.723	2.065904

Appendix A2

Equilibrium isotherm data values for CWS sample

q_e	Ce	Ce/q_e
1.14	5.865	5.144737
1.15	3.781	3.287826
1.15	2.98	2.591304
1.15	2.947	2.562609
1.15	2.52	2.191304
1.15	2.357	2.049565
1.15	2.326	2.022609
1.15	3.327	2.893043
0.69	3.034	4.397101

Appendix A3

Coefficient of correlation (R^2) in the adsorption models for CWO and CWS samples

SAMPLE ID	LANGMUIR	FREUNDLICH
CWO	1.00000	-
CWS	0.99995	0.69563

Appendix A4

FTIR Spectral features of tea used for adsorption

Wavenumber (cm^{-1}) Before Adsorption	Wavenumber (cm^{-1}) After Adsorption	Differences in wavenumbers	Functional group Assignment
3334.01	3327.73	6.28	OH Hydroxyl
2919.29	2918.57	0.72	C-H stretching
2851.14	2850.62	0.52	C-H stretching
1626.52	1627.34	-0.82	C=O stretch
1518.46	1542.30	-23.84	N-H secondary amine
1449.67	1449.15	0.52	Symmetric bending CH$_3$
1316,23	1315.83	0.4	Symmetric bending CH$_3$
1234.25	1235.72	-1.47	-SO$_3$ Stretching
1145.47	1145.34	0.13	C-O Stretching
1033.76	1033.24	0.52	C-O
429.27	-	-	-CN stretching