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Removal and Recovery of Heavy Metals by Nickel Smelter Slag

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A thesis submitted in partial fulfillment of the requirements for the Master of Engineering Science degree in Civil and Environmental Engineering

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REMOVAL AND RECOVERY OF HEAVY METALS BY NICKEL SMELTER SLAG

(Thesis format: Monograph)

by

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Graduate Program in Civil and Environmental Engineering

A thesis submitted in partial fulfillment
of the requirements for the degree of
Master of Engineering Science

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ABSTRACT

The research was performed to assess the potential of nickel smelter slag, an industrial waste, as an adsorbent in the removal of heavy metals from solution. Results from batch studies on the effect of pH, metal-slag contact time, particle size, competition by other ions and slag dose were used to estimate the optimum adsorption conditions of the slag as an adsorbent for Cu, Pb, Cd, Ni and Zn. Adsorption of Cu and Pb were akin to the pseudo second order kinetic model and followed the Langmuir adsorption isotherm model. The calculated k_2 values were 0.18 mg $g^{-1}min^{-1}$ for Pb and 0.14 mg $g^{-1}min^{-1}$ for Cu. The q_m and b values obtained for Pb from the Langmuir plot were 4.05 mg/g and 0.59 L/mg for Pb and q_m and b values for Cu were 3.83 mg/g and 0.17 L/mg. Nickel slag has affinity for the metals studied in the order of Pb>Cu>Zn>Cd>Ni. Multiple adsorptions showed that the slag could be used about five more times before it gets exhausted.

Keywords: adsorption, industrial waste, nickel smelter slag, heavy metals

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NOMENCLATURE

b	Langmuir constant related to apparent heat change (L/mg)
Cd	Cadmium metal
C_e	Concentration of solute at equilibrium (mg/L)
C_o	Initial concentration of solute (mg/L)
C_t	Concentration of solute at time, t (mg/L)
Cu	Copper metal
ICP-OES	Inductively Coupled Plasma-optical Emission Spectroscopy
k_1	Pseudo first order rate constant (min^{-1})
k_2	Pseudo second order rate constant ($mg\ g^{-1} min^{-1}$)
K_f	Freundlich constant related to adsorption capacity (mg/g)
n	Freundlich parameter depicting bond strength
Ni	Nickel metal
Pb	Lead metal
q_e	Amount of solute adsorbed at equilibrium (mg/g)
q_m	Langmuir constant related to adsorption capacity (mg/g)
q_t	Amount of solute adsorbed per unit mass of adsorbent at time, t (mg/g)
t	Contact time (hour)
XPS	X-ray Photoelectron Spectroscopy
Zn	Zinc metal

CHAPTER ONE

INTRODUCTION

1.1. Background

Heavy metals are a natural part of the earth's crust; they occur in rocks and are distributed in the environment (soil, water and air) through many pathways, both naturally such as through weathering, biodegradation, volcanic eruptions and water-rock interaction, and via human activity such as mining. As industrialization and civilization grew over the last century, there has been an increase in the release of contaminants and other waste products into the environment at levels that far exceed their natural production. Industries such as mining, ore smelting, and manufacturing release contaminants including heavy metals such as arsenic, lead, iron, chromium and nickel, and organic pollutants such as toluene and dichlorodiphenyl trichloroethane (DDT).

Mining is a major industry in the world accounting for the release of large amounts of waste geochemically comparable to the value of the minerals such as gold, oil, aluminum, coal, copper and silver, that are mined, serving manifold purposes in the life of the modern human being; this industry discards 90% of the material it handles as waste. The milling and smelting operation is known to release an estimated seven to seventy thousand metric tons of metals into the environment each year (Hochella et al., 1990; Jamieson, 2011). Mining operations produce effluents containing many toxic chemicals and metals such as chromium, lead, nickel, copper, arsenic, zinc, mercury, arsenic, selenium, iron, vanadium, bismuth, molybdenum, cobalt and cadmium which when released into the environment have deleterious effects on flora, fauna and humans. The number of metals and their quantities present in wastewater depend on the nature of the industry involved (Gupta et al., 2009). The major risks posed by these metals are their toxicity, their persistence or inability to degrade chemically or biologically in the environment, and their tendency to bioaccumulate in the food chain. Humans, being on top of the food chain, receive the most impact in the form of both chronic and acute health problems with their attendant skyrocketing health care costs and declining productivity. For example, the presence of lead in elevated amounted is believed to have contributed to the fall of a whole civilization, the Roman Empire (Lessler, 1988 and Gilfillan, 1965).

These toxins enter an organism's system by ingestion, inhalation and skin contact. Their presence in certain concentrations have been linked to many cancers and other diseases, such as hemochromastosis and brasschills, hence the need for limits set by organizations such as the World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA) (Akpor and Munchie 2010; Macek and Mackova, 2009; Reeder et al., 2006; Hernberg, 2000; and Volesky, 2000).

In a bid to reduce heavy metal presence in the environment, particularly the aquatic environment, many methods have been devised to treat wastewater laden with heavy metals before their release into the environment. These treatment methods include reverse osmosis, chemical precipitation, membrane filtration, ion exchange, adsorption, biosorption, oxidation-reduction, solvent extraction and adsorption (Barakat, 2011; Amin et al., 2010; Zhou and Haynes, 2010; Gupta et al., 2009; Hu et al., 2005; and Gupta and Ali, 2004). Of all these technologies for contaminant removal, adsorption offers the best advantage in terms of cost and removal efficiency. For example, in the case of precipitation, there often arises the need for oxidation-reduction to occur in order to change the metal's form to one that can be easily precipitated. Adsorption, the process where substances adhere to a surface by a combination of complex chemical action and physical forces has been found to be a very effective treatment method. For many years, activated carbon was the main material used in the treatment of waste water by adsorption but its high cost and relatively low regeneration ability has led to the birth of research devoted to the discovery of cheaper and efficient alternate adsorbents. Agricultural products such as peat, rice husk, pawpaw leaves, bagasse, orange peel, and industrial byproducts, for example, mud, fly ash, sludge and various slags, have thus been employed as adsorbents (Agarwal et al., 2012; Chiban et al., 2012; Raju et al., 2012; Zhou and Haynes, 2011 and 2010; Liu et al., 2009; Das et al., 2007 and 2008; Gupta and Ali, 2002). These byproducts have the added advantage of possessing functional groups that may be organic or inorganic. The functional groups are chemically reactive molecular units attached to the surface of the solid with their reactive groups in contact with the aqueous solution. Functional groups donate their electron pair and thus form complexes with heavy metals and other contaminants in solution leading to the latters' removal. Hydroxyl and silicones associated with metal oxides and silicates, respectively, are examples of inorganic functional groups while esters, carboxylic acids and phenols constitute examples of organic functional groups (Raju et al., 2012; Zhou and Haynes, 2010; and Sparks, 2003).

Slag is a waste material generated from smelting of ore in the production of metals. This by product is normally used as cement or filler in the construction industry (Ahmaruzzaman, 2011; Nilforoushan et al., 2008; Srivastava et al., 1997). The use of slag as adsorbent for heavy metal removal leads to economical environmental management by reducing the volume of waste since the slag was already earmarked for disposal.

1.2. Justification

Mining and other industry effluents contain many heavy metals generally existing at concentrations that exceed regulatory standards. Research has shown that many of the remediation technologies, such as ion exchange, precipitation and reverse osmosis are relatively expensive and may produce sludge whose disposal also raises concern. Adsorption has been shown to be a very effective means of wastewater treatment. Some agricultural and industrial waste byproducts, such as rice husk, pawpaw leaves and steel slag, have shown potential as a cost effective way to reduce heavy metal concentrations. Although some information exists on the use of various slags in the removal of heavy metals by adsoprtion, published data on the use of nickel smelter slag in wastewater treatment is almost non-existent.

The present study was therefore proposed to augment existing information on the use of nickel slag in heavy metal removal by adsorption.

Scientific and technological advancements in natural resource extraction have led to increased mineral production and growth in the extraction industry. Unfortunately, this growth has also resulted in a significant increase in the amount of waste generated by this industry. Research has shown that the waste from mines are equivalent in geochemistry to the rock mined (Jamieson, 2011). In order to increase the profitability of resource exploitation and at the same time protect the environment, there is the need to use more cost effective waste management options. This is the primary motivation for the present research.

1.3. Objectives

The main objective of the study is to assess the effectiveness of nickel smelter slag as adsorbent for the removal of lead (Pb), copper (Cu), nickel (Ni), zinc (Zn) and cadmium (Cd) from aqueous solution.

In line with this broad goal, the specific objectives are:

- To investigate the removal of Cu, Cd, Ni, Pb and Zn using nickel smelter slag.
- To determine the most cost effective particle size of nickel slag for heavy metal removal.
- To study the regeneration ability of the adsorbent through the use of an appropriate eluent.

1.4. Outline of thesis

Five chapters and an appendix make up the thesis. The introduction constitutes the first chapter and gives a background of the presence of heavy metals in the environment and methods currently used their mitigation.

A summary of the relevant literature reviewed in the study is discussed in Chapter two; this chapter provides the necessary information on the success of different types of adsorbents, particularly inexpensive adsorbents used in the removal of heavy metals from wastewater. Chapter three provides a detailed description of the materials and methods used in the research. The types of isotherms used to describe the adsorption of the test metals on slag are described here.

Chapter four provides the results of the study as well as a comprehensive discussion of the research findings. This chapter compares and contracts the findings of this research with those of other researchers and provides explanations.

The thesis is finally concluded with Chapter five-Conclusions and Recommendations. This chapter briefly states the conclusions drawn from the research and makes recommendations for future work based on the success and challenges from the present work. An Appendix of some of the tables produced from the research is provided to complete the write up.

CHAPTER TWO

LITERATURE REVIEW

2.1. Presence of heavy metals in the environment and their health effects.

The use of heavy metals has grown with civilization, particularly in the metallurgical, extractive, petrochemical, chemical, paint, electroplating, mining, mechanical and agricultural industries (Ziemarchi et al., 1989). Srivastava and Majumder (2008) define heavy metals as elements possessing atomic weight in the range of 63.5-206 and possessing a specific gravity greater than 5. These heavy metals take their sources from rocks and are distributed in the environment (water, soil, air) both naturally and by anthropogenic activities. Metals such as Pb, Cu, Zn, Ni, Hg and Cd are present as divalent cations in many soils, natural and wastewater at pH and Eh common to these systems; As and Cr are however found in multiple oxidation states (Zhou and Hynes, 2010, and Reeder et al., 2006). Although common in our environment, some of these heavy metals such as Mn and Zn in trace amounts may actually be good for our health but an excess of them leads to many deleterious effects (Zhou and Haynes, 2010, and Volesky, 2001). In addition to soil, air and water pollution caused by these heavy metals, their effect on public health has also been of a great concern. Diseases such as dyspnoea, "metal fume fever" and chronic bronchitis have been linked to the presence of Pb, Cr, As, Cd, Ni and other heavy metals occurring beyond certain limits in the human body and in other living organisms (Ahmaruzzaman, 2011; Fu and Wang, 2011; and Akpor and Muchie, 2010). Zhou and Haynes (2010) attribute the current pollution by heavy metals to both historical and current anthropological activities thus linking the release of metals into coastal waters and sediments of aquatic systems in the past to be a precursor to the current pollution in some environments.

2.1.1. Cadmium

Cadmium is the 48th element in the periodic table and occurs naturally in the environment as Cd^{2+} and rarely as Cd^{+}. The metallurgical, electroplating, pigment, fertilizers, batteries, mining and electroplating industries are major contributors to the increase of Cd in the environment (Gupta et al., 2009, and Sharma et al., 2009). Ziemacki et al. (1989) reported that Cd emissions in Europe have been closely linked to Zn production. The steel industry, volcanic eruptions and waste incineration pose the most problems. Exposure to cadmium over a long period leads to kidney failure and also plays a role in the development of dyspnoea hypertension and prostate cancer. High levels of cadmium in the body can also lead to death. Cadmium has been reported to be the most toxic element easily taken up by plants (Ahmaruzzman, 2011; Fu and Wang, 2011; and Bruce, 1990).

2.1.2. Copper

Copper, the 29th element in the periodic table is employed in metal finishing, paint, chemical, mining, wood manufacturing, fertilizer and electrical industries. It exists in nature in two oxidation states: Cu^{+} or Cu^{2+} (Hu, 2006). Copper is needed for metabolic processes but the central nervous system, hepatic and renal regions of living organism are affected by high levels of copper in the body. Conditions such as irritations in the eyes, nose and mouth, cramps, convulsions and sometimes death have been reported to be associated with high levels of copper in the tissues of living organisms. (Ahmaruzzaman, 2011; Fu and Wang, 2011; Paulino et al., 2006; Sharma et al., 2009). According to Patterson (1985) there is a strong connection between pH and the amount of copper available in waste water.

2.1.3. Nickel

Nickel and its compounds are widely used in modern industry such as electroplating, battery, alloy production and dye industries, due to its unique chemical and physical properties; the plating industry is recorded to be the most significant contributor of nickel in waste water (Hu, 2006; Jin et al., 2006, and Patterson, 1985). Apart from being carcinogenic, nickel exceeding certain limits have been found associated with health conditions including kidney and lung problems like chronic bronchitis, skin dermatitis, gastrointestinal distress and pulmonary fibrosis (Ahmaruzzaman, 2011 and Borba et al., 2006).

2.1.4. Lead

Lead, a very common element associated with the mining, waste incineration, pesticide, paint, battery, fuel and photographic industries, has been described as the most significant of toxic metals. The element occurs in the earth crust primarily as galena (PbS) but also occurs in other minerals such as cerrusite ($PbCO_3$) and anglesite ($PbSO_4$). Together with the sulfides of zinc, copper and iron, lead sulfide is highly associated with gold and silver ores. It occurs naturally in two oxidation states, +4 and +2 with the latter being the prevailing one (Reeder et al., 2006). Lead's toxicological and neurological effects on living organisms include dizziness, anaemia, hallucination, brain dysfunction, high blood pressure, renal, liver, and reproductive system damage as well as weakness of muscles (Ahmaruzzaman, 2011; Fu and Wang, 2011; Reeder et al., 2006; Gupta and Ali, 2004, and Naseem and Tahir, 2001).

Although solubility calculations reveal that the most effective pH at which lead precipitates as a hydroxide is near 10, literature is fraught with many conflicting views on the optimum pH at which it precipitates as a hydroxide. Values of 6 and higher have been recorded by Lancey et al. (1972), Patterson (1985), Maruyama et al. (1975), Joster and Taylor (1973) and many others. According to Reeder et al. (2006), the solubility of lead in most surface and ground waters is low with the highest values being recorded in soft acidic waters. Jamieson (2011) also confirms the release of cations such as Pb, Cu, Zn and Cd from their sulfide minerals in low pH water. Lead occurs as ions in fresh water at pH <7.5, as undissolved particles and colloids in surface waters, as precipitates of platterite (PbO_2) in municipal waters due to oxidation, and as precipitates of carbonates, hydroxides and sulphates in natural waters.

2.1.5. Zinc

The paint, pharmaceutical, plastic, newsprint, galvanizing and zinc plating industries are responsible for the release of zinc into the environment. Although essential for human health due to its regulation of biochemical processes and importance to the proper physiological functioning of living tissues, an excess of zinc in living organisms results in retardation of growth, skin irritations, nausea, restlessness and lung disorders (Ahmaruzzaman, 2011; Fu and Wang, 2011; Sharma et al., 2009, and Oyaro et al., 2007).

2.2. Remediation technologies

In order to safeguard the environment for current and future generations, many stringent measures have been taken by organisations such as the World Health Organization (WHO), Unites States Environmental Protection Agency (US EPA) to control the amount of contaminants released into the environment. Reduce, recycle, reuse and recovery are terms that have been very popular in the bid to achieve environmental management. Many industries have collaborated with researchers to develop effective waste management technologies to deal with environmental contaminants and also comply with environmental standards. Technologies developed to treat wastewater include precipitation, reverse osmosis, metal extraction, filtration and adsorption (Barakat, 2011; Fu and Wang, 2011; Akpor and Munchie, 2010; Kurniawan et al., 2006 Xue et al., 2009 and Hu, 2005). The concentration of heavy metals present in wastewater, the presence of other substances, the extent of contaminant removal, regulations regarding the quality of treated water, cost of technology, volume of wastewater to be treated and the amount and cost of treatment of residue generated are all factors that determine the type of technology to be used in any remediation scheme, hence treatment may involve just one method or a combination of several technologies (Hu, 2005; Sen and Gupta, 2002; and Petruzzelli et al., 1995).

2.2.1. Chemical precipitation, coagulation and flocculation

Precipitation involves the addition of chemicals to wastewater in order to form solid particles from dissolved solutes which are then removed by centrifugation, filtration or decantation. Coagulation and flocculation, on the other hand, involve chemical addition to cause small suspended particles to aggregate, followed by removal, just like precipitation (Akpor and Munchie, 2010). They are effective methods for the removal of metals, oils, grease and other inorganic substances. Precipitation is pH dependent and the pH at which this process occurs is a function of both the nature of the metal to be removed and the counter ions used (EPA, 2000). Lime, NaOH, ferrous sulfate, alum, ferric chloride and some polymers have been employed in as source of counter ions in precipitation (EPA, 2000 and 1980). Thus depending on the precipitant used, terms such as sulphide, carbonate and hydroxide precipitations are applied accordingly (Fu and Wang, 2011, and Akpor and Munchie, 2010). Sulphide precipitation has been noted to be the most effective method due to the low solubility of most metal sulphides; however, it has the drawback of releasing toxins at acidic pH values (Akpor and Munchie, 2010). Lee et al. (2007) reported 98% success in using granulated lime and calcium carbonate to remove nickel and arsenic from metal laden-water; however when calcium carbonate was used, the removal efficiency dropped to 97% for nickel and less than 5% for arsenic. Coagulants such as alum, organic polymers and iron salts are normally employed to remove precipitates that are light and tiny (Fu and Wang, 2011, and Akpor and Munchie, 2010).

Although the process of precipitation is inexpensive and simple, it requires large space, large amount of chemicals and produces voluminous sludge whose disposal raises another issue (Stankovic et al., 2009; Hu, 2005; and Chen and Holsen, 1991). The sludge, upon drying, has the potential to form dust whose entry into the environment poses a threat to environmental health and safety. The presence of certain compounds in the wastewater may also render this technology ineffective by interfering with the formation of metal hydroxides; for example, chelates in waste streams have been reported to reduce the effectiveness of precipitation as a treatment technology (Hu, 2005; Guclu and Apak, 2003; and Yang et al., 2001). Furthermore, a small pH adjustment may result in the dissolution of the precipitated metals and acid rain may also bring about leaching of the metal hydroxides. Low pH has been associated with the release of cations from their sulfates (Stankovic et al., 2009, and EPA, 2000). Chemical precipitation is sometimes used together with ion exchange for heavy metal removal. Akpor and Munchie (2010) and Feng et al. (2000) reported the use of both technologies for the treatment of acid mine water in South Africa at a reasonable cost.

2.2.2. Ion exchange

Ion exchange is usually a reversible reaction with a high resemblance to biosorption, and involves the displacement of a charged ion from a immobile solid by equivalent charged ion or ions of similar or smaller size (Akpor and Muchie, 2010). In a broader scope ion exchange refers to any substitution of ion by another while in a narrower scope it is used to characterize the substitution or replacement of an exchangeable ion that has been adsorbed by another ion (Stumm and Morgan, 1996; Stumm1992). Synthetic resins derived from hydrocarbons or natural zeolites are mostly employed in ion exchange; these have the ability to exchange either cations, often Ca, Na and K, or anions held electrostatically on the resin's surface for heavy metal ions in wastewater. The process does not result in any terminal alteration to the ion exchanger's structure. The heavy metals can then be collected from the surface of the resin in another process or destroyed together with the resin (Chiban et al., 2012; Akpor and Muchie, 2010; Hu, 2005; Inglezakis et al., 2005; Dabrowski et al., 2004 and 2003; and Mier et al., 2001). This technology has been in operation in drinking water treatment for reduction in water hardness. Sungur and Babaoglu (2005) synthesised a cellulose based resin with an exchange capacity of 3.3 meq/g, which was successful in the removal and recovery of Pb, Cd, Zn, Fe, Ni, Co and Cr from aqueous solutions.

Further research on this treatment method has been performed by Virgili et al. (2013), Mahmoud and Hoadley (2012), Silva et al. (2008 and 2001), Inglezakis et al. (2005, 2004 and 2001), Volesky et al. (2003 and 2001) and Vaca et al. (2001). In their review on ion exchange as a waste water treatment technology, Dabrowski et al. (2004) confirmed the effectiveness of ion exchange in the removal of Pb, Cu, Cr, Hg, Cd, Ni, and Zn; they asserted that in most cases involving a mixture of metals, Pb was the most highly selectively removed by many ion exchange resins. Selectivity for Pb is also confirmed by research performed by Trgo et al. (2006). A modified zeolite, clinoptilolite was brought in contact with a solution of Pb and Zn. The research showed a higher rate of exchange and capacity for Pb than for Zn.

Vaca et al. (2001) studied the removal of Pb, Cr, and Cd by clinoptilolite resin and reported higher than 95 % removal of these metals in the acidic pH range over 18 hours. Chern and Chang (2000) employed the use of ion exchange technology to treat a binary system of Cu and Ni. Batch and column experiments were performed on the binary system using a cation resin, IRC-718. The resin showed efficiency in the removal of Cu but not Ni. The Cu was recovered from the resin by treating it with 0.25 M sulphuric acid.

Silva et al. (2008) compared the effectiveness of calcium alginate beads with a commercial ion exchange resin, Lewatit TP 207, in the removal of heavy metals from wastewater. The performance of both materials were similar; the resin of dosage (0.27 g/L) was successful in reducing concentrations of zinc from 17.06 mg/L to 8.23 mg/L, iron from 5.34 mg/L to 0.716 mg/L, nickel from 0.395 mg/L to 0.059 mg/L and cadmium from 0.004 mg/L to less than the detectable limit. Silva et al. (2008) noticed that although the resin gave a higher performance metal uptake, the process was faster in the alginate beads. In both methods, recovery of the heavy metals was feasible.

Inglezakis et al. (2005) reported the use of clinoptilolite zeolite in the removal of Cu, Pb, Cr and Fe due to its attractive selectivity for heavy metals and cations. Their work also included a study of the effects of ions, such as Li^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Br^- and Cl^- on the heavy metals in both binary and mixed solutions. Although the presence of anions was insignificant in the removal of these heavy metals, the cations did affect the extent to which the heavy metals were removed. For example in the presence of competing ions, the removal of copper was 12 %- 40 % less than in the absence of other cations while the removal of lead was 1 % - 9 % less than in the absence of the competing cations. In the presence of the anions Br^- and Cl^-, there was less than 20 % decrease in heavy metal removal. The researchers concluded selectivity of clinoptilolite for heavy metals in a decreasing order of Pb, Fe, Cr and Cu.

Although ion exchange technology has been an effective technology for the removal of heavy metals for many years, it may not be suitable for concentrated solutions due to a higher tendency of fouling of ion exchanger or resin by solids present in the wastewater. Another disadvantage of ion exchange is it's sensitivity to pH (Barakat, 2011).

2.2.3. Membrane filtration

In many liquid and gas mixtures, some components are able to pass through selective barriers called membranes with greater ease than others. Membrane filtration may be of various types depending on the size of materials rejected by the membrane; suspended particles, higher molecular weight compounds and suspended particles, low molecular weight substances and suspended particles, are rejected by microfiltration, nano filtration and ultra filtration membranes, respectively (Barakat, 2011; Akpor and Muchie, 2010; Ahmedzeki et al., 2009; Kochany, 2007; McCabe et al., 2005; Saffaj et al., 2004; Juang and Shiau, 2000; and Amjad and Zibrida, 1998). Membrane filtration has been used successfully for the removal of heavy metals, organic substances, suspended and inorganic contaminants. Membrane filtration requires high pressure to cause water to move across the membrane form high concentration to low concentration of solute. Saffaj et al. (2004) used ultra filtration to successfully remove Cu(II), Cd (II), Cr (III) and Zn (II) and recorded over 80 % removal of these metals.

Reverse Osmosis is also a membrane technology which employs the use of a semi permeable membrane to separate water or other solvent from dissolved and particulate materials. It has sometimes been referred to as hyperfiltration (Chiban et al., 2012; Fu and Wang, 2011; and

Akpor and Munchie, 2010). Of the myriad of materials used in the production of membranes, cellulose acetate and polyamide thin film composite are the most common. Their configuration may be spiral plate and frame, or hollow tubular. The latter provides the greatest surface area but it is also the most susceptible to fouling (Ahmedzeki et al., 2009).

In a pilot study, Pawlak et al. (2005) succeeded in applying reverse osmosis for the treatment of arsenic and antimony contaminated groundwater water via two different types of reverse osmosis modules. They observed reductions in groundwater arsenic and antimony concentrations from 60 µg/L to less than 1 µg/L and 8.7 µg/L to less than 3 µg/L, respectively; other researchers who have worked with this technology include Waypa et al. (1997) and Ahmedzeki et al. (2009).

Reverse osmosis is becoming an increasing popular method in the treatment of wastewater due to ease of metal recovery, decreasing prices of membranes, stricter water quality standards, and high effectiveness in the removal of heavy metal species and dissolved compounds. However, its requirements of high power to restore the membrane and sustain the pumping pressure makes it less desirable (Fu and Wang, 2011; Akpor and Munchie, 2010; Ahmedzeki et al., 2009; Pawlak et al., 2005; and Volesky et al., 2003).

2.2.4. Electrochemical treatment

This technology employs electricity to remove heavy metals. It involves passing an electrical current through a metal -laden solution, with the cationic metals being attracted to the negatively charged cathode. This is an ineffective method due to the huge quantity of sludge produced and corrosion of the cathode plates (Barakat, 2011; Macek and Mackova, 2011; and Kurniawan et al., 2006). Electro- dialysis is a membrane process where metal solutions are passed through an ion exchange membrane by means of electrical potential thus the anions move towards the anode and the cations towards the cathode. This method combines ion exchange and electricity for better performance thus allowing the heavy metals to be recovered in a concentrated form (Barakat, 2011 and Chen, 2004).

2.2.5. Adsorption

The interaction of species in the fluid phase with a solid surface results in adsorption. Thus, adsorption, a term introduced by Kayser in 1881, can be referred to as the process whereby a solute or species in a liquid or gas mixture is removed onto an adsorbent or a solid that is in contact with the fluid. Apart from possessing a great surface area for attachment, the adsorbent also has a high affinity for the solute (McCabe et al., 2005; Felder and Rousseau, 2000; Tien, 1994; and Greg and Sing, 1982). Adsorption is a surface phenomenon and is the result of the forces of attraction between molecules of the asorbent and species of the adsorbate and may generally be described as physical adsorption or chemisorption depending on the interaction between the adsorbent and adsorbate; however, many intermediates do occur and both processes can occur either alternately or concurrently (Dabrowski, 2001; Tien, 1994; and Ruthven, 1984). Physisorption, the more common of the two, is a reversible process and involves weak hydrogen, van der Waal or electrostatic intermolecular forces including outer-sphere complexes while chemisorption involves the formation of chemical bond between the surface of the adsorbent and the adsorbate and occurs as a monolayer inner sphere complexation involving ligand exchange as well as covalent and hydrogen bonding. The reversibility of physisorption makes it more significant in engineering operations in that metals that adsorb by this mechanism can readily be recovered (Chowdhury, 2013; Sparks, 2005; Dabrowski, 2001; Paraffit and Rochester, 1983; and Gregg and Sing, 1982). According to Gregg and Sing (1982) adsorption could also be described as being positive or negative, in that the constituents of the interfacial stratum may be enriched or depleted accordingly. In all adsorbents except for porous adsorbents, the time taken to reach equilibrium may serve as a guide in determining the type of bonding between a solute and solvent. In addition to the above, the rate of desorption via a suitable eluent, the temperature of contact and the shape of the adsorption isotherm are good assessors of the adsorbate-adsorbent interaction (Parafitt and Rochester, 1983).

Water treatment by adsorption is mostly carried in fixed beds where the water to be treated is continuously passed through the bed until saturation is achieved although a contact of the water with tiny particles of the adsorbent would also yield good results (McCabe et al., 2005). McCabe et al. (2005) reported that adsorption largely occurs either at definite sites inside the adsorbent, or on its walls with the internal area larger than the outer surface by a range from 500 to 1000 m^2/g. Different adsorbate particles are attracted and attached to adsorbents at various degrees and this permits selective adsorption in a mixture of solutes as well as regeneration of adsorbent and recovery of the adsorbate.

Adsorption has been successfully used for the removal and recovery of heavy metals such as lead, chromium, nickel, mercury, arsenic, zinc, manganese, selenium, cobalt and iron; organic solvents such as paints, printing inks and fabric dyes. The way in which an adsorbent and adsorbate interact under set conditions is unique to that system and determines the level of contaminant removal and this is why a known contaminant may be removed by different adsorbents at varying degrees. This serves as the foundational principle on which adsorption-based separation operates (Mosca, 2009; McCabe et al., 2005; and Tien, 1994). Adsorbents such as activated carbon, iron oxides and zeolites have been used successfully for the treatment of wastewater laden with heavy metals with activated carbon as the most widely used. Difficulties with regeneration, and the high cost of activated carbon has led to the discovery and development of cheaper alternate adsorbents (Chiban et al., 2012; Zhou and Haynes, 2010; and Ajmal et al., 2000).

In the last few decades a category of low cost adsorbents, industrial waste and biosorbents such as agricultural waste have been developed with comparable removal effectiveness; they are either used in their natural state or with some form of modification either physical or chemical. They include corn starch, sawdust, peanut hulls and skins, bark of trees, xanthane, pawpaw leaves, peat, moss, orange peel, rice husk, seaweed, sugar cane bagasse, coffee beans , rice husk, rubber tyres, red mud, fly ash, slag and sludge from various industries (Lasheen et al., 2012; Raju et al., 2012; Ahmaruzzaman, 2011 and 2010; Zhou and Haynes, 2011; Das et al., 2008; Demirbas, 2008; Sud et al., 2008; Kumar, 2006; Kumar and Bandyophyay, 2006; Wang et al., 2003; Dimitrova, 2002; Ortiz et al., 2001; Volesky, 2001; and Ajmal et al., 1998). Lasheen et al. (2011) compared the removal rates of 10 mg/L each of Pb, Cd and Cu on both modified and unmodified orange peel at pH 5. The modified peel recorded a higher adsorption capacity of 11.2 mg/g while the unmodified had a capacity of 6.94 mg/g with removal rates of 99.5 %, 89.57 % and 81.03 % for Pb, Cu and Cd respectively. They ascribed the removal to the presence of hydroxyl and carboxyl groups on the orange peel which had a high affinity for the metals under study. An equilibrium time of 30 minutes was recorded for adsorption which was well described by the Langmuir and Freundlich isotherms.

Adsorbents may be porous materials possessing a high surface area-to-volume ratio and pore size range of up to tens of Angstroms; this serves as a significant factor in giving them the high adsorption capacity property. For example, surface areas of 800 m^2/g, >200 m^2/g and >500 m^2/g have been recorded for synthetically produced silica, an aluminium oxide- activated alumina, and activated carbon (Mosca, 2009).

Parfitt and Rochester (1983) have noted difficulty in reproducing an adsorbent with the same chemical nature. This challenge is as a result of contamination, variation in preparation methods as well as incomplete removal of surface impurities. For example the method of preparation may yield silica possessing different number of hydroxyl groups. This serves as a setback in providing unambiguous explanations on the role of adsorbent surface in adsorption studies.

2.3. Porosity and size distribution of adsorbents

The surface area available for adsorption is highly influenced by the porosity of the material; the surface area is made up of the internal and external surface areas and the proportion of these two may vary by many degrees. The presence of outward fissures and grooves as well as internal fractures may account for the difference in these two surface areas (Cornell and Schwertmann, 1996; and Greg and Sing, 1982). Many primary particles of fine powder may come together to form secondary particles such that there is presence of voids in the network. These voids increase the internal surface area of adsorbent available for adsorption. This internal surface of the secondary particles is usually smaller than the internal surface of the primary particles. The inner surface of the primary surface may include fractures and cracks which are deeper while the secondary inner surface is wider. Diffusion is the main process by which the pores, a constituent of the internal surface of adsorbents, become filled with adsorbate. These pores may be macro, micro, meso, nano or transitional depending on their size; they impose specific adsorption characteristics displayed by adsorption isotherms. These pores take a longer time to fill up than the external surface (Cornell and Schwertmann, 1996).

Adsorption has been used as a preferred technology for metal removal and recovery because more often than not, it produces a high quality effluent and adsorbents that can sometimes be generated by desorption with a suitable eluent; this makes this method cost effective (Fu and

Wang, 2011; Hue et al., 2006 and 2005). In a review, Fu and Wang (2011) noted a flexibility with design and operation for the use of adsorption technology. Factors such as pH, contact time, temperature and adsorbent dose have been noted from literature to affect adsorption. The pH effect varies depending on the type of adsorbent used and contact time plays an important role in batch experiments. Generally, the adsorption increases with contact time until equilibrium is attained. Temperature also affects adsorption variably; adsorption of different metals on adsorbents may either be endothermic where adsorption increases with increasing temperature due to an increase in adsorption capacity attributed to the enlargement of pores or activation of the adsorbent's surface when temperature is increased. On the other hand, with exothermic adsorption reactions, an increase in temperature leads to a decline in adsorption.

2.4. Iron oxides

"Iron oxides" is a term that generally encompasses iron oxides, hydroxides and oxide hydroxides. They are abundant in nature and are employed in many fields such as mineralogy, biology, soil science, environmental chemistry, medicine and geochemistry for various purposes. Sixteen iron oxides have been named of which jacobsite, magnetite, maghemite, hematite, ferrihydrite, wusite, geohite, lepidocrocite, and feroxyhyte are included; the main difference being in the arrangement of the foundational structure. They are formed from the protonation and release of Fe ions from primary and secondary minerals (Tang et al., 2013; Chowhury and Yanful, 2011 and 2010; Tiwari et al., 2008; Hu et al., 2004; and Cornell and Schwertmann, 1996). These iron oxides, consisting of Fe ions and oxide or hydroxides ions, are composed of packed arrays of anions with interstitial spaces partially occupied by Fe^{2+} or Fe^{3+}; hence the arrangement of the anions being the sole determinant of the structure of these oxides and the ease with which one oxide changes to another. These hydroxyl groups serve as the main functional groups of iron oxide. In addition to hydroxyl groups that are part of the structure, Fe ions may interact with water molecules to have more hydroxyl attached to the oxide's surface. Although there are situations where the interstitial spaces may be occupied by cations instead of Fe, the structure of the oxide is not affected but rather a modification of the unit cell size does occur. The properties which make them good sorbents include magnetism, the presence of minute crystals leading to high surface area required for sorption, and low solubility resulting in high stability (Cornell and Schwertmann, 1996; Muller and Joubert, 1974). Thus iron oxides of different size range have been shown to be effective in the removal of heavy metals by many authors. Nano-scale iron particles have been recorded as being the most effective. The availability of iron oxides in commercial quantities at an economical price in addition to not being as reactive as other sorbents like ferric chloride ($FeCl_3$) and ferrous sulphate ($FeSO_4$) make them excellent candidates as adsorbents (Chowdhury, 2008).

The magnetic properties possessed by this group of minerals make them suitable adsorbents in heavy metal removal. The immensely small size of nanoparticles (1-100 nm) makes them easy to transport as well as gives them the added advantage of a greater surface area -to -volume ratio resulting in high reactivity for heavy metal removal. In addition to these, magnetic nanoparticles have a high removal capacity, fast kinetics and exceptional adsorption properties provided by the varied supply of reactive surface sites and disordered zones (Tang and Lo, 2013; Tiwari et al., 2008; Yantasee et al., 2007; Hu et al., 2004; and Zhang, 2003). The last few decades have seen active research into the development of synthetic nanoparticles, alteration of surface properties and enhancement of application methods of nanoparticles for more effective removal of contaminants including dyes, heavy metals and organochlorine pesticides (Saleh et al., 2008; Sun et al., 2006; Liu et al., 2005; Hu et al., 2004; and Zhang, 2003). Injection of nanoparticles into some sites has yielded tremendous results. Zhang (2003) reported the successful reduction of TCE in a supersite in North Carolina by 99 % after a few days of injection of nanoparticles in the form of a slurry. The volume and concentration of the iron oxide nanoparticles were 6056 L and 1.9 g/L respectively; the initial concentration of VOCs was 140,000 ug/L and the total mass of iron oxides was 11.2 g injected at a rate of 0.6 gallons per minute.

Chen et al. (1991) reported the successful removal and recovery of Cr(VI) and Zn from wastewater via an adsorption and magnetic method using magnetite as the adsorbent. The experiment yielded greater than 90% removal in the first adsorption test. Subsequent adsorption steps resulted in a decrease in performance of the adsorbent which could be accounted for by the accumulation of adsorbed metal on the adsorbent from previous adsorptions. The researchers asserted that although adsorption may be a reversible process, the rate of reversibility may differ depending on the adsorbent and metal used.

Chowdhury and Yanful (2011 and 2010) reported on the removal of arsenic and chromium by mixed magnetite and maghemite, and magnetite nanoparticles. They observed a greater than 94 % removal of Cr (VI), As (III) and As (VI) at specific pH values. The highest removal of 2 g/L As (III) and As (VI) with 2 g/L magnetite nanoparticles was 95 % at pH 2. The authors noted that As removal by magnetite nanoparticles was dependent on contact time, pH, adsorbent concentration, initial As concentration and the concentration of phosphate in the water to be treated. Chowdhury and Yanful (2010) found that, in the presence of PO_4^{3-} greater than 6 mg/L, the removal rate dropped to less than 50 %.

An iron-bearing derivative from surface finishing operation of cast iron manufacturing was used in the removal of Pb, Zn and Cd, and the results were comparable to those of activated carbon and other commercial adsorbents. The iron-bearing material removed the heavy metals in a decreasing order of Pb, Zn and Cd respectively (Smith, 1996). In that study, Smith (1996) also noted that the main mechanism of uptake was surface complexation and factors such as pH, sorbent concentration, ionic strength, particle size and initial concentration of metals had different degrees of effect on adsorption, adsorption rate and adsorption kinetics. For example, Smith (1996) was of the view that while adsorption was sensitive to pH, in that adsorption increased with an increase in pH, the adsorption efficiency was impacted to a moderate degree by pH and to a lesser extent by sorbent dose. Huang et al. (2007) also reported on the successive use of a waste metal oxide (F1) from a fluidized bed reactor in the removal of 0.8 mol/dm^3 of Cu^{2+}; the greatest adsorption capacity was reported to be 0.21 mmol/g at pH 6 and temperature of 300K. These authors concentrated on the thermodynamics and kinetics to assess the effectiveness of F1 as an adsorbent for Cu; F1 was characterized to be similar to goethite. Huang et al. (2007) reported an increase in adsorption with increasing temperature, an enthalpy change, ΔH, of +9.2 kJmol/ L and a negative change in standard free energy, ΔG, of 6.12 kJ/mol at temperature of 318K to signify a spontaneous endothermic reaction. The Freundlich and pseudo second order rate model provided the best fit for the data. In similar work, Ren et al. (2012) used magnetic eggshell iron oxides for the removal of Cu and Pb. The authors reported spontaneous endothermic adsorption of the metals at optimal pH around 5.5. Characterisation of the interaction was done with FTIR and XPS; adsorption capacity values of 263.2 mg/g and 250.0 mg/g were recorded for Pb and Cu, respectively, and the adsorbent had a high adsorption capacity above 150 mg/g for both metals after 5 cycles of adsorption-elution. Of the eluents tested (deionized water, NH_4Cl, NH_4OH, HCl, HNO_3 and NaCl), HNO_3 proved the most effective. Ren et al. (2012) attributed the decline in adsorption capacity to the loss of active sites on the adsorbent.

2.4.1. Surface properties of iron oxides

Iron oxides occur generally as colloids; hence the majority of their atoms are exposed. The difference in bonding on the surface from the bulk of an adsorbent produces surface properties that differ from the rest of the material. The reaction between a mineral's surface and water results in the formation of hydroxyl functional groups that play a significant role in adsorption. These hydroxyl functional groups have the potential for ionization, yielding charged surfaces for ion uptake (Parks, 1990). Wesolowski et al. (2001) also note that the surface charge of an iron oxide is determined by the reaction between the terminal oxygen and the H and OH ions in an aqueous solution. According to Hu et al. (2004) redox reactions and electrostatic attraction between iron oxides and metals in aqueous solutions hasten the latter's removal from solution. Results reported by Chowdhury et al. (2011) and Chowdhury (2013) also confirm this fact. These authors attributed the removal of arsenic by mixed magnetite-maghemite to redox reactions. The authors used a mixture of magnetite-maghemite as adsorbent in the removal of As, Cr and Cd in columns and recorded high removal capacities: 1.5 mg/L of Cd was removed by 0.8 g/L adsorbent of size 20-60 nm while 3 mg/L each of As and Cr were removed by 0.4 g/L of the adsorbent of the same size as that used in the Cd removal study. The redox reactions were confirmed by the results of XPS analysis performed on the adsorbent before and after adsorption as well as the simultaneous decrease in magnetite and increase in maghemite. Adsorption of metals onto adsorbents have the potential to change the electronic structure of surfaces and make the latter more susceptible to undergo redox reactions that would otherwise not occur when the metals are in solution (Reeder et al., 2006).

2.5. Slag

Slag, an industrial waste, is currently receiving attention as an inexpensive adsorbent for the removal of contaminants from waste water. Industries that release slag as their by-product include steel mill and iron smelters as well as non ferrous smelters and to an extent municipal solid waste incineration (Das et al., 2006; Shen and Frossberg, 2002). Slags from different operations and industries contain a variety of compounds and minerals at varying amounts which makes them a very good choice as adsorbents. Common among these compounds are TiO_2, Fe_2O_3, FeO,Fe_3O_4, BaO, MgO, CaO, Al_2O_3, MnO and SiO_2 (Liu et al., 2010 and 2009; Nilforoushan et al., 2008; Das et al., 2007; Dimitrova, 2002; Ortiz et al., 2001; and Waypa et al., 1997). The composition of these compounds in varying amounts makes no two slags the same; hence their capacity for the removal of various contaminants including metals like Cu, Ni, Cd, Cr, As, Pb, Zn, Se and Hg.. The presence of iron and manganese on these surfaces make them good electron acceptors or donors (Reeder et al., 2006). Workers who have championed research on these waste materials include Chen et al. (2011), Zhou and Haynes (2010 and 2011), Liu et al. (2009), Ortiz et al. (2001) and Nilforoushan et al. (2008). The majority of slag research has been carried out with iron or blast furnace (BF) slag and steel slag. The composition of these two slags is shown in Table 1.

Table 1: Composition of major slags

Constituent	**Composition**	
	Iron/ Blast furnace slag	**Steel slag**
Fe_2O_3	0.02 - 0.45 %	42 - 84 %
SiO_2	30 - 40 %	9 - 18 %
CaO	30 - 40 %	25 - 55 %
Al_2O_3	5 -15 %	0 - 3 %
MnO	Not recorded	1-6%

Source: Zhou and Hynes (2010)

The presence of these compounds offers unique adsorption characteristics to these slags and sometimes makes it difficult to determine the specific surface sites on which sorption occurs (Zhou and Haynes, 2010, and Nilforoushan et al., 2008). Zhou and Haynes (2010) noted that due to the possession of sites with different charges, the calcium aluminosilicate in blast furnace slag serves as the main adsorption region in blast furnace whereas the iron oxides provide the major adsorption sites in steel slag. Furthermore, Nilforoushan et al. (2008) noted that while difficulty lies in ascribing a surface for removal of contaminants in a slag constituted of many compounds such as SiOH, SiO, AlOH and CaO, the element whose compounds predominate can be reported as the dominant adsorption site (Nilforoushan et al., 2008). Zhou and Haynes (2010) also noted that at high metal concentrations, surface precipitation may also be a mechanism for the removal of toxic metals by slag materials.

Several authors have reported that industrial slags are basic in nature with pH values ranging from 8.9 to 12.2 having been reported (Chen et al., 2011; Zhou and Haynes, 2011; Liu et al., 2009; Dimitrova, 2002; and Srivasta et al., 1997). In addition to the constituent silicates, the addition of limestone in slag formation process may be the principal precursor to their alkaline nature, offering a buffering effect to keep pH well in the basic region (Zhou and Haynes, 2010). The basic nature of slags provides them with an abundance of hydroxide ions which facilitates the attraction of metal cations for effective removal as well as precipitation as oxides and hydroxides. Reeder et al. (2006) have also confirmed that pH is a significant determinant of the level of removal by inorganic sorbents. High removal of metals has been reported for metals under alkaline pH conditions on adsorbents of hydrated oxides, oxyhydrates and aluminosilicates (Dimitrova and Mehandgiev, 1998; Huang and Rhoads, 1989; and James and MacNoughton, 1977). Huang and Rhoads (1989) recorded that pH above 6 yielded high removal rates in a study on the removal of Zn by aluminosilicates while Dimitrova and Mehandgiev (1998) reported insignificant sorption at pH below 5. These workers further asserted that irrespective of the initial pH, once it is neutral or slightly basic, a sorbent with the alkaline effect will still be effective.

Liu et al. (2009) reported the successful removal of Cr^{3+}, Cu^{2+}, Pb^{2+} and Zn^{2+} from aqueous solution by steel slag in batch experiments. A contact time of 1 hour was enough to yield a 99.2 % removal of Cr^{3+} from an aqueous solution. In a multi-element solution of the four above-mentioned metals at a concentration of 25 mg/L each, Liu et al. (2009) recorded high removal rates >82 % for all metals using 3 g of slag. The adsorption capacity of the steel slag for the metals was in a decreasing order of Cr > Zn> Cu> Pb. There was an increase in adsorption with a reduction in particle size of slag from 2.5 mesh till 80 mesh after which there was no significant effect on the removal of the metals. In another work Nilforoushan et al. (2008) recorded better removal of Pb at higher concentrations in column experiments with electric arc and blast furnace. Ortiz et al. (2001) also reported similar results in the removal of Ni by steel converter slag. Their results appear to be contrary to those of many other researchers who have observed removal rates to decrease with an increase in initial concentration at the same adsorbent dose (Srivastava et al., 1997). The electric furnace slag, being crystalline, yielded slightly better results than the amorphous blast furnace slag. Although removal was very fast in the first half hour, equilibrium was not attained until after 48 hours. In general, crystalline natured slag have a high adsorption capacity and surface area than amorphous types and the temperature at which the crystallization is achieved may lead to different degrees of increase in adsorption capacity. For example, 41 % increase in adsorption capacity for Pb was recorded for granulated blast furnace slag crystallized at 860^{o}C while 25 % increase was recorded for crystallization at temperatures of 960^{o}C and 925^{o}C (Mihailova et al., 2013). These authors believed the difference in adsorption capacities was the result of the different minerals produced at the different temperatures.

Gregg and Sing (1982) are in agreement that, by and large, in addition to chemical nature, the condition under which an adsorbent is produced influences its behaviour. In support of this, Cornell and Schwertmann (1996) have also reported porosity and particle size, which determines surface area, to be dependent on the conditions of formation and growth of iron oxides. Prevailing conditions during the formation of an adsorbent may yield some imperfections in the lattice structure of the adsorbent. This in turn influences adsorption by bringing about a variation in the proportion of faces available for solute-adsorbent interaction. Point defects, cleavage steps, kinks and dislocations are some defects that occur at an adsorbent's surface; most of the significant interfacial chemical reactions of oxides are known to occur at these defect regions (Brown et al., 1999; Greg and Sing, 1982).

In their work, Srivastava et al. (1997) used air-activated blast furnace slag in the removal of Pb and Cr in batch and column tests. They reported adsorption to follow both the Langmiur and Freundlich models and adsorption to be higher for Pb than for Cr. The results obtained from the removal of Pb and Cr by activated slag were comparable to those of commercial activated carbon. Factors investigated by Srivastava et al. (1997) included pH, adsorbent dose, initial concentration of metals and contact time. They reported that adsorption increased with increasing temperature and was thus endothermic; they attributed this to the increase in adsorption sites caused by the breaking of bonds as temperature increased. These authors reported a point of zero charge (PZC) of slag to be 2.8, with low pH favouring Cr removal and high pH favouring Pb removal. At pH values above the PZC, there is an abundance of negative charges on the adsorbent (blast furnace slag) which favours Pb removal and vice versa. Higher sorption of 80-90 % was recorded at low solute concentration while 26-42 % was recorded at high solute concentrations.

2.5.1. Mechanisms of metal removal by slag

The removal of heavy metals from solution by slag surfaces has been attributed to sorption, which consists of three main processes: adsorption, precipitation and co precipitation, and ion exchange (Zhou and Haynes, 2010). The term, sorption, was first proposed by McBain in 1909 to encompass surface adsorption, absorption by penetration into the solid network and condensation within the pores of a solid. These may also be referred to as adsorption, co-precipitation and precipitation. These processes may occur in continuum in the removal of contaminants. Sorption behaviour of a contaminant is dependent on its properties: acid-base chemistry, redox reactions, ionic character, pH, concentration of aqueous species, nature of adsorbent and surface coverage, among many others (Sparks, 2005; Cornell and Schwertmann, 1996; Piwoni and Keeley, 1990; and Gregg and Sing, 1982). Zhou et al. (2010) proposed that precipitation and co- precipitation are the principal mechanisms for heavy metal removal at high concentrations while specific adsorption occurs at lower metal concentrations.

Sorption is most effectual at low adsorbate concentration and large surface area. Sorption of anion species is greatest at pH values nearer to the pKa values of the species, while cationic sorption is influenced by complexation which depends on pH and ligand concentration. Between pH 3 and 10, typical for most waters and soils, there is a variation in the proportion of hydration products present for most ions being adsorbed. For example, Cu will be present as Cu^{2+}, $CuOH^{+}$ and $[Cu(OH)_2]^{o}$ while Pb will be present as Pb^{2+}, $PbOH^{+}$ and $[Pb(OH)_2]^{o}$ (Cornell and Schwertmann, 1996; Reeder et al., 2006; and Olin, 1960). Sparks (2005) also reported of the presence of a narrow pH range, the adsorption edge, where almost complete sorption of cations takes place; the pH position of this edge is related to the acid-base attributes or hydrolysis of exact cations. The selectivity of adsorbents for cations is dependent on properties of both entities as well as the medium or solvent. The selectivity of most hydrous oxides for alkali metals is the order of $Li^{+} > Na^{+} > K^{+} > Rb^{+} > Cs^{+}$. This trend has been attributed to electrostatic attractions and the size (hydrated radius) of the species involved (Sparks 2005; Stumm, 1992). However, there seems to be no similar trend involved in the sorption of divalent cations whose sorption is usually stronger. The trend in the case of divalent cations depends on the nature of surface and pH. The inconsistency in divalent cation sorption has been proposed to be caused by the difference in the hydrogen ion: metal ion (H^+: M^{n+}) ratio; selectivity in this case increases with increase in the ratio (Sparks, 2005).

Specific adsorption could lead to precipitation and co-precipitation in the presence of many adsorbates. In such a scenario, the monolayer formed in the initial sorption serves as a site on which further adsorbates are collected. The term co precipitate is used when the precipitates are made up of chemical species formed by the dissolution of components of the adsorbent and the sorbing species or adsorbates. Adsorbates capable of forming co-precipitates are those that have comparable ionic radii to the components of the adsorbent (Sparks, 2005). Figure 1 provides a summary of the removal of metals by the process of sorption.

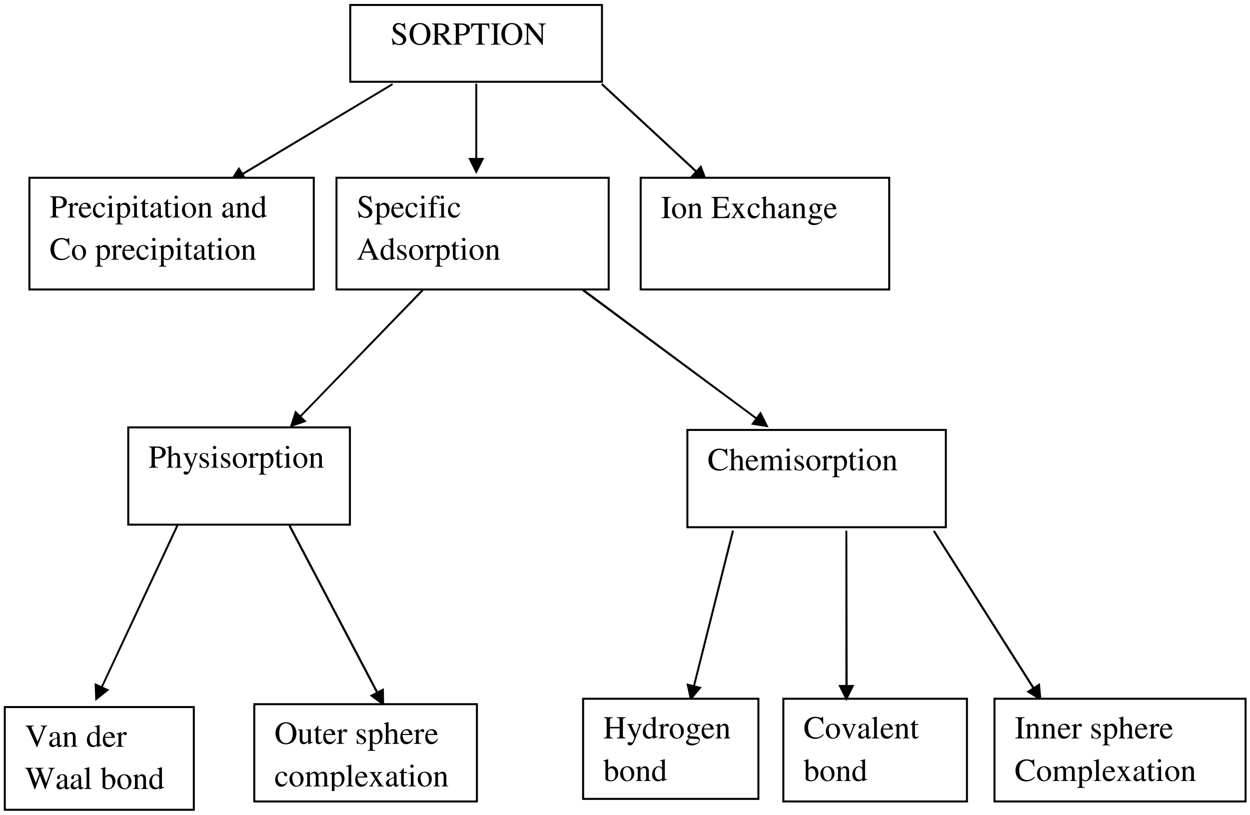

Figure 1: Summary of removal of contaminants by sorption

Iron oxide properties change with an increase in substitution but it is not conclusive to say a change in property is solely as a result of cation substitution. Cation substitution may also lead to colour modification in iron oxides (Cornell and Schwertmann, 1996). Iron oxides, being amphoteric in nature can dissolve in both acidic and basic media hence depending on how far pH changes from acidity or basicity, solubility can increase or decrease. Ionic strength, temperature, particle size and crystal defects also influence iron oxide solubility (Cornell and Schwertmann, 1996). Solubility is determined by surface properties such as surface free energy, hence solubility increases with crystal size of less than 1µm.

All amphoteric oxides have $MOH_2^{0.5+}$ and $MOH^{0.5-}$ groups whose protonation and deprotonation lead to a charge on the oxide's surface thus influencing the type of ions in solution to be bonded to the oxide. The surface charge is further altered by the introduction of acids or bases such that the surface may be positive, negative or with no charge; the surface charge density is also influenced by the ionic strength of the system. The pH at which the surface becomes uncharged is the point of zero charge (pzc); this is one of the most significant factors in describing variable-charge surfaces. Above this value the oxide removes cations due to the negative charge on the surface; the opposite is true for anions. When the surface charge is created exclusively by hydrogen ion exchange, then the term, point of zero net proton charge (pznpc) is used (Zhou and Haynes, 2010; Torodoric and Milonjic, 2004; Apel et al., 2003; Stumm, 1992; Parks, 1967). The mechanism for removal of metals by slag may sometimes be difficult to tell due to the buffering effect of the adsorbent; the adsorption process may be controlled by the pH of the slag. Table 2 lists the point of zero charge of oxides and other adsorbents reported by other researchers.

Table 2: Point of zero charge of selected adsorbents

Adsorbent	Point of Zero charge	Reference
Aluminium hydroxide ($\propto Al(OH)_3$)	5.0	Sparks (2003); Stumm (1992)
Alumina ($\propto Al_2O_3$)	7.2 -9.1	Sparks (2003); Brown et al. (1999)
Magnetite	6.4-7.5	Cornell and Schwertmann (1996)
Maghemite	6.3-8.4	Vayssieres (2009); Hu et al. (2006)
Goethite	7.4-9.7	Apel et al. (2002); Cornell and Schwertmann (1996)
Magnesium oxide	10.9-12.7	Sverjensky and Sahai (1996); Stumm (1992)
Silica	2.0-3.5	Brown et al. (1999); Sverjensky and Sahai (1996); Stumm (1992)
Calcium oxide	11.0-12.3	Brown et al.(1999)

2.6. Alumina

Al_2O_3, an amphoteric compound heavily employed in the aluminium metal production industry, has served as an effective adsorbent for the removal of pollutants from water. In nature, aluminium oxide is present in its crystal form as corundum. Aluminium oxides exist in many phases but two phases, γAl_2O_3 and α Al_2O_3, have been employed the most in many research activities. The former has a higher adsorptive capacity which can further be increased upon modification of the surface. The modification which involves the introduction of supplier functional groups like oxygen and phosphorus changes the mechanism of adsorption to include surface attraction of the contaminant by the introduced functional groups (Hua et al., 2012; Li et al., 2008; and Hiraide et al., 1995 and 1994). Hossein and Ebrahim (2012) used three types of modified γAl_2O_3 for the removal of Cd, Pb, Co, Ni and Cu in column studies. These authors reported >96 % removal of all metals and high sorption capability of the adsorbent after five cycles of adsorption-desorption and in the presence of other competing ions. The pH of removal varied between 1 and 10 and was dependent on the type of ligand used in the modification of the alumina. For example, the authors reported pH 5-9 as the range for simultaneous recovery of the afore-mentioned metals with dithizone modified alumina. Points of zero charge reported for alumina are in the range of 6.8 and 9.1 (Sparks, 2003; Todorovic and Milonjic, 2004). According to Todorovic and Milonjic (2004), in a study of the intrinsic ionisation and complexation constants, recorded pzc of 7.2 for alumina. They noted an insignificant effect of crystallisation on pzc and hence reported similar values for both $\propto Al_2O_3$ and γAl_2O_3. These authors further noted that the point of zero charge of alumina depends on the alumina: solution ratio and increasing the ratio increases the pzc until a constant value is attained.

2.7. Silicate

Silicates have been shown to be effective as adsorbents in the removal of heavy metals. They form the major components of minerals such as kaolinite and montmorillonite. Mechanisms such as adsorption, precipitation and ion exchange have been reported as being associated with the removal of contaminants from silicate surfaces with ion exchange as the primary removal mechanism by silicates (Nilforoushan et al., 2008).

2.8. Manganese oxides

Manganese oxides have proved effective in the removal of heavy metals from aqueous solutions with the nano-oxides having shown greater removal capacity than their bulk equivalent; the superiority being a result of higher surface area and the possession of polymorphic structures. The forms popularly used in research are hydrous manganese oxide and nanoporous manganese oxide. Sorption of heavy metal cations like Zn, Pb and Cd onto hydrous manganese oxides has been by ion exchange resulting in inner sphere complexation. The divalent cations are adsorbed in two steps, the first being a rapid process of attachment onto the surface sites and the second being the slow movement of the ions into the inner micro pores of the adsorbent by diffusion (Hua et al., 2012; and Fan et al., 2005). The sorption sites on these manganese oxides are heterogeneous, hence the better fit with the Freundlich isotherm. In a solution with mixed metals, the adsorbates' selective removal by manganese oxide will be according to the softness of the metal, thus for example Pb > Cd > Zn. The hardness classification was done in order to explain chemical and equilibrium reactions involving metal ions and ligands that cannot be classified as acids or bases based on their protonation (Hua et al., 2012 and Misono et al., 1967). Hocella et al. (1990) have also described transition metal cations to be soft acids and their adsorption on iron oxides to be independent of ionic strength due to the greater dependency of adsorption on co-ordination chemistry than on electrostatic attraction.

CHAPTER THREE

MATERIALS AND METHODS

3.1. Adsorbent

Nickel smelter slag, was obtained from Vale Canada Copper Cliff Smelter, Sudbury, Ontario. The slag, a byproduct of smelting nickel ore, was received as small rock particles from the company, which were subsequently crushed into smaller fragments with a pestle and mortar and later further ground into finer particles with a mortar and pestle. Prior to its use in the experiments, the slag was stored in air tight containers. The components of the bulk slag was also analysed using PAN-analytical PW-2400 Wavelength Dispersive XRF (X-Ray Fluorescence) after roasting 1 g of slag to loss of ignition .

3.2. Adsorbates

Analytical grade chemicals were employed in all experiments. The compounds, $Pb(NO_3)_2$, $Cd(NO_3)_2.4H_20$, $Cu(NO_3)_2.2.5H_20$, $Zn(NO_3)_2.6H_20$ and $N_2NiO_6.6H_20$, were purchased from Sigma Aldrich (USA) and used in the experiments. Appropriate amounts of the metal salts were dissolved in mega-pure or de-ionized water (DIW) to yield the lead, cadmium, copper, zinc and nickel stock solutions of concentration 1000 mg/L. The stock solutions were further diluted with DIW water to obtain the various concentrations used in the adsorption studies. All glassware were thoroughly washed with soap, followed by 10 % HNO_3 and then rinsed many times with DIW before use. The pH of the solutions were measured with an Orion Model 410 pH meter (Boston, USA). The adjustment of pH was done using either 0.1 M HNO_3 or 0.1M NaOH.

3.3. Batch experiments

Adsorption studies were performed by shaking known amounts of nickel slag with 50 mL metal solutions in 125-mL Erlenmeyer flask at room temperature ($23^oC \pm 2^oC$). All experiments were carried out in triplicate on the rotary shaker (New Jersey, USA) at a shaking speed of 170 rpm. The speed of 170 rpm was chosen since it allowed good contact between the adsorbent and adsorbate and yielded good results similar to 200 rpm used in the trial experiments; this speed was also within the range of those used by many authors (Chowdhury, 2013; Mohapatra et al., 2010; Liu et al., 2009). In all experiments, there were control blanks to check if there was adsorption of the metal ions onto the walls of the Erlenmeyer bottles. There was no adsorption on the walls of the bottles. Unless otherwise stated the experimental conditions were pH:5; contact time: 10 hours, shaking speed: 170 rpm; slag dose 10 g/L; temperature: 25ºC; slag size: 75-128 µm; initial concentration of metals: 10 mg/L.

3.3.1. pH studies

In order to obtain information on the optimal pH for Pb adsorption, 10 mg/L of Pb solution was shaken with 10 g/L of nickel slag for 10 hours at pH 2-11. Solution samples were taken at the end of the experiment and filtered with 0.2 µm filters. The filtrates were acidified with 2 % HNO_3 and analyzed for Pb concentrations using the Varian Vista Pro inductively coupled plasma-optical emission spectroscopy (ICP-OES). Similar experiments were run for 10 mg/L of Cu and also for a mixed metal system of Cd, Cu, Ni, Pb and Zn at a concentration of 10 mg/L of each metal except Cd whose concentration was 7 mg/L. The volume of the Pb and Cu solutions were 50 mL each and that of the mixed system was also 50 mL.

3.3.2. Contact time and kinetic studies

Experiments to determine the optimum contact time necessary for adsorption studies were performed by separately reacting 10 g/L of slag with 10 mg/L of Pb and 10 mg/L Cu in a 125 mL Erlenmeyer flask at pH 5. Samples were taken periodically and analyzed for metal concentrations at the various contact times using ICP-OES. This was continued until equilibrium. The adsorption efficiency (percentage metal removal) at a specific contact time was calculated using equation 1. The pseudo first order kinetic model (Lagergren, 1898) and the pseudo second order kinetic model (Ho and McKay, 1999) were also used to describe the kinetics involved in the adsorption of Pb and Cu by nickel smelter slag. The generalised forms of the models were used in the calculations and shown in equation 2 (pseudo first order model) and equation 3 (pseudo second order)

$$Adsorption\ efficiency\ (\%) = \left(\frac{Co-Ct}{Co}\right) \times 100 \qquad (1)$$

$$\log(qe - qt) = \log qe - \frac{k_1}{2.303}t \qquad (2)$$

$$\frac{1}{qt} = \frac{1}{k_2 qe^2} + \frac{1}{qe}t \qquad (3)$$

Where,

C_o = the initial concentration (mg/L)

C_t = concentration at time, t (mg/L)

q_e = amount of solute adsorbed at equilibrium (mg/g)

q_t= amount of solute adsorbed at any time, t (mg/g)

k_1= pseudo first order rate constant (min^{-1})

k_2= pseudo second order rate constant (mg $g^{-1}min^{-1}$)

t= time (min)

3.3.3. Adsorbent dose

The amount of slag needed to effectively remove the target metals was also studied. Different amounts of slag, ranging from 10 g/L to 60 g/L, were separately reacted with 10 mg/L and 100 mg/L each of Pb and Cu, a for contact time of 10 hours and pH of 5 (natural pH of the system). At the end of the experiment, the mixtures were filtered through 0.2 micron syringe filters and the filtrates were analysed for metal concentrations using ICP-OES. Similar experiments were also conducted for a mixed metal system containing 10 mg/L of Pb, Cu, Ni and Zn and 7 mg/L of Cd; in this case, the slag amount was from 10 g/L to 80 g/L.

3.3.4. Particle size studies

In another set of experiments, different particle sizes of slag at a dose of 10 g/L were reacted with 10 mg/L lead and copper solutions for 10 hours. The rotary lab sifter (Burlington, Canada) and the Canadian Standard Sieve Series (St Catharine's, Canada) were employed in sorting the sample into different sizes. The mesh openings that retained the samples were 425 µm, 250 µm, 150 µm, 106 µm, 75 µm, <75 µm corresponding to the standard sieves of mesh numbers 40, 60, 100, 140, 200 and >200 (pan), respectively.

3.3.5. Effect of competing ions

Adsorption has been shown to favour some elements better than others. In order to study the effect of other ions on the adsorption of Pb and Cu by nickel smelter slag, a 50 mL solution containing a mixture of metals was reacted with 10 g/L of nickel smelter slag until equilibrium was achieved. The elements in the mixed system were 10 mg/L each of Cu, Ni, Pb, Zn, and 7 mg/L of Cd. After the 10 hour contact time, the mixture was filtered with a 0.2 µm Nalgene syringe filter; the filtrate was acidified with 2 % nitric acid and then analyzed for metal concentrations using ICP-OES.

3.3.6. Adsorption isotherm

Adsorption data were interpreted using published adsorption isotherms. Such isotherms include the Langmuir, Freundlich, BET and Temkin isotherms. They can be used to describe the properties of the adsorbent surface as well as explain the adsorption behaviour of many adsorbents and adsorbates. These isotherm equations typically relate the amount of adsorbed solute on the adsorbent to that remaining in solution at equilibrium at a given temperature. (McCabe et al., 2005; and Felder and Rousseau, 2000). The Langmuir and Freundlich isotherms were used in this study.

The Langmuir model (Langmuir, 1916) operates on the assumption that the adsorbent has a uniform surface and adsorption occurs as a monolayer adsorption, and that there are no negligible forces of interaction between the adsorbed ions. Hence once a site is occupied by an ion or molecule, there is no other adsorption on that site. The equation for this model is expressed as:

$$\frac{Ce}{qe} = \frac{Ce}{qm} + \frac{1}{bqm} \qquad (4)$$

Where,

C_e = equilibrium concentration

q_e = amount of solute adsorbed at equilibrium

q_m = Langmuir constant related to adsorption capacity. It represents the maximum monolayer adsorption capacity (mg/g)

b = Langmuir constant related to apparent heat change (L/mg).

The efficiency of the Langmuir adsorption process is further assessed by the equation:

$$r = \frac{1}{(1+bCo)} \qquad (5)$$

Where,

r = separation factor

b= Langmuir constant related to apparent heat change (L/mg)

C_o = Initial concentration of solute (mg/L)

The Freundlich model (Freundlich, 1926) assumes that adsorption takes place in a multilayer on a heterogeneous surface. The equation is expressed as:

$$qe \ = Kf \ \times Ce^{\frac{1}{n}} \qquad (6)$$

where,

C_e = concentration of solute at equilibrium (mg/L)

q_e = mass of solute adsorbed per unit mass of adsorbent (mg/g)

K_f = Freundlich constant related to adsorption capacity (mg/g)

n = Freundlich constant depicting bond strength or intensity

This equation is written in a linear form as a log function, thus:

$$log\ qe = log\ Kf + \frac{1}{n}\ log\ Ce \qquad (7)$$

3.3.7. Desorption tests

In this set of experiments, separate solutions containing 10 mg/L each of Pb and Cu were placed in 125 mL Erlenmeyer flasks and shaken with 10 g/L of slag in a rotary shaker for 10 hours at a speed of 170 rpm. The speed of 170 rpm was maintained in the desorption test in order to provide the same conditions of adsorption as desorption. After adsorption, the solutions were filtered with 0.2 micron syringe filters; the filtrate was analysed for metals using ICP-OES. The metal-loaded slag was washed with deionised water in order to wash off any loosely attached metal ions and also prepare the surface for desorption. The loaded slag was shaken with 50 mL of 0.1 M HNO_3 for 10 hours; this constituted the desorption step. The adsorption-desorption process was repeated 4 times; a step of adsorption and desorption constitute one cycle. Samples were taken and analysed by ICP-OES for both adsorption and desorption. A similar test of 5 cycles of adsorption and desorption was also carried out for a mixed metal solution of Cd, Cu, Ni, Pb and Zn at concentration of 7-10 mg/L and slag dose of 80 g/L.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1. Characteristics of nickel smelter slag

The XRF tests performed on the slag revealed major constituents as shown in Table 3.

Table 3: Composition of nickel smelter slag

Constituent	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	Na_2O	P_2O_5	Cr_2O_3
%	36.90	0.20	2.44	56.72	0.04	1.23	1.26	0.63	0.26	0.11	0.20

The results from Table 3 show the major components of the slag to be iron oxides and silicon dioxides at 56.34 % and 36.90 % respectively. Compared to the values of slag constituents shown in Table 1, the nickel smelter slag appears to have a greater resemblance to steel slag than to blast furnace slag. It should then follow that sorption on the sites would be in a decreasing order of abundance of the compounds Fe_2O_3, SiO_2, Al_2O_3, CaO, and MgO. Many authors have recorded high affinity of SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO and TiO_2 for heavy metals (Zhou and Haynes, 2011; and Feng et al., 2004). An 89 % and 95 % removal of Pb and Zn at an initial concentration of 300 mg/L and 160 mg/L respectively using iron oxide adsorbent has been reported (Sidhaarth et al., 2012). Similarly, steel slag containing 38.8 % Fe_2O_3, 12.33 % SiO_2 and 32.73 % CaO was efficient in reducing a Pb concentration of 150 mg/L by 99 % (Liu et al., 2010). These oxide compounds are alkaline in nature and responsible for the neutralization property possessed by oxide-rich adsorbents. The buffering effect possessed by these adsorbents make preliminary pH adjustment unnecessary (Nilforoushan et al., 2008). Due to the presence of different mineral phases on adsorbents such as slag, samples of the same material may have different specific sorption features (Zhou and Haynes, 2010).

In a review, Ahmaruzzaman (2011) reported the successful use of red mud, fly ash, waste hydroxide and sludge, all possessing an abundance of alumina, silicates and iron oxides in various amounts for the removal of Pb, Zn, Hg, Ni, Cu, As, Cr and many other contaminants. For example, red mud has been identified to consist of approximately 60 % silica, 25 % alumina and 6 % magnetite. Taha (2006) employed bagasse fly ash for the removal of chromium, nickel, copper and zinc, and reported as high as 99.2 %, 98.8 %, 99.2 % and 96 % removal of the above-mentioned metals respectively under optimum conditions. Likewise, Das et al. (2008) attributed the removal of Cu and Pb to the iron and aluminosilicates present in blast furnace flue dust. Similarly, fly ash containing 25.90 % alumina and 56.04 % silica was excellent in removing Cu ions from solution. Surface ionization and complexation were reported to be the factors responsible for the difference in adsorption of Cu at varying pH. These authors noted that diffusion might also have accounted for the removal of copper; they reported up to 100 % removal of Cu at an initial concentration of 1.0×10^{-4} M and pH of 6.5 (Panday et al., 1985).

4.2. pH Studies

The pH of a solution is a very strong indicator of the extent of adsorption. The effect of pH on the removal of Cu, Cd, Ni, Pb and Zn was studied at pH 2-11. Figures 2-4 show the results obtained from the series of experiments performed to study the effect of pH on metal removal by nickel smelter slag.

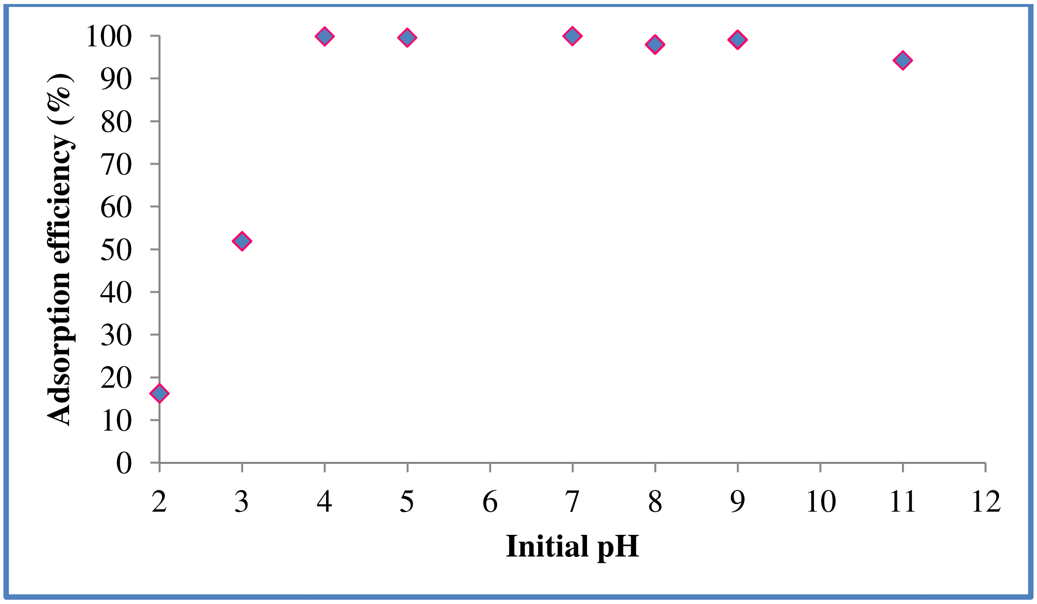

Figure 2: Effect of pH on removal of Pb by nickel smelter slag (initial concentration: 10 mg/L, slag dose: 10 g/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25° C)

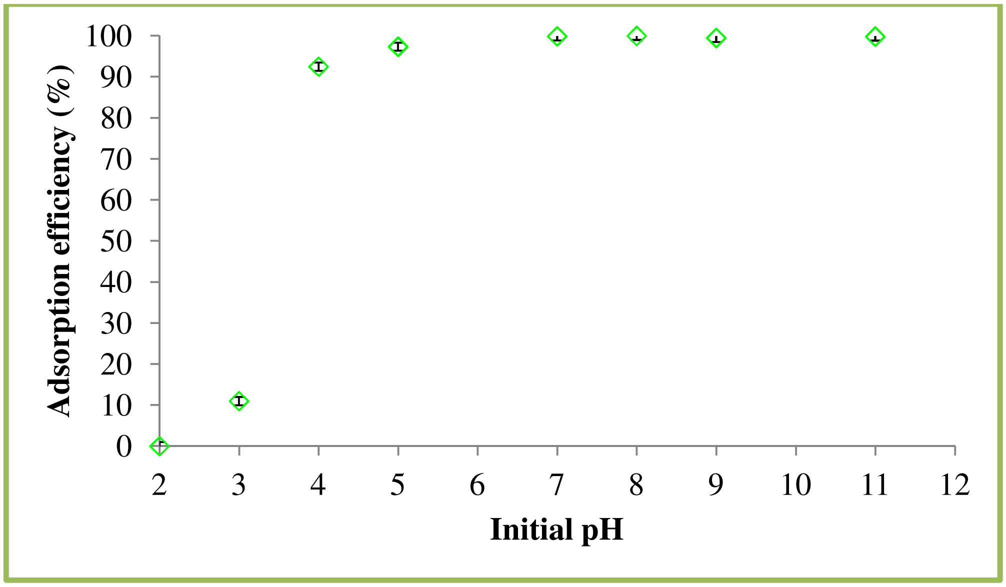

Figure 3: Effect of pH on removal of Cu by nickel smelter slag (initial concentration: 10 mg/L, slag dose: 10 g/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25º C)

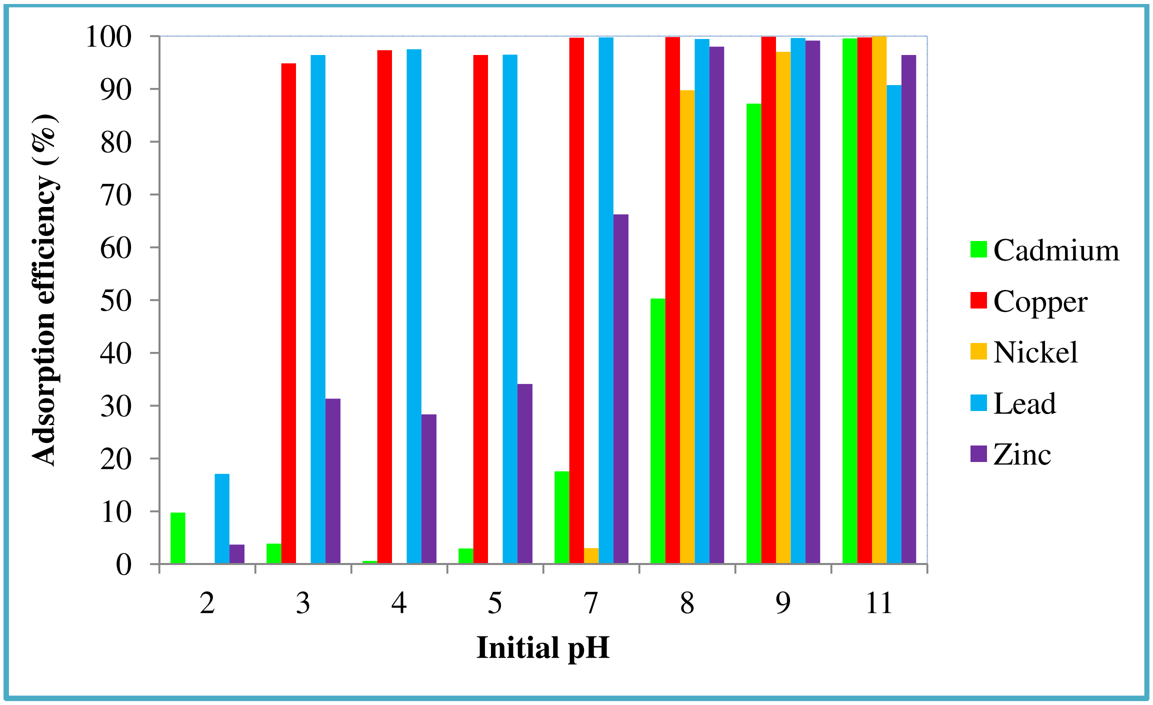

Figure 4: Effect of pH on removal of Cd, Cu, Ni, Pb and Zn by nickel smelter slag (initial concentration: 7-10 mg/L, slag dose: 10 g/L, contact time: 10 hours, shaking speed: 170 rpm, 25º C)

The experiments revealed a general increase in metal removal with increasing pH for all five metals in both the single and the mixed systems. The sharp increase in removal for Pb and Cu from pH 2 to 5 may be accounted for by the adsorption edge. Reeder et al. (2006) confirmed that although there is a general increase in adsorption of cations with increasing pH, there exists a narrow pH range, the adsorption edge, at which the adsorption efficiency is very high. This change may vary for different metals on the same adsorbent due to different mechanisms operating for the removal of the metals. For the same metal, the range of pH at which it is removed may vary due to the presence of different adsorption sites and surface charge on the same adsorbent.

At pH 5 the removal of Cd, Cu, Ni, Pb and Zn are 3.00 %, 96.42 %, 0.00 %, 96.48 % and 34.15 %, respectively. There is a dramatic increase in removal of Cd, Ni and Zn at pH above 5. Modelling of experimental data with Visual MINTEQ revealed that 99 % of the metals were present as Me^{2+} with <0.3 % as $Me(OH)^+$ and negligible amounts of other hydroxide species (where Me is the metal). Saturation indices of <0 were recorded in all cases suggesting that the metals at this pH were understurated and thus in their aqueous forms. This confirms the absence of precipitation in the removal of these metals at pH 5. Several workers such as Raju et al. (2012), Chen et al. (2011), and Amin et al. (2010), have reported a general increase in removal of cations with increasing pH and vice versa for anionic species.

Zhou and Haynes (2011) have attributed the change in pH during experiments with slag and other industrial byproducts to be as a result of the high surface alkalinity possessed by these adsorbents. This surface alkalinity property may be said to provide a buffering capacity during the experiments thus making it difficult to determine the actual pH at which adsorption takes place although regular adjustment helped to keep the pH at a close enough value. However, it may also be said that the high removal rate achieved at pH 5, similar to those in the alkaline range may be attributed to ion exchange between the hydrogen ions and adsorbates, the presence of some hydroxyl on the surface of the slag and the net negative charge on the surface of the slag shown by the point of zero charge.

The effect of pH on removal of the cations could also be explained in terms of the point of zero charge. Generally the point of zero charge of silica, manganese oxides and clay minerals are below 4 while those of aluminium and iron oxides are above 7 (Sposito, 2000). However, in this study, the point of zero charge of the nickel smelter slag was approximately 3.1 (as shown in the appendix). Below the point of zero charge, the surface of the adsorbent is positive and cations (Me^{2+}, $Me(OH)^+$ will be removed through ion exchange with H^+. When the adsorbent's surface becomes negative at pH above the point of zero charge, cations are then adsorbed through electrostatic attraction. This accounts for the high removal rates of metals at pH 5 and higher. All other experiments were run at this pH since it required no addition of chemical (acid or base) that comes at an extra cost. Srivastava et al. (1997) also showed that blast furnace waste had point of zero charge of 2.8 although its constituent alumina and silica had point of zero charges of 8.2 and 2.3 respectively, the slag had optimum removal of Pb and Cr at pH of 4 and 1 respectively. According to Wang et al. (2010), for amphoteric iron oxides such as magnetite with pzc of about 7.33, even at pH < pzc, where $FeOH_2^+$ dominate, there is still some amount of FeO^- groups capable of removing cations from solution. Chang and Chen (2005) recorded pH >2 to be favourable for the removal of Cu by chitosan-bound Fe_3O_4 nanoparticles whose point of zero charge was recorded to be 5.95.

At pH 8 and above, visible precipitates were seen in the metal solution; however these could not be recovered for X-ray analysis to determine the type of precipitates. Saturation indices above zero were recorded for some species of all metals except Cd, using Visual MINTEQ; this confirmed the presence of precipitates of all metals under study with the exception of Cd at pH of 8 and above. At such high pH, precipitates such as CuO, $Cu(OH)_2$, $Ni(OH)_2$, $Pb(OH)_2$, ZnO and $Zn\ (OH)_2$ are formed. The presence of precipitates at high pH suggest that removal of the metals at such pH may not be attributed solely to adsorption. Chang and Chen (2005) also confirmed the presence of white precipitate of Cu at pH >5 and adsorption not being the main mechanism of Cu removal at such pH.

Although there was a general increase in removal with pH, Zn and Pb recorded a slight decrease in removal at pH 11. The values decreased from 99.63 % to 90.74 % for Pb from pH 9 to 11 and a reduction from 99.15 % to 96.45 % for Zn at the same pH change. Chen et al. (2011) recorded similar findings in their work on using two types of slag to remove Cu, Cd, Zn and Pb. The reduction in Zn and Pb removal at higher pH could be due to the dissolution of these metals from their oxides at higher pH. Zn and Pb are known to form amphoteric oxides, $Zn(OH)_2$ and $Pb(OH)_2$ that are soluble at high pH.

The increase in pH results in a reduction in H^+ ions that serve as competitive species with the heavy metals for adsorption sites. The adsorption sites are now available to be occupied by more metal ions than H^+ ions. In alkaline pH there is an abundance of OH^- on the slag surface which promotes the adsorption of cations. These results are in agreement with observations made by several workers who have reported significantly higher adsorption of cations in alkaline pH range than in acidic range. Thus from this study, ion exchange and electrostatic attraction contribute to the removal of cations by the nickel smelter slag.

4.3. Effect of contact time

Adsorption was measured as a function of time in order to establish the optimum contact time as well as the kinetics involved in the removal of Pb and Cu with the slag. In this experiment, 10 g/L of nickel smelter slag was reacted with 10 mg/L each of Pb and Cu over 24 hours. Samples were taken periodically and analysed by ICP-OES.

The graphs in Figures 5 and 6 show that the removal of Pb and Cu increased with increasing time; removal is very fast in the initial stages of the experiments and then becomes gradual towards the end of the experiments. In the first 5 and 20 minutes, 55.85 % and 91.58 % of Pb was been adsorbed while 34.55 % and 88.65 % of Cu was adsorbed respectively. By the first hour, there was 92.49 % and 94.06 % removal for Pb and Cu, respectively, at initial concentration of 10 mg/L and optimum slag dose of 10 g/L. This may be attributed to the presence of the large exterior surface being fully available at the initial stage; as the exterior sites become filled with ions, the ions are then moved from the exterior to the interior, thus accounting for the slower rate of adsorption following the initial fast rate (Chen et al., 2011; and Liu et al., 2009).

After the first hour, interparticle and intraparticle diffusion may account for the gradual increase in removal of Cu and Pb. Furthermore, it can be seen that at the end of 10 hours, 99.60 % of Pb was removed while 99.89 % was removed in 24 hours. A similar result occurs in Cu where 97.97

% and 98.90% were removed in 10 hours and 24 hours respectively. Contact time of 10 hours was then chosen for other experiments since it gave very high adsorption efficiency. The high removal amount of the two metals by the nickel smelter slag confirms the effectiveness of the adsorbent for the two metals under study.

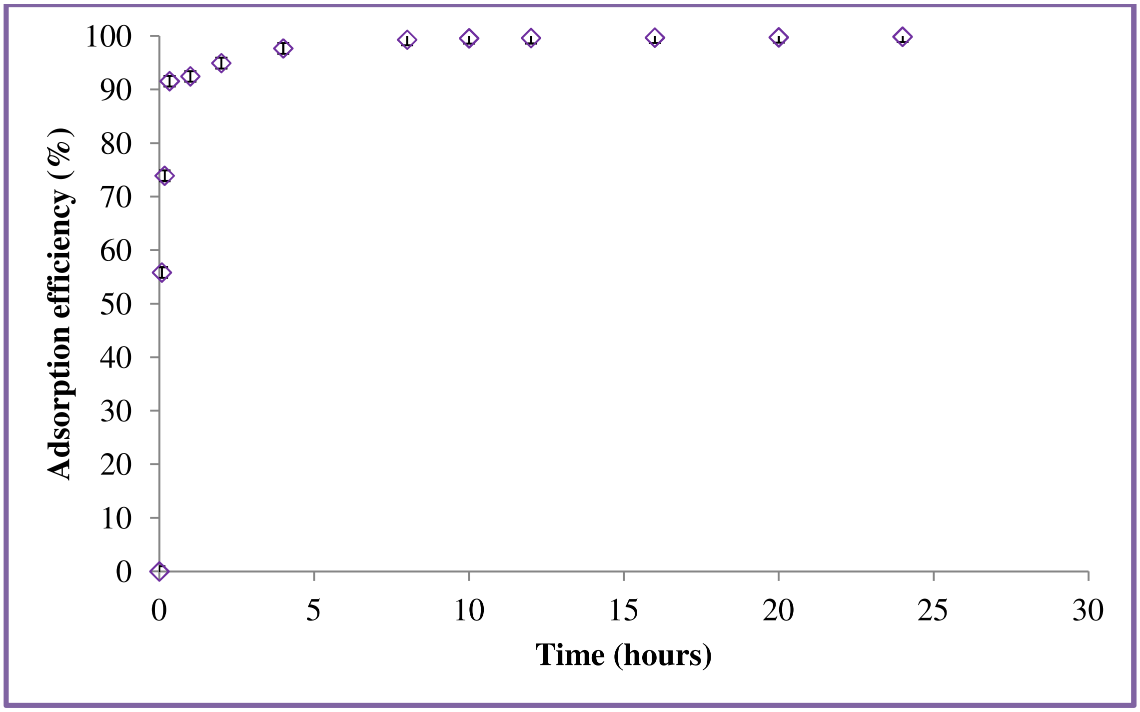

Figure 5: Effect of contact time on removal of Pb by nickel smelter slag (initial concentration: 10 mg/L, slag dose: 10 g/L, shaking speed: 170 rpm, temperature: 25° C)

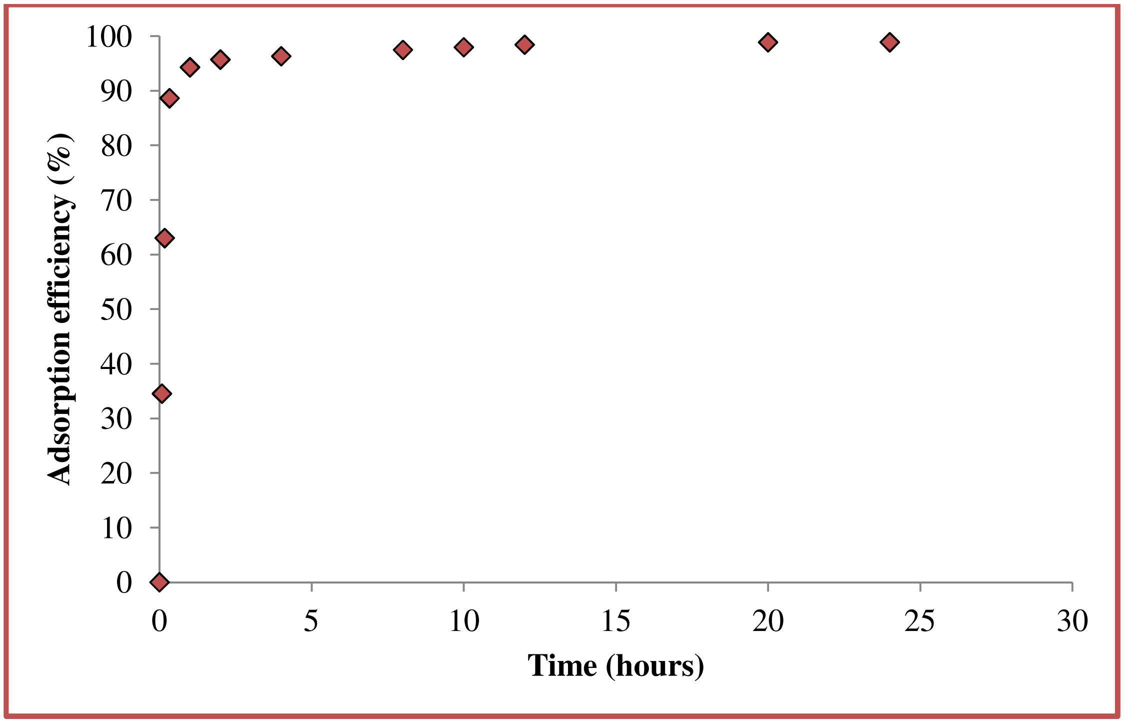

Figure 6: Effect of contact time on removal of Cu by nickel smelter slag (initial concentration: 10 mg/L, slag dose: 10 g/L, shaking speed: 170 rpm, temperature: 25º C)

The sorption kinetics of Pb and Cu on nickel smelter slag was analyzed using the pseudo first order and pseudo second order kinetic models. Table 4 shows the parameters obtained from fitting the data to the pseudo first order and pseudo second order kinetic rate models.

Kinetic studies give an understanding of the mechanisms of sorption as well as the pathways of reactions. This information obtained from the rate law, helps to predict the uptake of contaminants by sorbents and overall helps in efficient design of an industrial waste water treatment plant. The data from this study shows a better fit for the pseudo second order model than the pseudo first order model with R^2 values being unity for both Pb and Cu. The pseudo first order model is based on the assumption that an ion is sorbed onto one site on an adsorbent's surface. In this study, k_1 value of 4.84×10^{-3} min^{-1} was recorded for Cu and 3.68×10^{-3} min^{-1} was recorded as k_1 value for Pb suggesting Cu was adsorbed faster than Pb. The qe values of 0.11 mg g^{-1} and 0.05 mg g^{-1} recorded for Cu and Pb were very different from the qe values of 1.05 mg/g and 1.08 mg/g obtained for Cu and Pb respectively from the experimental data.

On the other hand, a contrary trend is provided by the pseudo second order which presents a better fit of the experimental data. The pseudo second order model operates on the assumption that a metal ion is sorbed on two sites of an adsorbent's surface. In this study, Pb is adsorbed at a rate (k_2) of 0.18 mg $g^{-1}min^{-1}$ while Cu is adsorbed at a rate (k_2) of 0.14 mg $g^{-1}min^{-1}$. Furthermore, the qe values obtained in the pseudo second order model is the same as those obtained from the experimental data; 1.08 and 1.05 mg/g for Pb and Cu respectively. Liu et al. (2009) reported a better fit of pseudo second order model with the removal of Pb ions with steel slag; with this model the authors recorded R^2 value of 0.995 while that of the pseudo first order model was 0.872. The pseudo second order has been used to describe chemisorption involving covalent bonds between an adsorbate and an adsorbent as well as ion exchange (Ahmaruzzaman, 2011; Boparai et al., 2011; Wang et al., 2010). The results from this experiment show that adsorption of Pb and Cu by the nickel smelter slag occurs by chemical interaction between the metal ions and the adsorbent. Chemisorption could be said to be a signifcant mechanism in the interaction between the nickel slag and the metals under study. Contrary to this, authors such as Chen et al. (2011) and Srivastava et al. (1997) have reported first order kinetics as the better fit for the removal of metals such as Cu, Cd, Zn, Pb and Cr by electric arc blast furnace slag and activated blast furnace slag respectively.

Ho and Mckay (1999) in a review of literature on removal of polluted aqueous effluents have recorded a greater fit of sorption kinetics to the pseudo second order model. The authors studied over 70 systems; the authors reported a better fit of the pseudo second order kinetic model of 11 out of 12 systems previously described as being pseudo first order. According to these authors, the pseudo first order model provides a fit for the initial period of the reaction time; over a long period the pseudo second order model gives the best correlation. However, there are some complex systems that fit both the pseudo first order and pesudo second order kinetic models; the sorption of Hg by kaolinite is one such example (Ho and Mckay, 1999; Sing et al., 1996; Varshney et al., 1996).

Table 4: Parameters of adsorption kinetic models

Kinetic Model	Parameters	Cu	Pb
Pseudo first order	k_1	4.84×10^{-3} min^{-1}	3.68×10^{-3} min^{-1}
	qe	0.11 mg/g	0.05 mg/g
	R^2	0.94	0.91
Pseudo second order	k_2	0.14 mg g^{-1}min^{-1}	0.18 mg g^{-1}min^{-1}
	qe	1.05 mg/g	1.08 mg/g
	R^2	1.0	1.0

4.4. Effect of slag dose

The graphs in Figures 7-10 reveal the optimum dose of nickel smelter slag needed to effectively remove heavy metals from solution. The plots show that the percentage removal increased with an increase in slag dose from 2 g/L to 40 g/L for Pb and Cu and 10 g/L to 80 g/L for the mixed metal solution. As shown in Figures 8 and 9, a slag dose of 10 g/L was sufficient to remove over 90 % of Pb and Cu from 10 mg/L solutions while 40 g/L effectively removed 100 mg/L Pb and Cu from solution. In the mixed metal system, 80 g/L was also sufficient to remove over 99 % of all five metals from solution. Adsorption is dependent on the amount of adsorbent and also on initial concentration of metal ions; this is exhibited in the difference in adsorption efficiency for the various amounts of slag in contact with 10 mg/L of Cu and Pb; furthermore, this is seen in the ability of 40 g/L slag to effectively remove 100 mg/L of Pb but not by 10 g/L of slag as displayed in Figures 9 and 10.

The adsorption capacity of the nickel smelter slag for Pb and Cu in the mixed metal solution at a slag dose of 10 g/L is less than that of the single element solution and this could be due to the effect of competition by the other three metals.

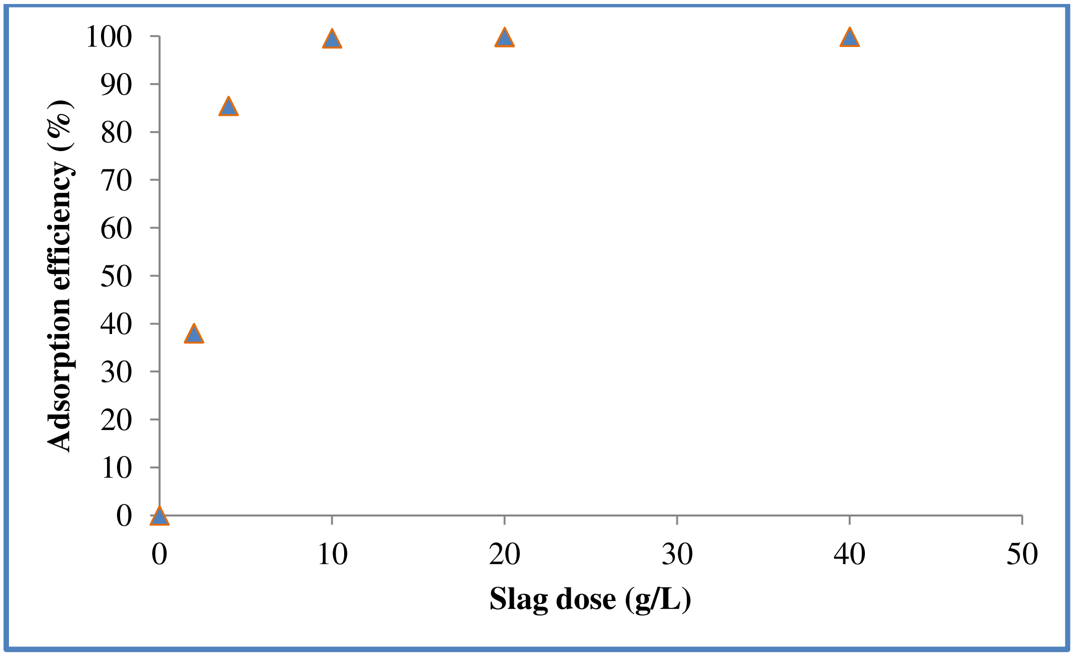

Figure 7: Effect of slag dose on removal of Pb by nickel smelter slag (initial concentration: 10 mg/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25º C)

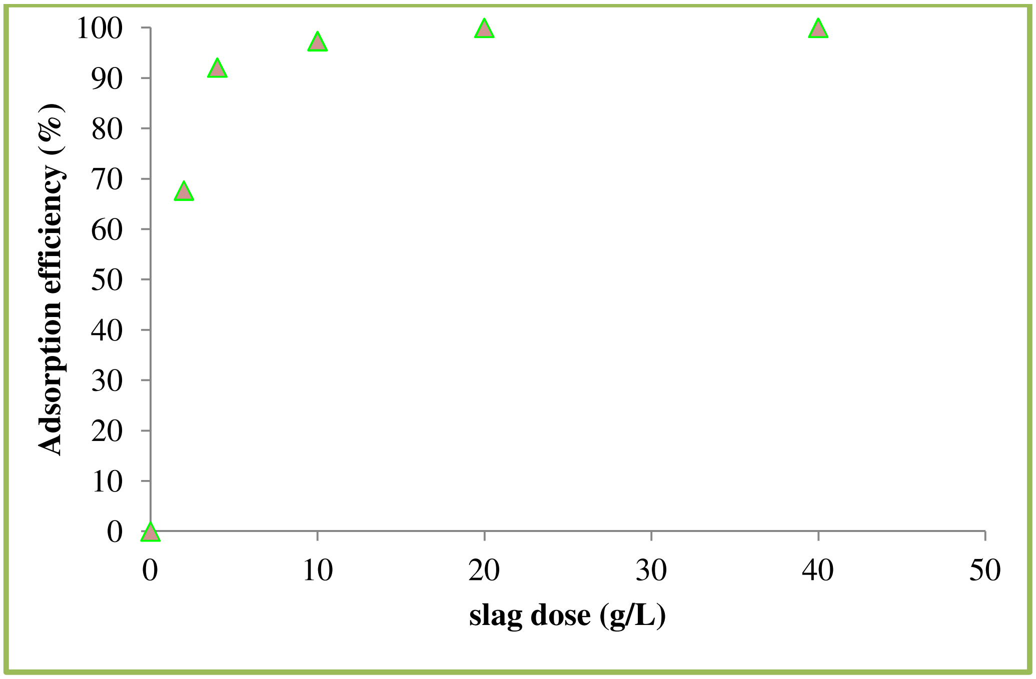

Figure 8: Effect of slag dose on removal of Cu by nickel smelter slag (initial concentration: 10 mg/L, contact time:10 hours shaking speed: 170 rpm, temperature: 25º C)

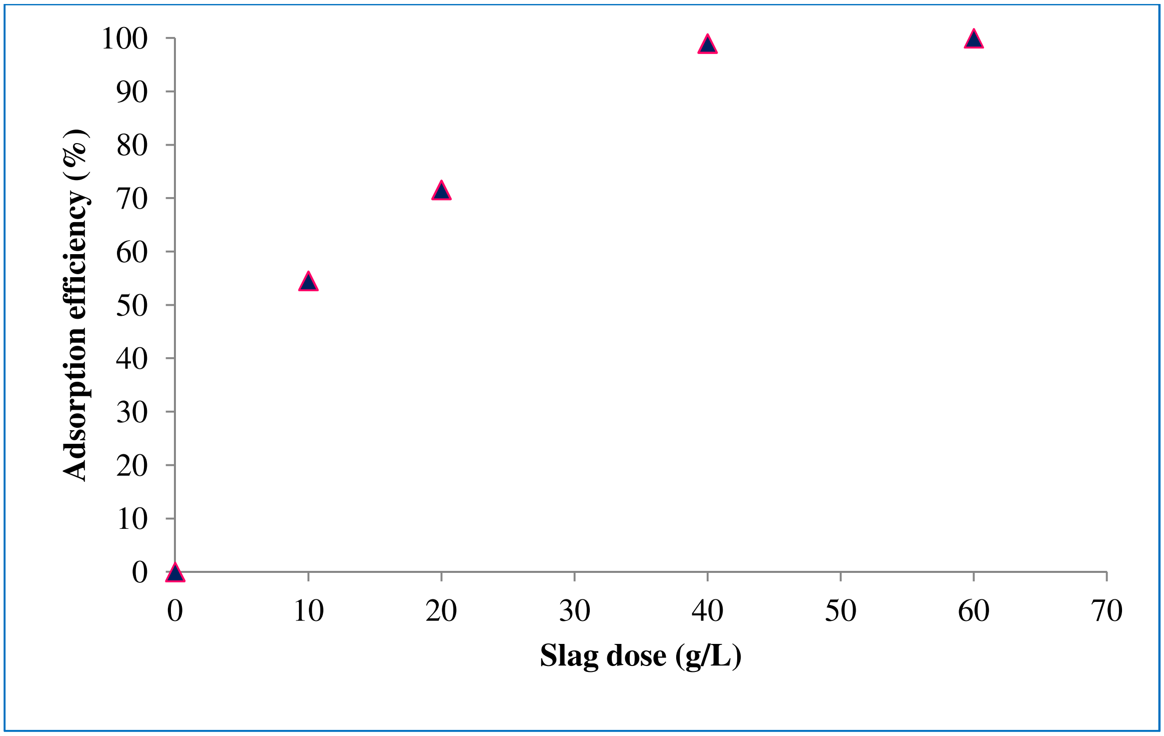

Figure 9: Effect of slag dose on removal of Pb by nickel smelter slag (initial concentration: 100 mg/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25º C)

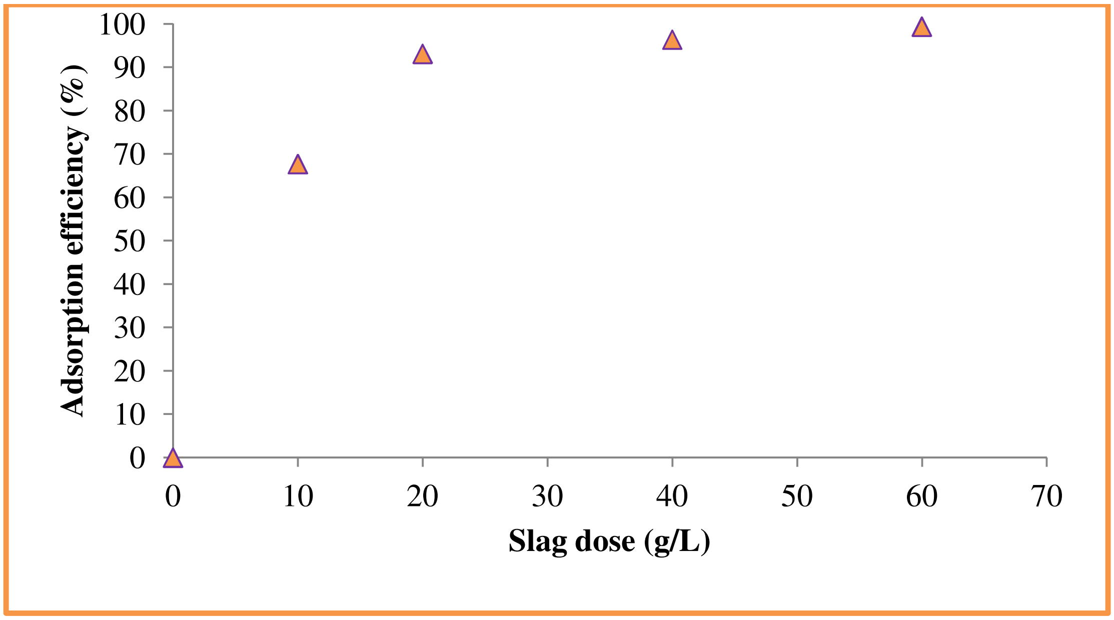

Figure 10: Effect of slag dose on removal of Cu by nickel smelter slag (initial concentration: 100 mg/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25º C)

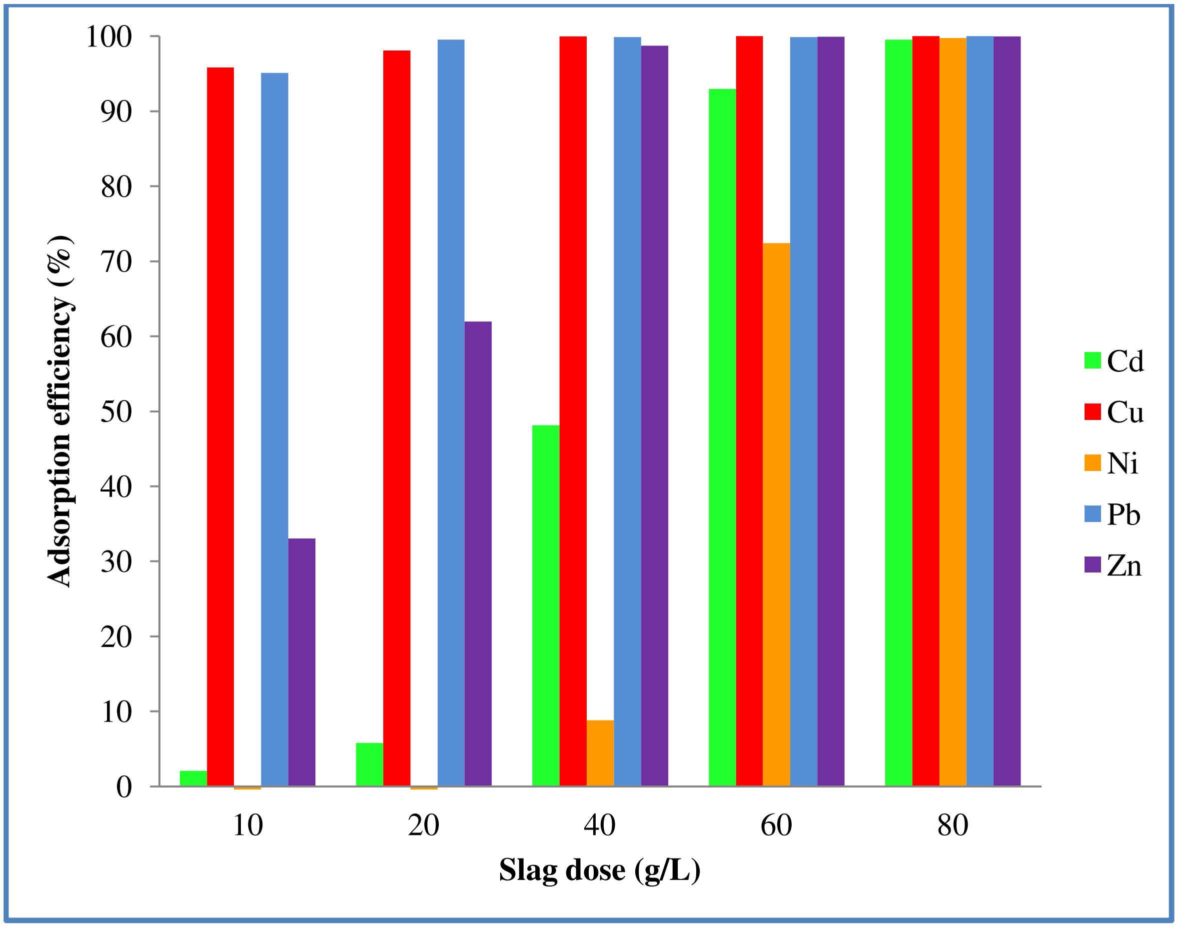

Figure 11: Effect of slag dose on removal of Cd, Cu, Ni, Pb and Zn by nickel smelter slag (initial concentration: 7-10 mg/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25º C)

Figure 11 also shows that there is a general increase in adsorption of all metals with an increase in slag dosage. At low slag adsorbent dose, there is small surface for attachment of the heavy metals hence the low adsorption efficiency. However as the adsorbent amount increases, more sites become available for attachment hence the increased removal in the metals under study.

At low adsorbent dose, the surface area available for adsorption is limited and competition for the few sites is higher. Cu and Pb, having a higher affinity for the adsorbent are removed first and as the dosage of adsorbent increases, more surface area becomes available and the metals are adsorbed. Pb and Cu generally have high removal rates over the range of dosage studied;

however, Cd, Zn and Ni show a significant increase in adsorption with increase in dosage from 10 g/L to 80 g/L. Slag dose of 60 g/L results in over 60% removal of all metals under study and slag dose of 80 g/L is capable of removing all metals above 90%. At slag dose of 20 g/L and below, no Ni was removed from solution but rather an increase in Nickel in the aqueous phase. This could also be attributed to the low affinity of the slag for this metal. The slag already had some Ni bound to it from the production source. In the presence of metals of higher affinity, Ni bound to the slag surface from the smelter operations could have desorbed into solution in order for the metals such as Cu and Pb with higher affinity for the slag to be adsorbed. Ion exchange can be said to be a contributor to the increased amount of Ni in solution at low slag dose. As the surface area increases due to an increase in dosage, some of the Ni in solution is then adsorbed onto the slag.

4.5. Effect of particle size

Adsorption occurs on the surface of an adsorbent. An inverse relationship exists between surface area of a solid and particle size such that for an ideal case with cubes:

$$S = \frac{6}{\rho l} \qquad (8)$$

where S is the specific surface, ρ is density and l is the particle size. The results of the study on the effect of average particle size on the removal of Cu and Pb are shown in Figures 12 and 13.

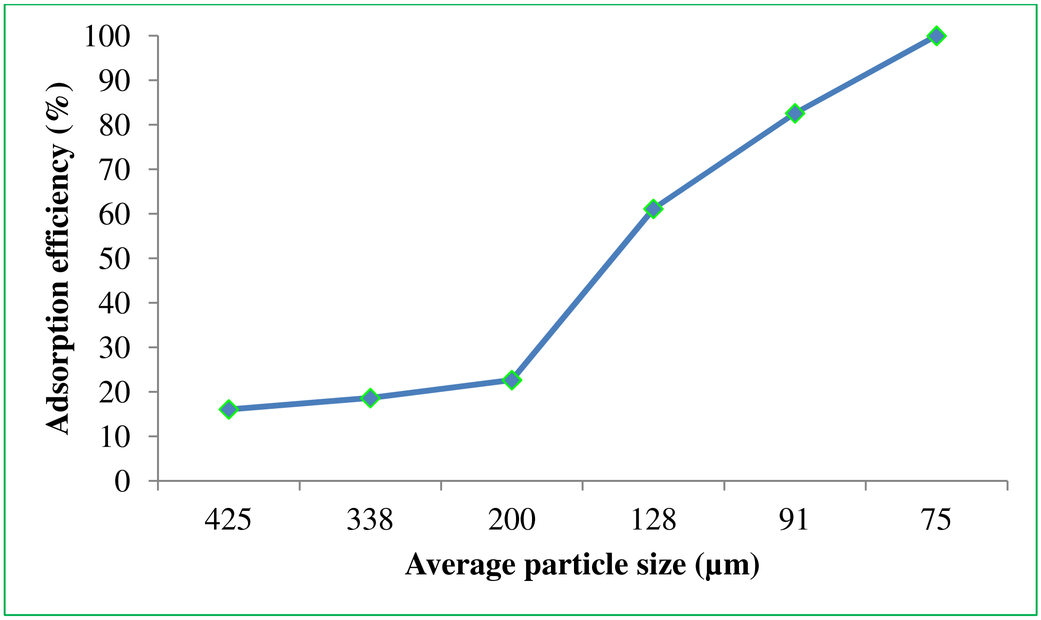

Figure 12: Effect of particle size on removal of Pb by nickel smelter slag (initial concentration: 10 mg/L, slag dose: 10 g/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25° C)

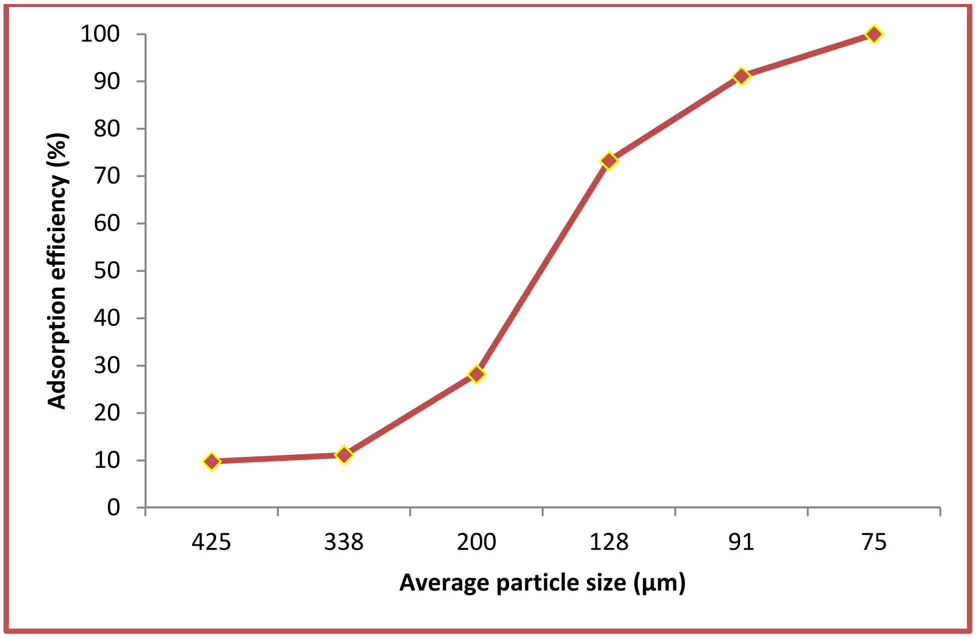

Figure 13: Effect of particle size on removal of Cu by nickel smelter slag (initial concentration: 10 mg/L, slag dose: 10 g/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25° C)

The removal of heavy metals is shown to increase with a decrease in particle size. Removal between 9.75 % -100 % is achieved for Cu and 16.08 %-100 % for Pb over the size range studied. Significant increase in adsorption is achieved when the particle size reduces from 200 µm to 128 µm for both Cu and Pb. For both metals, there was a gradual increase in adsorption from particle size of 425 µm to 200 µm with removal rates below 40 %; however, at particle size of 128 µm and smaller, the removal rates were all above 60 % thus slag of size 128 µm and below were used in all experiments. The results of this study do not show consistent proportional increase in adsorption with finer particle size hence an exact relationship of adsorption efficiency with particle size could not be expressed by an equation. For example while a decrease in size by half, from 425 µm to 200 µm resulted in a 20% increase in adsorption of Cu, reducing the particle size from 200 µm to 91 µm resulted in a 60% increase in adsorption.

These results are in conformity to those obtained by many researchers. Liu et al. (2009) recorded an increase in removal of Cr with decreasing particle size. The removal rate increased from 44 % at mesh size 2.5 to 99 % at sieve number 80. The general increase in removal with increasing sieve number and thus decreasing particle size can be accounted for by the presence of a much larger surface to volume ratio. As the particles get smaller, the surface area increases thus, making more sites available on the outer surface of the slag for adsorption. In other words, adsorption capacity increases with increase in surface area. According to Chen et al. (2011) decrease in particle size also leads to an increase in ion exchange although in the case of porous materials the pores might be crushed and hence a reduction in adsorption would result. Liu et al. (2009) also suggested that longer diffusion paths, blockages and longer contact time associated with larger particles may account for the lower removal rates. These authors recorded from their experiment that for slag particle size ranging from 1.25-2.5 mesh to 80-120 mesh, intraparticle diffusion was the adsorption rate determining step in the removal of Pb with steel slag. Within these two points adsorption removal increased from 45 % to 96 %.

According to Chowdhury (2013), crushing is the major cost associated with the use of nickel smelter slag as reactive barriers in metal removal; a cost of $8 per ton is involved in crushing the slag to various size ranges. Based on this study, particle size of 128 µm corresponding to 140 mesh opening provides the most economical size at which the slag can be crushed for high adsorption efficiency.

4.6. Effect of other ions

Mining effluents always contain a combination of many heavy metals and the presence some metals may affect the removal of others. A solution containing 7 mg/L of Cd and 10 mg/L each of Cu, Ni, Pb and Zn were reacted together with 10 g/L of nickel smelter until equilibrium in order to study the effect of the presence of other ions on the removal of Pb and Cu. The results are shown Table 5 below.

Table 5: Effect of other ions on the removal of Pb and Cu

Metal	Initial concentration (mg/L)	Final concentration (mg/L)	Removal (%)	Adsorption capacity (mg/g)
Cd	7	5.3555	23.49	0.16
Cu	10	0.1965	98.03	0.98
Ni	10	15.3575	-53.57*	-0.54*
Pb	10	0.0280	99.72	1.00
Zn	10	3.9927	60.07	0.60

* negative sign refers to desorption of Ni from slag surface

The nickel smelter slag possessed the ability to remove all test metals except Ni at a slag dosage of 10 g/L. The adsorption capacity of nickel slag for the five test metals were in decreasing order of Pb > Cu > Zn > Cd > Ni at values of 1.00, 0.98, 0.60, 0.162 and -0.54 mg/g repectively. Values such as 2.5, 8.05 and 64.79 mg/g have been reported for the removal of Pb with bagasse fly ash, granular slag and red mud respectively. Uptake capacities of 1.2, 0.6, 0.2 and 0.027 mg/g have also been reported for the removal of Cd by bagasse fly ash, biological activated carbon, granular activated carbon and activated charcoal respectively (Yadanaparthi et al., 2009).

According to literature, there is no consistent universal rule governing the removal of cations by adsorbents. The selectivity of adsorbents for metals is dependent on a combination of factors such as (1) adsorbent:adsorbate ratio; (2) the ability to form hydroxo complexes (dependent on chemical nature surface reactive groups); (3) electronegativity; (4) charge to radius ratio; (5) preferential adsorption site for particular metals; (6) pH (competition between metals and H^+ vary for metals); and (7) the presence of soluble ligands (Mohapatra, 2010; McBride, 2000). The affinity for iron and aluminum oxides follows the trend: Cu > Pb > Zn > Ni > Cd with an exchange between Pb and Cu in some iron oxides; this trend is consistent with the order of their pKa values of 7.7, 7.9, 9.0, 9.9 and 10.1 for Cu, Pb, Zn, Ni and Cd respectively. However based on electronegativity, the trend should have been Pb (2.33) > Cu (2.00) > Ni (1.91) > Cd(1.69) > Zn (1.65) (Mohapatra, 2010; Zhou and Haynes, 2010; McBride, 2000; Sparks, 2005 and 2003). According to McBride (2000), because Pb and Cu are the most easily hydrolysed of all divalent metals, they are the most adsorbed on silica and oxides of aluminium and iron.

As compared to the single metal solution of Pb and Cu, there was a reduction in adsorption capacity for Pb and Cu in the mixed metal solution. Pb reduced from 1.08 mg/g to 1.00 mg/g while Cu reduced from 1.05 mg/g to 0.98 mg/g. It can thus be said that competition for the same adsorption sites by other metals resulted in the decrease in removal efficiency and adsorption capacity of nickel smelter slag for Pb and Cu. Liu et al. (2009) in the study of adsorption of heavy metals by steel slag, also recorded a decrease in adsorption capacity of steel slag for Cr, Cu, Zn and Pb from the single element system to the mixed elements system. The results of this study show that although the presence of other metals reduce the adsorption capacity of the nickel smelter slag for Pb and Cu, the adsorption efficiency of the adsorbent for these two metals still remain the highest; the selectivity of the slag for the metals cannot be explained based on electrostatic attraction and covalent bonding alone.

4.7. Adsorption isotherms

Different models have been used to describe adsorption behaviour. Different concentrations (10-100 mg/L) of single element solutions of Pb and Cu were reacted with 10 g/L nickel smelter slag and the equilibrium concentrations were measured using ICP-OES. Linear graphs of C_e/q_e against C_e; and log q_e against log Ce were used in the Langmuir and Freundlich plots respectively and the equations of the straight lines were recorded. The slope and intercept of these graphs were used in the calculation of the Langmuir (q_m, b) and Freundlich (K_f and n) parameters respectively. Figures 14-17 show the adsorption isotherm plots.

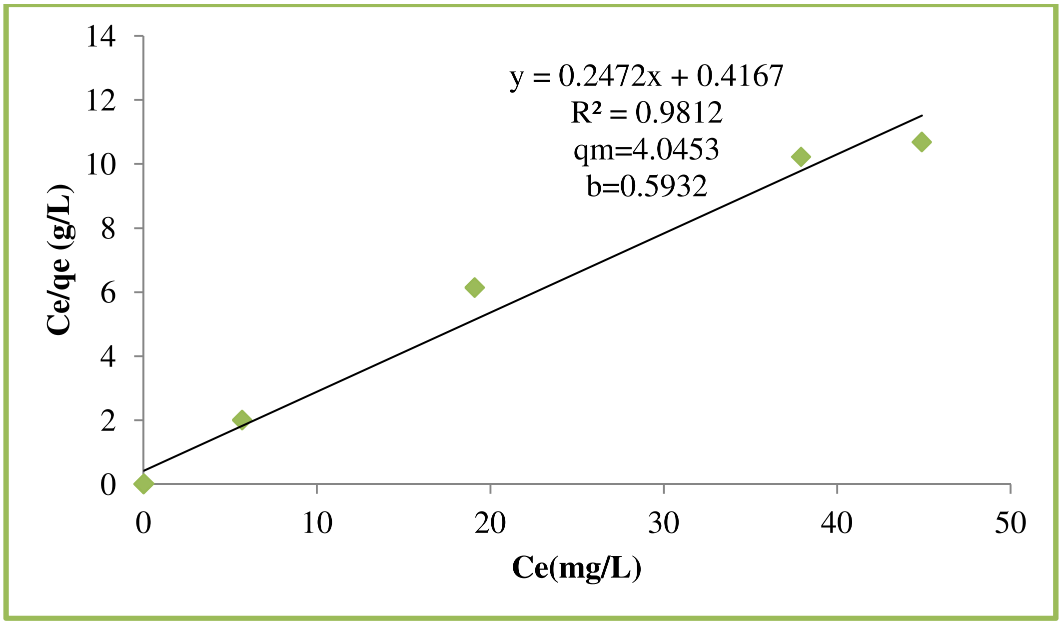

Figure 14: Langmuir isotherm plot for adsorption of Pb by nickel smelter slag (initial concentration: 10 -100 mg/L, slag dose: 10 g/L, contact time: 24 hours, shaking speed: 170 rpm, temperature: 25º C)

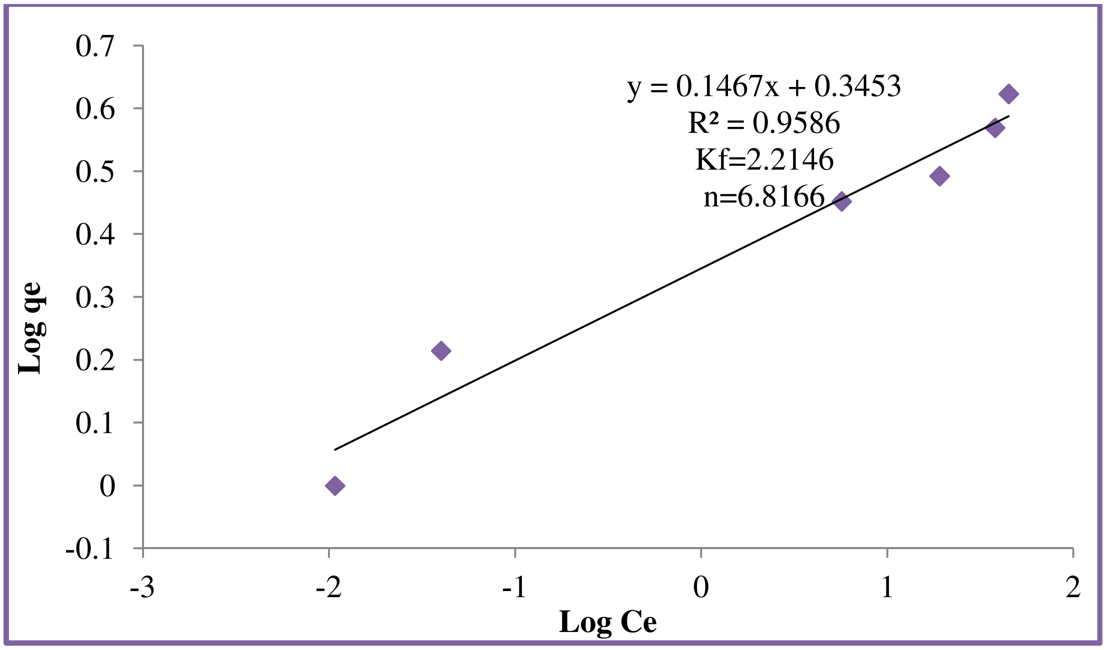

Figure 15: Freundlich isotherm plot for adsorption of Pb by nickel smelter slag (initial concentration: 10-100 mg/L, slag dose: 10 g/L, contact time: 24 hours, shaking speed: 170 rpm, temperature: 25º C)

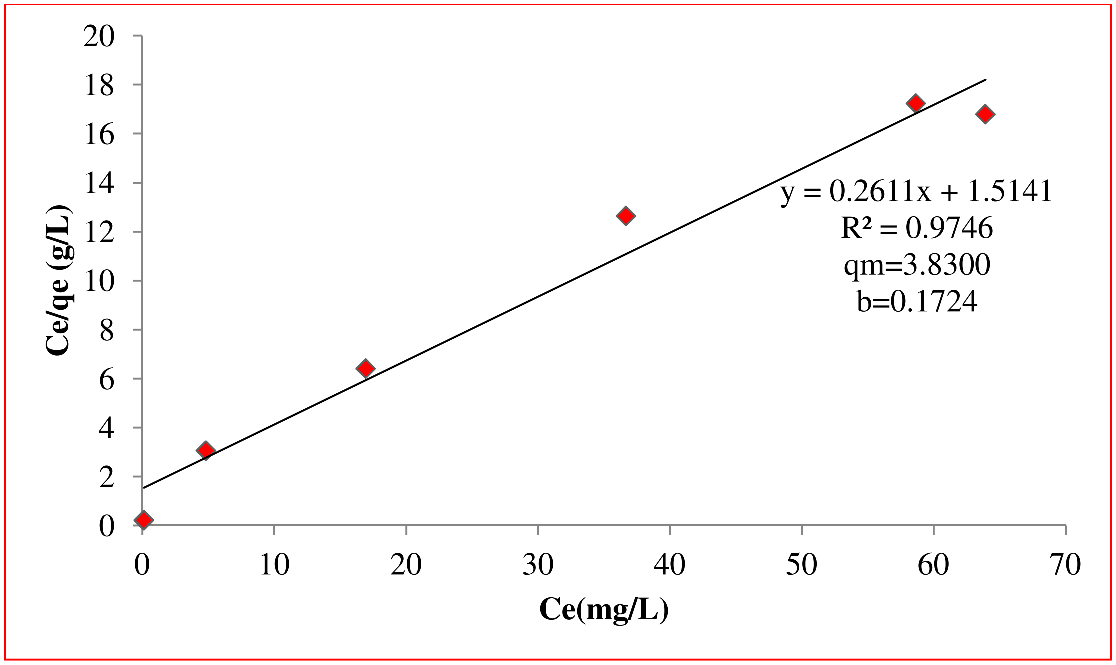

Figure 16: Langmuir isotherm plot for adsorption of Cu by nickel smelter slag (initial concentration: 10-100 mg/L, slag dose: 10 g/L, contact time: 24 hours, shaking speed: 170 rpm, temperature: 25º C)

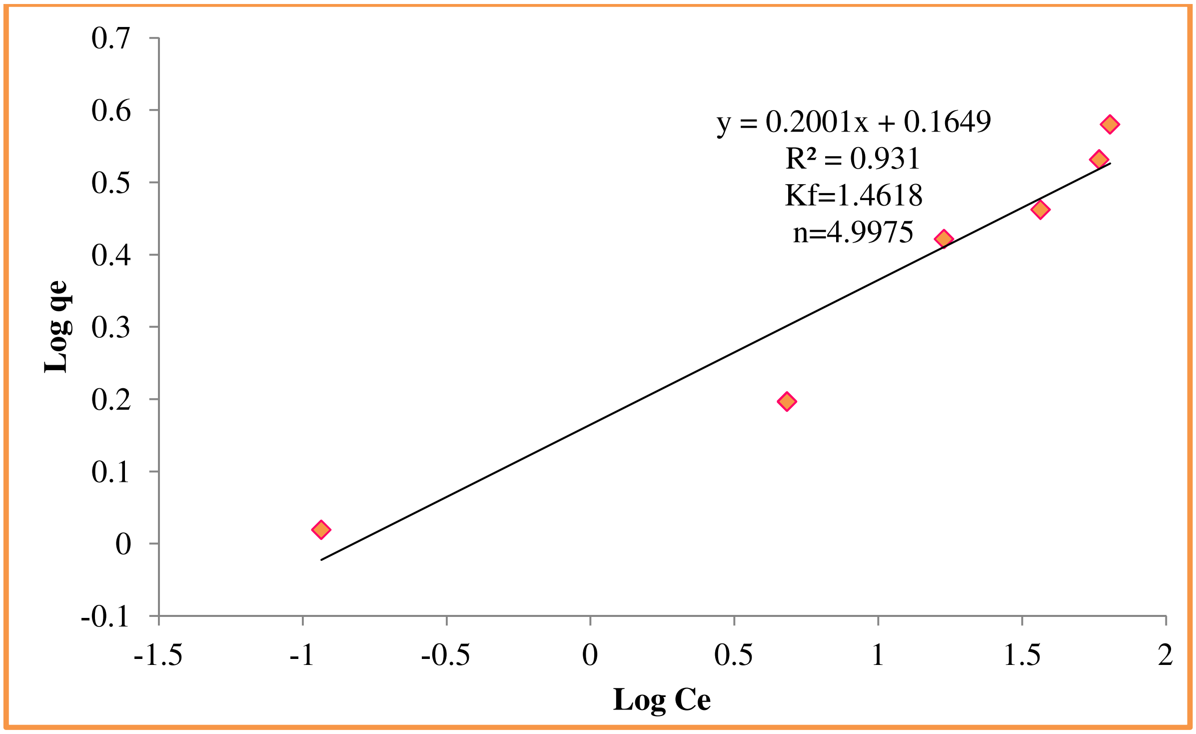

Figure 17: Freundlich isotherm plot for adsorption of Cu by nickel smelter slag (initial concentration: 10-100 mg/L, slag dose: 10 g/L, contact time: 24 hours, shaking speed: 170 rpm, temperature: 25º C)

A comparison of the results show that for both Pb and Cu, the Langmuir isotherm provides a slightly better fit due to higher R^2 (>0.97) values. The maximum capacity, q_m, for the two metals were 4.05 mg/g and 3.83 mg/g, respectively, while values of the Langmuir constant, b, were 0.59 L/mg and 0.17 L/mg for Pb and Cu in that order. Varying results such as q_m values of 36.36 mg/g, 88.50 mg/g and 16.21 mg/g have been recorded for Cu while values of 35.84 mg/g, 95.24 mg/g and 32.26 mg/g have been reported for electric arc furnace, iron and steel slags, respectively (Chen et al., 2011; Zhou and Haynes, 2010; Feng et al., 2004; Dimitrova, 2000). The nickel smelter slag has a low adsorption capacity in comparison to commercial and low cost adsorbents. Adsorption capacity of 16.58, 26.94 and 100 mg/g have been reported activated cabon while capacities of 122.25, 290.08, 198.9 and 325 mg/g have been reported for Duolite GT-73, amberlite IRC-718, amberlite 200 and Lewit TP 207 respectively in the adsorption of Pb. Similarly adsorption capacities of activated carbon for Cu are 5.08, 4.45 and 11.05 mg/g; adsorption capacities as high as 61.60, 127.00, 88.90 and 85.09 mg/g have been recorded for the adsorption of Cu on the commercial adsorbents Duolite GT-73, amberlite IRC-718, amberlite 200 and Lewit TP 207 respectively (Bohli et al., 2013; Kumar, 2006; Zacaria et al., 2002)

The Langmuir isotherm assumes that there is a specific number of sites on an adsorbent's surface and once these are filled, no more adsorption takes place. This isotherm has hence been described as indicative of monolayer chemisorption (Chen et al., 2011; Zhou and Haynes, 2010; Taha et al., 2004). The assumption of the fixed sites q_m, gives this isotherm an advantage over the Freundlich isotherm which does not place any limit on the number of adsorption sites. The constant, b, calculated from the Langmuir isotherm is related to the free energy of adsorption.

The features of a Langmuir isotherm are represented by the dimensionless separation constant r. This separation factor gives an indication of the shape of Langmuir isotherm as irreversible ($r = 0$), linear ($r =1$), favourable ($0< r < 1$), and unfavourable ($r >1$) (Hu et al., 2006; Kadiverlu et al., 2001; McKay et al., 1985). In this study, the dimensionless separation factor, r, for Pb was 0.03 - 0.1 and that of Cu was 0.09 - 0.3. The results obtained in this study reveal that nickel smelter slag is a good adsorbent for the removal of Pb and Cu from solution.

The Freundlich isotherm parameters K_f and n were 2.21 mg/g and 6.82 for Pb and 1.46 mg/g and 5.00 for Cu. The Freundlich isotherm assumes that an adsorbent has heterogeneous surface on which an adsorbate is adsorbed both in chemisorption and physisorption. The heat of adsorption on such an adsorbent's surface is not uniform. The Freundlich parameter K_f is related to adsorption capacity and the results from this research shows a higher capacity of the slag for Pb than Cu. Values of K_f are in the range of 1 and 10, with 10 signifying favourable adsorption (Zhou and Hynes, 2011). The empirical value, n, from the Freundlich isotherm gives an indication of the intensity with which an adsorbate is adsorbed onto an adsorbent. Values of $n >1$ are classified as L-type isotherms and depict a high affinity of an adsorbent for an adsorbate. Such values also indicate chemisorption as occurring between the adsorbate and adsorbent. Values of $n<1$ indicate unfavourable adsorption and hence a greater amount of solution than adsorbed on the adsorbent (Boparai et al., 2011; Taha et al., 2004; Apak, 2002). K_f values of 0.10, 0.17 and 0.12 have been recorded for Pb and Cu; n values of 3.45, 5.92; 3.46 and 3.92 have similarly been recorded for adsorption of Cu and Pb on electric arc furnace. From this study, nickel slag is an effective adsorbent for the removal of Pb and Cu since in both cases $n > 2$.

4.8. Desorption

Adsorbents that can be used several times before disposal are more cost effective since they also add the advantage of recovery of metals from the adsorbent. Adsorption-desorption tests were carried out on the nickel smelter slag to assess its ability for reuse. Although hysteresis exists between adsorption and desorption, many authors in their study of the number of times an adsorbent can be reused have maintained equal time for adsorption and desorption (Castañeda et al., 2012; Pandey et al., 2007; Hameed, 2006; Lodeiro et al., 2006; Ajmal et al., 2000). This method, used in this research is more practical since in real life applications, complete desorption may not follow adsorption. In this study 10 g/L of nickel smelter slag was reacted with 10 mg/L each of Pb and Cu under experimental conditions. Similarly, 80 g/L of the slag was reacted with a solution of mixed metals at concentration of 7-10 mg/L. Trial experiments with 0.01- 2 M HNO_3 showed that 0.1M was the most suitable eluent for desorption studies. Elution with 50 mL of 0.1 M HNO_3 was carried out for 10 hours after 10 hours adsorption. The results for the adsorption stage of 5 cycles of adsorption -desorption cycle are presented in Figures 18, 19 and 20.

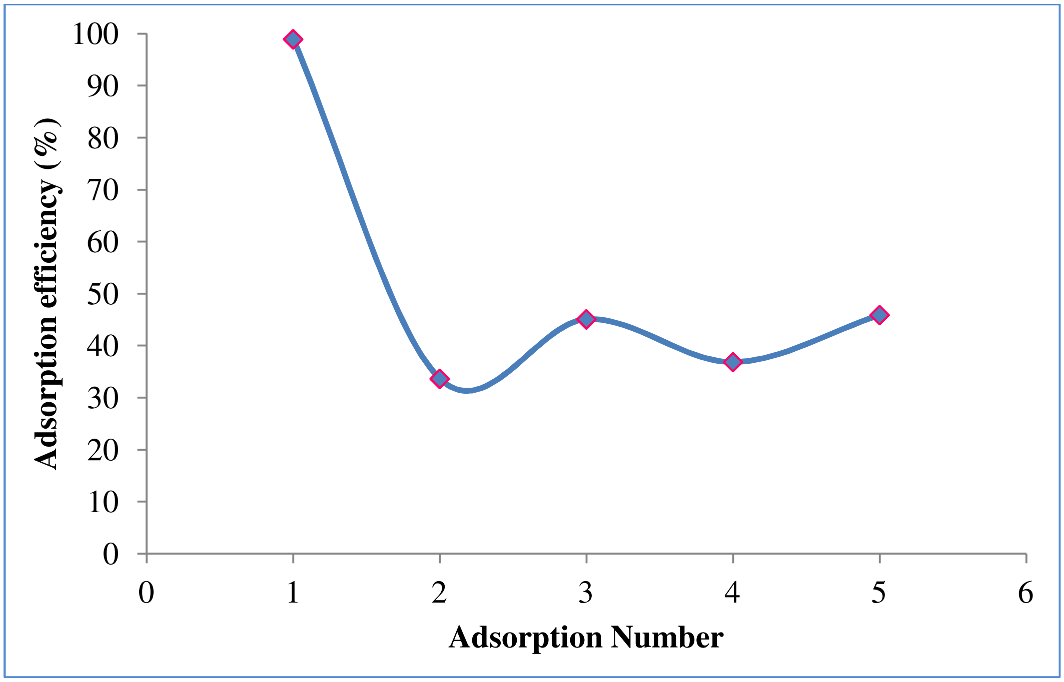

Figure 18: Removal of Pb by nickel smelter slag over 5 cycles of Adsorption (initial concentration: 10 mg/L, slag dose: 10 g/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25º C)

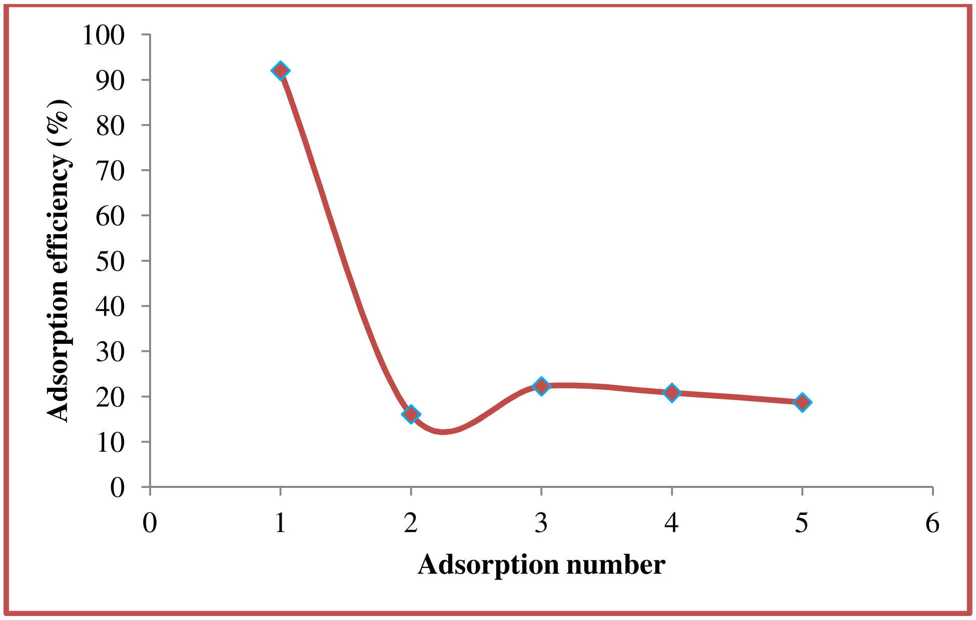

Figure 19: Removal of Cu by nickel smelter slag over 5 cycles of Adsorption (initial concentration: 10 mg/L, slag dose: 10 g/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25º C).

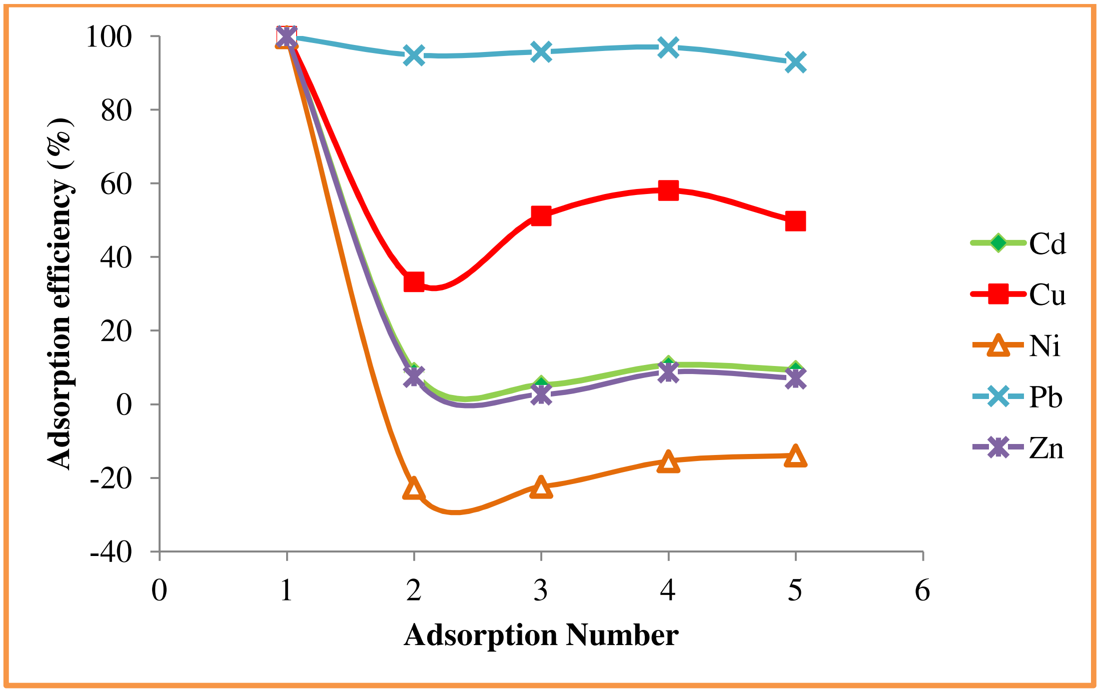

Figure 20: Removal of mixed metals by nickel smelter slag in 5 cycles of adsorption (initial concentration: 7-10 mg/L, slag dose: 80 g/L, contact time: 10 hours, shaking speed: 170 rpm, temperature: 25º C)

There is a general decrease in the adsorption of all five metals at the end of the five cycles. The adsorption of the five metals from the 1st to the 5th cycle are as follows: Pb (100 to 92.96 %); Cu (100 to 49.79 %); Zn (99.90 to 7.04 %); Cd (99.88 to 9.27 %); and Ni (99.72 to -13.87 %). In the single system, over the 5 cycles adsorption efficiency of Pb and Cu reduced from over 90 % in the first cycle to < 60% and < 20% in the 5th cycle for Pb and Cu respectively. The nickel in solution at the end of the experiments exceeded the initial concentration which implied that nickel originally present in the slag was desorbed. At the end of the 5th cycle of the mixed system, Pb showed greater than 90 % removal which suggests that nickel slag had the high affinity for Pb than the other metals. Higher removal efficiency for Pb and Cu in the mixed metal system than the single system is as a result of the presence of a slag dose hence larger surface in the mixed system (80 g/L) than the single system (10 g/L).

The decrease in adsorption over the cycles could be a result of the loss of active sites. Desorption requires higher activation energy and time than adsorption; rate constant for desorption is reported to be about 3 orders of magnitude slower than adsorption in pure oxides (McBride, 2000). All these factors coming into play may account for low adsorption in the subsequent adsorption after the first adsorption since a desorption step preceded each adsorption. The adsorption of heavy metals by adsorbents may involve the process of complexation which consists of inner and outer sphere complexation. Depending on the type of complex formed, desorption may either be easy or difficult. Inner complexes have been reported to involve stronger bonds whose breaking pose a challenge and results in incomplete stripping of metals from the surface of the adsorbent (Reeder et al., 2006 and Sparks, 2003). Thus, in the present study, it could be said that the presence strong bonds between the adsorbent and adsorbate in each cycle of adsorption accounted for the partial desorption of the heavy metals in each of the desorption stages; this could be one of several factors that led to lower desorption in each cycle. The loss of less adsorbent in some stages could account for the inconsistency in the adsorption and desorption rate in succeeding cycles (Pandey et al., 2007; Reeder et al., 2006,).

In a review, Hochella and White (1990) describe hysteresis between adsorption and desorption of strongly bound ions. Thus desorption requires a longer time to attain equilibrium than adsorption. Longer times are required to dissociate bidentate complexes associated with transition metal cations due to their possession of higher activation energies for dissociation. The hysteresis may also be due to the slow diffusion of ions out of the pores and void spaces in porous and aggregated-particle adsorbents. According to these authors, the solid solutions and precipitates formed during adsorption may also require longer time to discharge the ions in desorption. Chen et al. (1991) have reported that the decline in adsorbent performance is caused by build-up of adsorbate on the adsorbent's surface rather than loss of adsorbent. According to these authors, although an increase in desorption time could reduce the rate of accumulation, it would not get rid of slowly desorbing or irreversible adsorption. Diffusion limitations, surface precipitation change in the structure of the adsorbent with probable creation of higher energy sites as well formation of dilute hydrous oxide have been recorded as mechanisms accounting for the slowly reversible sorption by an iron oxide, such as ferrihydrite (Schultz et al.,1987).

Complete desorption of a single Pb adsorbed nickel slag after 24 hours showed 91% desorption. Although complete desorption experiments and mass balance calculations were not performed to ascertain the complete adsorption capacity of the slag for each cycle, the results obtained from this research suggest that nickel smelter slag can be used about five times more before disposal in a landfill or as a stabilization material, for example, in road construction.

4.9. Application of technology

The results from the present study indicate that nickel smelter slag has the potential to be used in the treatment of heavy metals from wastewater. Although the maximum adsorption capacity, qm (about 4 mg/g) of slag is less than many conventional adsorbents, the results indicate that the slag has a high affinity for Pb and Cu and as such can be used in the treatment of mine effluents containing these two metals. Mine effluents typically contain many metals and while Pb and Cu may be the primary metals to be treated, the slag can also be used in the finishing process in the treatment of other metals like Cd and Zn.

The nickel slag can be employed as permeable reactive barriers in in-situ treatment of the mine effluent since the present study has shown adsorption efficiencies above 95% for Pb and Cu. Desorption experiments which mimicked cyclical environmental conditions that may occur, for example acid rain, showed that the slag has the potential for reuse after which the spent slag could be burnt to recover the metals or stored in a landfill.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The primary goal of the present research was to assess the effectiveness of nickel smelter slag for the removal of selected heavy metals from solution. This was accomplished through laboratory batch experiments involving known amounts of crushed slag and predetermined concentrations of the following heavy metals: Pb, Cu, Zn, Cd and Ni. All experiments were carried out at a laboratory room temperature of $23\pm2^{o}C$. Batch adsorption tests were modelled using both the Langmuir and Freundlich equations and adsorption kinetics was also analyzed. Based on the results, the following is concluded:

1. The slag was effective in removing Pb, Cu, Ni, Cd and Zn from aqueous solutions at varying degrees. The affinity of the slag for the metals was in the order of Pb> Cu>Zn>Cd>Ni; the order is as a result of a combination of different factors.
2. The key factors found to control the adsorption efficiency of the slag were: pH, metal-slag contact time, adsorbent dose, particle size and the presence of competing ions.
3. The following conditions were found to be the best for the removal of the metals from solution: pH of 5, slag dose of 10 g/L, shaking speed of 170 rpm and contact time of 10 hours. These conditions provided the most cost-effective removal, based on the amounts of reagents or chemicals used in the experiments; they can be used as an initial basis for pilot scale evaluation. Adsorption of Cu and Pb was described by the Langmuir isotherm plot and the kinetics of adsorption followed the pseudo second order model.
4. Crushing the nickel smelter slag to a particle size of 128 µm or less would provide the most economical and efficient removal of heavy metals. Nickel smelter slag, an industrial waste material, has the potential for use in waste water treatment although it has a low maximum adsorption capacity (< 5 mg/g) compared with commercial adsorbents.
5. Regeneration studies showed potential reuse of the slag, about five times more before exhaustion (that is, <10% metal recovery from solution).

5.2. Recommendations

The present study provided an insight into the interactions between the crushed Ni smelter slag and the metals studied. A number of issues, however, require further investigation and are recommended here as follows:

1. Although batch tests provided a quick and reliable estimate of the operating conditions of the slag-metal solutions system, column tests and field studies should be conducted to determine the feasibility of using nickel smelter slag in industrial applications.
2. Activation of an adsorbent's surface by physical or chemical process has been shown to enhance sorption of adsorbates onto adsorbents. Studies on removal of heavy metals with activated nickel smelter slag should be conducted to ascertain whether activation might produce a significant increase in adsorption capacity of this slag for heavy metals.
3. Surface analysis and modelling of results from this study should be conducted to clearly distinguish between the mechanisms responsible for the removal of heavy metals by nickel smelter slag.

BIBLIOGRAPHY

Agarwal, A., Agarwal, M., & Saxena, M. (2012). Removal of cu & zn from industrial wastewater by using steel industry waste (slag) as an adsorbent. *International Journal of Modern Engineering Research, 2*(3), 1348-1353.

Ahmaruzzaman, M. (2010). A review on the utilization of fly ash. *Progress in Energy and Combustion Science, 36*(3), 327-363. doi:10.1016/j.pecs.2009.11.003

Ahmaruzzaman, M. (2011). Industrial wastes as low-cost potential adsorbents for the treatment of wastewater laden with heavy metals. *Advances in Colloid and Interface Science, 166*(1–2), 36-59. doi:http://dx.doi.org/10.1016/j.cis.2011.04.005

Ahmedzeki, N. S., Abdullah, S. M., & Salman, R. H. (2009). Treatment of industrial waste water using reverse osmosis technique . *Journal of Engineering, 15*(4), 4356-4363.

Akpor, O. B., & Munchie, M. (2010). Remediation heavy metals in drinking water and waste water treatment systems: Processes and applications. *International Journal of the Physical Sciences, 5*(12), 1807-1817.

Amin, M. M., Khodabakhshi, A., Mozafari, M., Bina, B., & Kheiri, S. (2010). *Environmental Engineering and Management Journal, 9*(7), 921-927.

Appel, C., Ma, L. Q., Dean Rhue, R., & Kennelley, E. (2003). Point of zero charge determination in soils and minerals via traditional methods and detection of electroacoustic mobility. *Geoderma, 113*(1–2), 77-93. doi:http://dx.doi.org/10.1016/S0016-7061(02)00316-6

Barakat, M. A. (2011). New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry, 4*(4), 361-377. doi:10.1016/j.arabjc.2010.07.019

Barone, F. S., Yanful, E. K., Quigley, R. M., & Rowe, R. K. (1989). Effect of multiple contaminant migration on diffusion and adsorption of some domestic waste contaminants in a natural clayey soil. *Canadian Geotechnical Journal, 26*(2), 189-198.

Bohli, T., Villaescusa, I., & Quederni, A. (2013). Comparative study of bivalent cationic metals adsorption pb(II), cd(II), ni(II) and cu(II) on olive stones chemically activated carbon. *Chemical Engineering & Process Technology, 4*(4), 158. doi:10.4172/2157-7048.1000158

Boparai, H. K., Joseph, M., & O'Carroll, D. M. (2011). *Kinetics and thermodynamics of cadmium ion removal by adsorption onto nano zerovalent iron particles* Elsevier. doi:10.1016/j.jhazmat.2010.11.029

Bradl, H. B. (2004). Adsorption of heavy metal ions on soils and soils constituents. *Journal of Colloid and Interface Science, 277*(1), 1-18. doi:http://dx.doi.org/10.1016/j.jcis.2004.04.005

Brown, G. E., Henrich, V. E., Casey, W. H., Clark, D. L., Eggleston, C., Felmy, A., . . . Zachara, J. M. (1999). Metal oxide surfaces and their interactions with aqueous solutions and microbial organisms. *Chemical Reviews, 99*(1), 77-174. doi:10.1021/cr980011z

Castañeda, M., Mirasol, M. S., Raymundo, L. A., & Solidum, J. (2012). Biosorption and desorption of lead (Pb+2) from simulated waste water using freshwater snail shells, melanoides tuberculata muller (family thiaridae) . *2012 2nd International Conference on Environment and BioScience,* Singapore. , *44*(12) 54-59. doi:10.7763/IPCBEE. 2012. V44. 12

Chang, Y., & Chen, D. (2005). Preparation and adsorption properties of monodisperse chitosan-bound Fe3O4 magnetic nanoparticles for removal of cu(II) ions. *Journal of Colloid and Interface Science, 283*(2), 446-451. doi:http://dx.doi.org/10.1016/j.jcis.2004.09.010

Chen, W. Y., Anderson, P. R., & Holsen, T. M. (1991). Recovery and recycle of metals from wastewater with a magnetite-based adsorption process. *Research Journal of the Water Pollution Control Federation, 63*(7), 958-964.

Chen, G. (2004). Electrochemical technologies in wastewater treatment. *Separation and Purification Technology, 38*(1), 11-41. doi:10.1016/j.seppur.2003.10.006

Chern, J., & Chang, F. C. (2000). Study of nonlinear wave propagation theory. III. removing heavy metals from wastewater by ion-exchange process. *Separation Science and Technology, 35*(8), 1099-1116.

Chiban, M., Zerbert, M., Carja, G., & Sinan, F. (2012). Application of low-cost adsorbents for arsenic removal: A review. *Journal of Environmental Chemistry and Ecotoxicology., 4*(5), 91-102. doi:10.5897/JECE11.013

Chowdhury, S. R., & Yanful, E. K. (2011). Arsenic removal from aqueous solutions by adsorption on magnetite nanoparticles. . *Water and Environment Journal, 25*(3), 429-437. doi:10.1111/j.1747-6593.2010.00242.x

Chowdhury, S. R. (2008). *Removal of arsenic and chromium form water using magnetite nanoparticles*. London, Ont.: School of Graduate and Postdoctoral Studies, University of Western Ontario.

Chowdhury, S. R. (2013). *Application of mixed iron oxides in subsurface remediation technologies*. London, Ont.: School of Graduate and Postdoctoral Studies, University of Western Ontario. Retrieved from http://ir.lib.uwo.ca/etd/

Chowdhury, S. R., & Yanful, E. K. (2010). Arsenic and chromium removal by mixed magnetite–maghemite nanoparticles and the effect of phosphate on removal. *Journal of Environmental Management, 91*(11), 2238-2247. doi:10.1016/j.jenvman.2010.06.003

Cornell, R. M., & Schwertmann, U. (1996). *The iron oxides :Structure, properties, reactions, occurrences and uses*. Weinheim ;; New York: Vch.

Da□browski, A., Hubicki, Z., Podkościelny, P., & Robens, E. (2004). Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosphere, 56*(2), 91-106. doi:http://dx.doi.org/10.1016/j.chemosphere.2004.03.006

Das, N., Karthika, P., Vimala, R., & Vinodhini, V. (2008). , Use of natural products as biosorbent of heavy metals: An overview. *Atural Product Radiance, 7*(2), 133-138.

Das, B., Prakash, S., Reddy, P. S. R., & Misra, V. N. (2007). An overview of utilization of slag and sludge from steel industries. *Resources, Conservation and Recycling, 50*(1), 40-57. doi:http://dx.doi.org/10.1016/j.resconrec.2006.05.008

Dimitrova(M), S. V. (1996). Metal sorption on blast-furnace slag. *Water Research, 30*(1), 228-232. doi:10.1016/0043-1354(95)00104-S

Dimitrova, S. V. (2002). Use of granular slag columns for lead removal. *Water Research, 36*(16), 4001-4008. doi:10.1016/S0043-1354(02)00120-3

Dimitrova, S. V., & Mehandgiev, D. R. (1998). Lead removal from aqueous solutions by granulated blast-furnace slag. *Water Research, 32*(11), 3289-3292. doi:http://dx.doi.org/10.1016/S0043-1354(98)00119-5

Fan, M., Boonfueng, T., Xu, Y., Axe, L., & Tyson, T. A. (2005). Modeling pb sorption to microporous amorphous oxides as discrete particles and coatings. *Journal of Colloid and Interface Science, 281*(1), 39-48. doi:10.1016/j.jcis.2004.08.050

Feng, D., Aldrich, C., & Tan, H. (2000). Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Minerals Engineering, 13*(6), 623-642. doi:http://dx.doi.org/10.1016/S0892-6875(00)00045-5

Fu, F., & Wang, Q. (2011). Removal of heavy metal ions from wastewaters : A review. . *Journal of Environmental Management, 92*(3), 407-418.

Gilfillan, S. C. (1965). Lead poisoning and the fall of rome . *Journal of Occupational Medicine, 7*, 53-60.

Grassi, M., Kaykioglu, G., Belgiorno, V., & Lofrano, G. (2012). Removal of emerging contaminants from water and wastewater by adsorption process. In G. Lofrano (Ed.), *Emerging compounds removal from wastewater: Natural and solar based treatments* (pp. 15-37). Netherlands: Springer. doi:10.1007/978-94-007-3916-1

Gregg, S. J., & Sing, K. S. W. (1982). *Adsorption, surface area, and porosity* (2nd ed.). London; Toronto: Academic Press.

Gupta, V. K., & Ali, I. (2004). Removal of lead and chromium from wastewater using bagasse fly ash—a sugar industry waste. *Journal of Colloid and Interface Science, 271*(2), 321-328. doi:http://dx.doi.org/10.1016/j.jcis.2003.11.007

Gupta, V. K., Carrott, P. J. M., Ribeiro Carrott, M. M. L., & Suhas, . (2009). Low-cost adsorbents: Growing approach to wastewater Treatment—A review. *Critical Reviews in Environmental Science and Technology, 39*(10), 783-842. doi:10.1080/10643380801977610

Hameed, M. S. A. (2006). Continuous removal and recovery of lead by alginate beads, free and alginate-immobilized chlorella vulgaris. *African Journal of Biotechnology, 5*(19), 1819-1823.

Hernberg, S. (2000). Lead poisoning in a historical perspective. *American Journal of Industrial Medicine, 38*(3), 244-254. doi:10.1002/1097-0274(200009)38:3<244::AID-AJIM3>3.0.CO;2-F

Ho, Y. S., & McKay, G. (1999). Pseudo-second order model for sorption processes. *Process Biochemistry, 34*(5), 451-465. doi:10.1016/S0032-9592(98)00112-5

Hochella, M. F., White, A. F., Bancroft, G. M., & Mineralogical Society of America. (1990). *Mineral-water interface geochemistry*. Washington, D.C.: Mineralogical Society of America.

Hu, J., Chen, G., & Lo, I. (2006). Selective removal of heavy metals from industrial waste water using maghemite nanoparticles: Performance and mechanisms. *Journal of Environmental Engineering, 132*(7), 709-715.

Hu, J., Lo, I., & Chen, G. (2005). Fast removal and recovery of cr(VI) using surface-modified jacobsite (MnFe2O4) nanoparticles. *Langmuir 2005, 21, 11173-11179, 21*(24), 11173-11179. doi:10.1021/la051076h

Hua, M., Zhang, S., Pan, B., Zhang, W., Lv, L., & Zhang, Q. (2012). Heavy metal removal from water/wastewater by nanosized metal oxides: A review. *Journal of Hazardous Materials, 211–212*(0), 317-331. doi:http://dx.doi.org/10.1016/j.jhazmat.2011.10.016

Huang, C. P., & Rhoads, E. A. (1989). Adsorption of zn(II) onto hydrous aluminosilicates. *Journal of Colloid and Interface Science, 131*(2), 289-306. doi:http://dx.doi.org/10.1016/0021-9797(89)90174-4

Huang, Y. H., Hsueh, C. L., Cheng, H. P., Su, L. C., & Chen, C. Y. (2007). Thermodynamics and kinetics of adsorption of cu(II) onto waste iron oxide. *Journal of Hazardous Materials, 144*(1-2), 406-411. doi:10.1016/j.jhazmat.2006.10.061

Inglezakis, V. J., Papadeas, C. D., Loizidou, M. D., & Grigoropoulou, H. P. (2001). Effects of pretreatment on physical and ion exchange properties of natural clinoptilolite. *Environmental Technology, 22*(1), 75-82. doi:10.1080/09593332208618308

Inglezakis, V. J., Zorpas, A. A., Loizidou, M. D., & Grigoropoulou, H. P. (2005). The effect of competitive cations and anions on ion exchange of heavy metals. *Separation and Purification Technology, 46*(3), 202-207. doi:10.1016/j.seppur.2005.05.008

Inglezakis, V. J., Loizidou, M. M., & Grigoropoulou, H. P. (2004). Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility. *Journal of Colloid and Interface Science, 275*(2), 570-576. doi:http://dx.doi.org/10.1016/j.jcis.2004.02.070

Jackson, S. D., & Hargreaves, J. S. J. (2009). *Metal oxide catalysis*. Weinheim: Wiley - VCH.

Jamieson, H. E. (2011). Geochemistry and mineralogy of solid mine waste: Essential knowledge for predicting environmental impact. *Elements, 7*(6), 381-386. doi:10.2113/gselements.7.6.381

Jin, J., Zhao, W. -., Xu, X. -., Hao, Z. -., & Liu, Y. (2006). **Remediation of ni(2+)-contaminated water using iron powder and steel manufacturing byproducts**. *Journal of Environmental Sciences, 18*(3), 464-467.

Kadirvelu, K., Thamaraiselvi, K., & Namasivayam, C. (2001). Adsorption of nickel(II) from aqueous solution onto activated carbon prepared from coirpith. *Separation and Purification Technology, 24*(3), 497-505. doi:10.1016/S1383-5866(01)00149-6

Karthikeyan, K. G., & Elliott, H. A. (1999). Surface complexation modeling of copper sorption by hydrous oxides of iron and aluminum. *Journal of Colloid and Interface Science, 220*(1), 88-95. doi:http://dx.doi.org/10.1006/jcis.1999.6507

Kotrba, P., Mackova, M., Macek, T., & SpringerLink. (2011). *Microbial biosorption of metals*. Dordrecht: Springer Science+Business Media B.V.

Kumar, U. (2006). Agricultural products and by-products as a low cost adsorbent for heavy metal removal from water and wastewater: A review. *Scientific Research and Essay, 1*(2), 33-37.

Kurniawan, T. A., Chan, G. Y. S., Lo, W., & Babel, S. (2006). Physico–chemical treatment techniques for wastewater laden with heavy metals. *Chemical Engineering Journal, 118*(1–2), 83-98. doi:http://dx.doi.org/10.1016/j.cej.2006.01.015

Lasheen, M. R., Ammar, N. S., & Ibrahim, H. S. (2012). Adsorption/desorption of cd(II), cu(II) and pb(II) using chemically modified orange peel: Equilibrium and kinetic studies. *Solid State Sciences, 14*(2), 202-210. doi:http://dx.doi.org/10.1016/j.solidstatesciences.2011.11.029

Lessler, M. A. (1988). Lead and lead poisoning from antiquity to modern times. *The Ohio Journal of Science., 88*(3), 78-84.

Li, J., Shi, Y., Cai, Y., Mou, S., & Jiang, G. (2008). Adsorption of di-ethyl-phthalate from aqueous solutions with surfactant-coated nano/microsized alumina. *Chemical Engineering Journal, 140*(1–3), 214-220. doi:http://dx.doi.org/10.1016/j.cej.2007.09.037

Liu, S. Y., Gao, J., Qu, B., & Yang, Y. J. (2009). Adsorption behaviors of heavy metal ions by steel slag-an industrial solidwaste *The 3rd International Conference on Bioinformatics and Biomedical Engineering.* , Beijing, China.

Liu, Y., Majetich, S. A., Tilton, R. D., Sholl, D. S., & Lowry, G. V. (2005). TCE dechlorination rates, pathways, and efficiency of nanoscale iron particles with different properties. *Environmental Science Technology, 39*, 1338-1345.

Liu, S., Gao, J., Yang, Y., Yang, Y., & Ye, Z. (2010). Adsorption intrinsic kinetics and isotherms of lead ions on steel slag. *Journal of Hazardous Materials, 173*(1–3), 558-562. doi:http://dx.doi.org/10.1016/j.jhazmat.2009.08.122

Lodeiro, P., Herrero, R., & Sastre de Vicente, M. E. (2006). Batch desorption studies and multiple sorption–regeneration cycles in a fixed-bed column for cd(II) elimination by protonated sargassum muticum. *Journal of Hazardous Materials, 137*(3), 1649-1655. doi:http://dx.doi.org/10.1016/j.jhazmat.2006.05.003

Mahmoud, A., & Hoadley, A. F. A. (2012). An evaluation of a hybrid ion exchange electrodialysis process in the recovery of heavy metals from simulated dilute industrial wastewater. *Water Research, 46*(10), 3364-3376. doi:http://dx.doi.org/10.1016/j.watres.2012.03.039

McCabe, W. L., Smith, J. C., & Harriott, P. (2005). *Unit operations of chemical engineering* (7th ed.). Boston: McGraw-Hill.

Merrikhpour, H., & Jalali, M. (2013). Comparative and competitive adsorption of cadmium, copper, nickel, and lead ions by iranian natural zeolite. *Clean Technologies and Environmental Policy, 15*(2), 303-316. doi:10.1007/s10098-012-0522-1

Mihailova, I., Dimitrova, S., & Mehandjiev, D. (2013). EFFECT OF THE THERMAL TREATMENT ON THE pb (II) ADSORPTION ABILITY OF BLAST FURNACE SLAG . *Journal of Chemical Technology and Metallurgy, 48*(1), 72-79.

Misono, M., Ochiai, E., Saito, Y., & Yoneda, Y. (1967). A new dual parameter scale for the strength of lewis acids and bases with the evaluation of their softness. *Journal of Inorganic and Nuclear Chemistry, 29*(11), 2685-2691. doi:http://dx.doi.org/10.1016/0022-1902(67)80006-X

Mosca, A., Hedlund, J., Webley, P. A., Grahn, M., & Rezaei, F. (2010). Structured zeolite NaX coatings on ceramic cordierite monolith supports for PSA applications. *Microporous and Mesoporous Materials, 130*(1–3), 38-48. doi:http://dx.doi.org/10.1016/j.micromeso.2009.10.010

Muller, J., & Joubert, J. C. (1974). Synthese en milieu hydrothermal et caractérisation de l'oxyhydroxyde de vanadium V3+OOH et d'une nouvelle variété allotropique du dioxyde VO2. *Journal of Solid State Chemistry, 11*(2), 79-87. doi:10.1016/0022-4596(74)90101-7

Neufeld, R. D., & Hermann, E. R. (1975). Heavy metal removal by acclimated activated sludge. *Journal (Water Pollution Control Federation), 47*(2), 310-329. Retrieved from http://www.jstor.org/stable/25038631

Nilforoushan, M. R., & Otroj, S. (2008). Absorption of lead ions by various types of steel slag. *Iranian Journal of Chemistry and Chemical Engineering (Ijcce), 27*(3), 69-75.

Ortiz, N., Pires, M. A. F., & Bressiani, J. C. (2001). Use of steel converter slag as nickel adsorber to wastewater treatment. *Waste Management, 21*(7), 631-635. doi:10.1016/S0956-053X(00)00123-9

Panday, K. K., Prasad, G., & Singh, V. N. (1985). Copper(II) removal from aqueous solutions by fly ash. *Water Research, 19*(7), 869-873. doi:http://dx.doi.org/10.1016/0043-1354(85)90145-9

Pandey, A., Bera, D., Shukla, D., & Ray, L. (2007). Studies on cr(VI), pb(II) and cu(II) adsorption – desorption using calcium alginate as biopolymer. *Chemical Speciation and Bioavailability, 19*(1), 17-24. doi:http://dx.doi.org/10.3184/095422907X198031

Parfitt, G. D., & Rochester, C. H. (1983). *Adsorption from solution at the solidliquid interface*. London ;; Toronto: Academic Press.

Patterson, J. W. (1985). *Industrial wastewater treatment technology* (2nd ed.). Boston ;; Toronto: Butterworths.

Pawlak, Z., Zak, S., & Zablock, L. (2006). Removal of hazardous metals from groundwater by reverse osmosis. *Polish Journal of Environmental Studies, 15*(4), 579-583.

Payne, T. E., Brendler, V., Ochs, M., Baeyens, B., Brown, P. L., Davis, J. A., . . . Altmann, S. (2013). Guidelines for thermodynamic sorption modelling in the context of radioactive waste disposal. *Environmental Modelling & Software, 42*(0), 143-156. doi:http://dx.doi.org/10.1016/j.envsoft.2013.01.002

Piwoni, M. D., Keeley, J. W., & Superfund Technology Support Center for Ground Water. (1990). *Basic concepts of contaminant sorption at hazardous waste sites*. Ada, OK: United States Environmental Protection Agency, Office of Research and Development, Office of Solid Waste and Emergency Response. Retrieved from http:// purl.access.gpo.gov/GPO/LPS49292

Popuri, S. R., Vijaya, Y., Boddu, V. M., & Abburi, K. (2009). Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. *Bioresource Technology, 100*(1), 194-199. doi:10.1016/j.biortech.2008.05.041

Reeder, R. J., Schoonen, M. A. A., & Lanzirotti, A. (2006). Metal speciation and its role in bioaccessibility and bioavailability. *Reviews in Mineralogy and Geochemistry, 64*(1), 59-113. doi:10.2138/rmg.2006.64.3

Saleh, N., Kim, H., Phenrat, T., Matyjaszewski, K., Tilton, R. D., & Lowry, G. V. (2008). Ionic strength and composition affect the mobility of surface-modified Fe0 nanoparticles in water-saturated sand columns. *Environmental Science & Technology, 42*(9), 3349-3355. Retrieved from http://resolver.scholarsportal.info/resolve/0013936x/v42i0009/3349_isacatfniwsc

Schultz, M. F., Benjamin, M. M., & Ferguson, J. F. (1987). Adsorption and desorption of metals on ferrihydrite: Reversibility of the reaction and sorption properties of the regenerated solid. *Environmental Science and Technology, 21*(9), 863-869.

Sharma, Y., Srivastava, V., Singh, V., Kaul, S., & Weng, C. (2009). Nano-adsorbents for the removal of metallic pollutants from water and wastewater. *Environmental Technology, 30*(6), 583-609.

Shen, H., & Forssberg, E. (2003). An overview of recovery of metals from slags. *Waste Management, 23*(10), 933-949. doi:http://dx.doi.org.proxy1.lib.uwo.ca/10.1016/S0956-053X(02)00164-2

Silva, R. M. P., Manso, J. P. H., Rodrigues, J. R. C., & Lagoa, R. J. L. (2008). A comparative study of alginate beads and an ion-exchange resin for the removal of heavy metals from a metal plating effluent. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering, 43*(11), 1311-1317.

Singh, J., Huang, P. M., Hammer, U. T., & Liaw, W. K. (1996). Influence of citric acid and glycine on the adsorption of mercury (II) by kaolinite under various pH conditions. *Clays and Clay Minerals, 44*(1), 41-48.

Smith, E. H. (1996). Uptake of heavy metals in batch systems by a recycled iron-bearing material. *Water Research, 30*(10), 2424-2434. doi:10.1016/0043-1354(96)00105-4

Sparks, D. L. (2005). SORPTION | metals. In Editor-in-Chief: Daniel Hillel (Ed.), *Encyclopedia of soils in the environment* (pp. 532-537). Oxford: Elsevier. doi:http://dx.doi.org/10.1016/B0-12-348530-4/00554-3

Sparks,Donald L.,,. (2003). *Environmental soil chemistry*. Amsterdam; Boston: Academic Press.

Stankovic, V., Božic, D., Gorgievski, M., & Bogdanovic, G. (2009). Heavy metal ions adsorption from mine waters by sawdust. *Chemical Industry & Chemical Engineering Quarterly, 15*(4), 237-249. doi:10.2298/CICEQ0904237S

Stumm, W., & American Chemical Society. (1967). *Equilibrium concepts in natural water systems :A symposium*. Washington, D.C.: American Chemical Society.

Stumm, W., Sigg, L., & Sulzberger, B. (1992). *Chemistry of the solid-water interface :Processes at the mineral-water and particle-water interface in natural systems*. New York ;; Toronto: Wiley.

Sungur, S., & Babaoglu, S. (2005). Synthesis of a new cellulose ion exchanger and use for the separation of heavy metals in aqueous solutions. *Separation Science and Technology, 40*(10), 2067-2078. doi:10.1081/SS-200068481

Sverjensky, D. A. (1994). Zero-point-of-charge prediction from crystal chemistry and solvation theory. *Geochimica Et Cosmochimica Acta, 58*(14), 3123-3129. doi:10.1016/0016-7037(94)90184-8

Sverjensky, D. A., & Sahai, N. (1996). Theoretical prediction of single-site surface-protonation equilibrium constants for oxides and silicates in water. *Geochimica Et Cosmochimica Acta, 60*(20), 3773-3797. doi:10.1016/0016-7037(96)00207-4

Taha, M. R., Ahmad, K., Aziz, A. A., & Chik, Z. (2004). Geoenvironmental aspects of tropical residual soils. In B. B. K. Huat, G. S. Sew & F. H. Ali (Eds.), *tropical residual soils engineering* (pp. 377-403). London: Balkema.

Taha, G. M. (2006). Utilization of low-cost waste material bagasse fly ash in removing of Cu2+, Ni2+, Zn2+, and Cr3+ from industrial waste water. *Ground Water Monitoring & Remediation, 26*(4), 137-141. doi:10.1111/j.1745-6592.2006.00120.x

Tang, S. C. N., & Lo, I. M. C. (2013). *Magnetic nanoparticles: Essential factors for sustainable environmental applications* Elsevier. doi:10.1016/j.watres.2013.02.039

Tiwari, D. K., Behari, J., & Sen, P. (2008). . "Application of nanoparticles in waste water treatment." *world appl sci J* 3 (2008): 417-433. *World Applied Sciences Journal, 3*(3), 417-433.

Todorovic, Ž. N., & Milonjic, S. K. (2004). Determination of intrinsic equilibrium constants at an alumina/electrolyte interface. *Journal of the Serbian Chemical Society, 69*(12), 1063-1072.

Trgo, M., Peric, J., & Medvidovic, N. V. (2006). A comparative study of ion exchange kinetics in zinc/lead-modified zeolite-clinoptilolite systems. *Journal of Hazardous Materials, 136*(3), 938-945. doi:10.1016/j.jhazmat.2006.01.032

Tsakiridis, P. E., Papadimitriou, G. D., Tsivilis, S., & Koroneos, C. (2008). Utilization of steel slag for portland cement clinker production. *Journal of Hazardous Materials, 152*(2), 805-811. doi:http://dx.doi.org/10.1016/j.jhazmat.2007.07.093

United States. (2000). *Wastewater technology fact sheet*. Washington, D.C.: United States Environmental Protection Agency, Office of Water. Retrieved from http://purl.access.gpo.gov/GPO/LPS50744

Vaca Mier, M., López Callejas, R., Gehr, R., Jiménez Cisneros, B. E., & Alvarez, P. J. J. (2001). Heavy metal removal with mexican clinoptilolite. *Water Research, 35*(2), 373-378. doi:10.1016/S0043-1354(00)00270-0

Varshney, K. G., Khan, A. A., Gupta, U., & Maheshwari, S. M. (1996). Kinetics of adsorption of phosphamidon on antimony (V) phosphate cation exchanger: Evaluation of the order of reaction and some physical parameters. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 113*(1-2), 19-23. doi:10.1016/0927-7757(96)03546-7

Vayssieres, L. (2009). On the effect of nanoparticle size on water-oxide interfacial chemistry. *The Journal of Physical Chemistry C, 113*(12), 4733-4736. doi:10.1021/jp810721f

Vergili, I., Soltobaeva, G., Kaya, Y., Gönder, Z. B., Çavus, S., & Gürdag, G. (2013). Study of the removal of pb(II) using a weak acidic cation resin: Kinetics, thermodynamics, equilibrium, and breakthrough curves. *Industrial and Engineering Chemistry Research, 52*(26), 9227-9238.

Volesky, B. (2001). Detoxification of metal-bearing effluents: Biosorption for the next century. *Hydrometallurgy, 59*(2-3), 203-216. doi:10.1016/S0304-386X(00)00160-2

Wang, J., Huang, C. P., & Allen, H. E. (2003). Modeling heavy metal uptake by sludge particulates in the presence of dissolved organic matter. *Water Research, 37*(20), 4835-4842. doi:10.1016/j.watres.2003.08.021

Waypa, J. J., Elimelech, M., & Hering, J. G. (1997). Arsenic removal by RO and NF membranes.
. *American Water Works Association.Journal, 89*(10), 102-114.

Wesolowski, D., Machesky, M., Ziemniak, S., Xiao, C., Palmer, D., Anovitz, L., & Benezeth, P. (2001). *Solubility and Surface Adsorption Characteristics of Metal Oxides to High Temperature,*

Xue, Y., Hou, H., & Zhu, S. (2009). Competitive adsorption of copper(II), cadmium(II), lead(II) and zinc(II) onto basic oxygen furnace slag. *Journal of Hazardous Materials, 162*(1), 391-401. doi:http://dx.doi.org/10.1016/j.jhazmat.2008.05.072

Yadanaparthi, S. K. R., Graybill, D., & von Wandruszka, R. (2009). Adsorbents for the removal of arsenic, cadmium, and lead from contaminated waters. *Journal of Hazardous Materials, 171*(1–3), 1-15. doi:http://dx.doi.org/10.1016/j.jhazmat.2009.05.103

Yang, C. (1998). Statistical mechanical study on the freundlich isotherm equation. *Journal of Colloid and Interface Science, 208*(2), 379-387. doi:10.1006/jcis.1998.5843

Yantasee, W., Warner, C. L., Sangvanich, T., Addleman, R. S., Carter, T. G., Wiacek, R. J., . . . Warner, M. G. (2007). Removal of heavy metals from aqueous systems with thiol functionalized superparamagnetic nanoparticles. *Environmental Science & Technology, 41*(14), 5114-5119.

Zacaria, R., Gerente, C., Andres, Y., & Cloirec, P. (2002). Adsorption of several metal ions onto a low-cost biosorbent:Kinetic and equilibrium studies . *Environmental Science & Technology, 36*(9), 2067-2073. doi:10.1021/es0102989

Zhang, W. (2003). Nanoscale iron particles for environmental remediation: An overview. *Journal of Nanoparticle Research, 5*(3-4), 323-332.

Zhou, Y., & Haynes, R. (2011). A comparison of inorganic solid wastes as adsorbents of heavy metal cations in aqueous solution and their capacity for desorption and regeneration. *Water, Air, & Soil Pollution, 218*(1-4), 457-470. doi:10.1007/s11270-010-0659-7

Zhou, Y., & Haynes, R. J. (2010). Sorption of heavy metals by inorganic and organic components of solid wastes: Significance to use of wastes as low-cost adsorbents and immobilizing agents. *Critical Reviews in Environmental Science and Technology, 40*(11), 909-977. doi:10.1080/10643380802586857

APPENDIX

BATCH EXPERIMENT TEST RESULTS

Table A.1: Operating conditions of Varian ICP-OES

Parameter	Value
Power	1.1 kW
Plasma flow	15 L/min
Frequency	40 MHz
Sample uptake delay	30 s
Rinse time	25 s
Replicate read time	5 s
Cd wavelength	214-228
Cu wavelength	224-327
Ni wavelength	221-231
Pb wavelength	217-261
Zn wavelength	202-214

*All experiments were run in triplicate and the average concentrations from ICP-OES analysis were used in the calculations employed in plotting all graphs

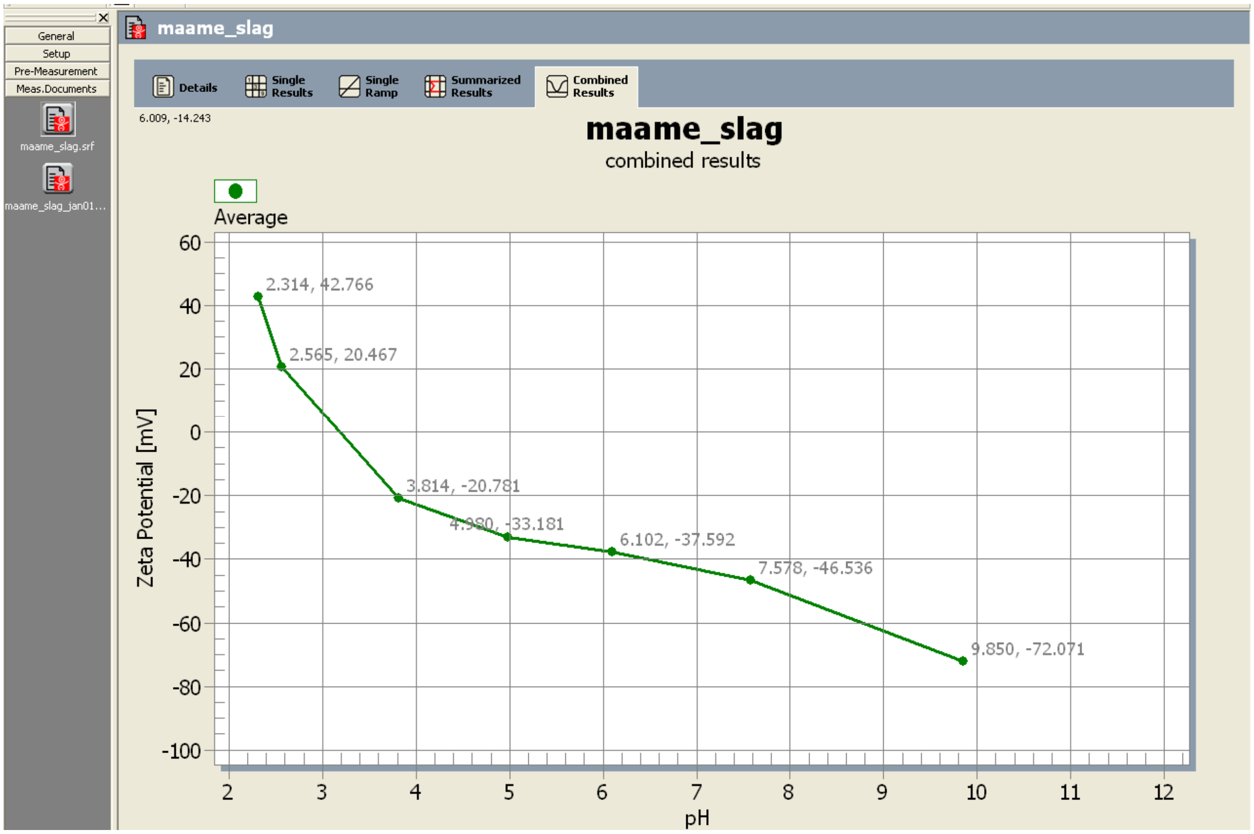

Figure A-1 : Figure: Electro kinetic Analysis of Nickel smelter slag showing pzc using the Surpass Anton Parr Analyser

Table A.2: Data on effect of pH on removal of Pb

Ph (Pb)	Co (mg/L)	Average Cf(mg/L)	Standard deviation	Standard error	Removal(%)
2	10	8.797133	0.470147	0.27144	16.27041
3	10	4.9397	0.28665	0.165498	51.9199136
4	10	0.011243	0.005903	0.003408	99.88757
5	10	0.040124	0.008278	0.004779	99.59876
7	10	0.003737	0.003693	0.002132	99.96263
8	10	0.201626	0.012656	0.007307	97.98374
9	10	0.088631	0.025546	0.014749	99.11369
11	10	0.57288	0.105498	0.060909	94.2712

Table A.3: Data on effect of pH on removal of Cu

Ph (Cu)	Co (mg/L)	Cf(mg/L)	Std deviation	Std error	Removal(%)
2	10	18.6061	1.3143	0.7588	0.0000
3	10	8.1073	0.3288	0.1898	10.9907
4	10	0.751647	0.394099	0.227533	92.48353
5	10	0.2793	0.0031	0.0018	97.3584
7	10	0.009807	0.002109	0.001218	99.90193
8	10	0.0100	0.0003	0.0002	99.9901
9	10	0.0508	0.0009	0.0005	99.4919
11	10	0.0162	0.0008	0.0004	99.8384

Table A.4: Results for effect of pH on mixedmetal removal

Ph	Adsorption efficiency (%)				
	Cd	Cu	Ni	Pb	Zn
2	9.76	0	0	17.14	3.69
3	3.92	94.84	0	96.46	31.36
4	0.601467	97.34847	0	97.52887	28.38067
5	3	96.42	0	96.48	34.15
7	17.58643	99.72738	3.079	99.7492	66.25183
8	50.295	99.83	89.76	99.48	98.03
9	87.21	99.88	97.03	99.63	99.16
11	99.58	99.75	99.96	90.74	96.44

Table A.5: ICP results on concentration of Pb with time

Time	Pb in solution (mg/L)	Standard deviation	Standard error	Adsorption efficiency (%)
0 min	10	0	0	0
5 min	4.414967	0.773274	0.44645	55.85033
10 min	2.607317	0.548325	0.316576	73.92683
20 min	0.841523	0.222286	0.128337	91.58477
1hour	0.751216	0.127051	0.073353	92.48784
2 hour	0.504049	0.12005	0.069311	94.95951
4 hour	0.22937	0.048636	0.02808	97.7063
8 hour	0.067672	0.019434	0.01122	99.32328
10 hour	0.040124	0.008278	0.004779	99.59876

12 hour	0.035616	0.013635	0.007872	99.64384
16 hour	0.027253	0.01259	0.007269	99.72747
20 hour	0.022458	0.010743	0.006202	99.77542
24 hour	0.010774	0.005104	0.002947	99.89226

Table A.6: ICP results on Cu concentration with time

Time	Cu in solution (mg/L)	Standard deviation	Standard error	Adsorption efficiency (%)
0 min	10.5735	0	0	0
5 min	6.545067	0.346036	0.199784	34.54933
10 min	3.696633	0.303052	0.174967	63.03367
20 min	1.135383	0.086026	0.049667	88.64617
1 hour	0.64331	0.013912	0.008032	94.30923
2 hour	0.480003	0.005764	0.003328	95.73176
4 hour	0.53331	0.009138	0.005276	96.33104
8 hour	0.264263	0.032775	0.018922	97.50071
10 hour	0.213988	0.003681	0.002125	97.97619
12 hour	0.164368	0.012287	0.007094	98.44548
20 hour	0.11766	0.009597	0.005541	98.88722
24 hour	0.116075	0.020576	0.011879	98.90221

Table A.7: Data for study on kinetics of Cu adsorption

Sample label	Cu unadsorbed (mg/L)	Cu adsorbed (mg/l)	Ce-Ct (mg/L)	Co-Ct	Qt	Time (minutse)	log Qe-Qt
Aug 25-66 Cu 5 ini	10.5735						
Cu ph5 0.5g AB 1hr	0.64331	9.93019	0.527235	9.93019	0.993019	60	-1.278
Cu ph5 0.5g AB 2hr	0.4800025	10.0935	0.363927	10.0935	1.00935	120	-1.439
Cu ph5 0.5g AB 4hr	0.53331	10.04019	0.417235	10.04019	1.004019	240	-1.38
Cu ph5 0.5g AB 8hr	0.2642625	10.30924	0.148187	10.30924	1.030924	480	-1.829
Cu ph5 0.5g AB 10hr	0.2139875	10.35951	0.097912	10.35951	1.035951	600	-2.009
Cu ph5 0.5g AB 12hr	0.1643675	10.40913	0.048293	10.40913	1.040913	720	-2.316
Cu ph5 0.5g AB 20/1hr	0.11766	10.45584	0.001585	10.45584	1.045584	1200	-3.8
Cu ph5 0.5g AB 24hr	0.116075	10.45743	0	10.45743	1.045743		

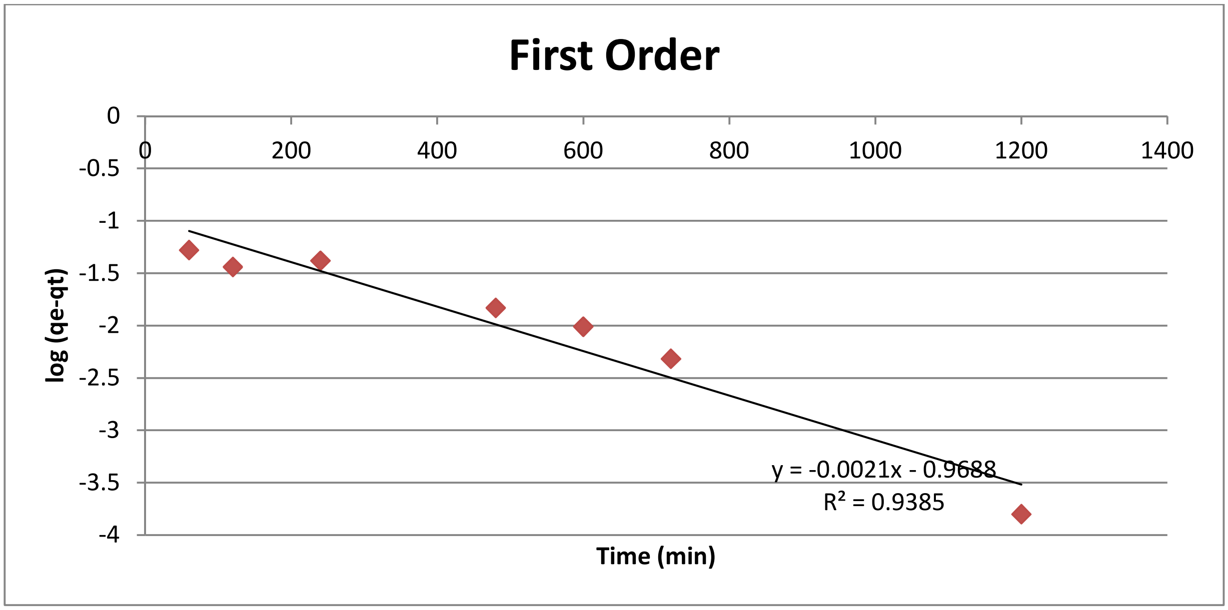

Figure A.2: Pseudo first order plot for Cu

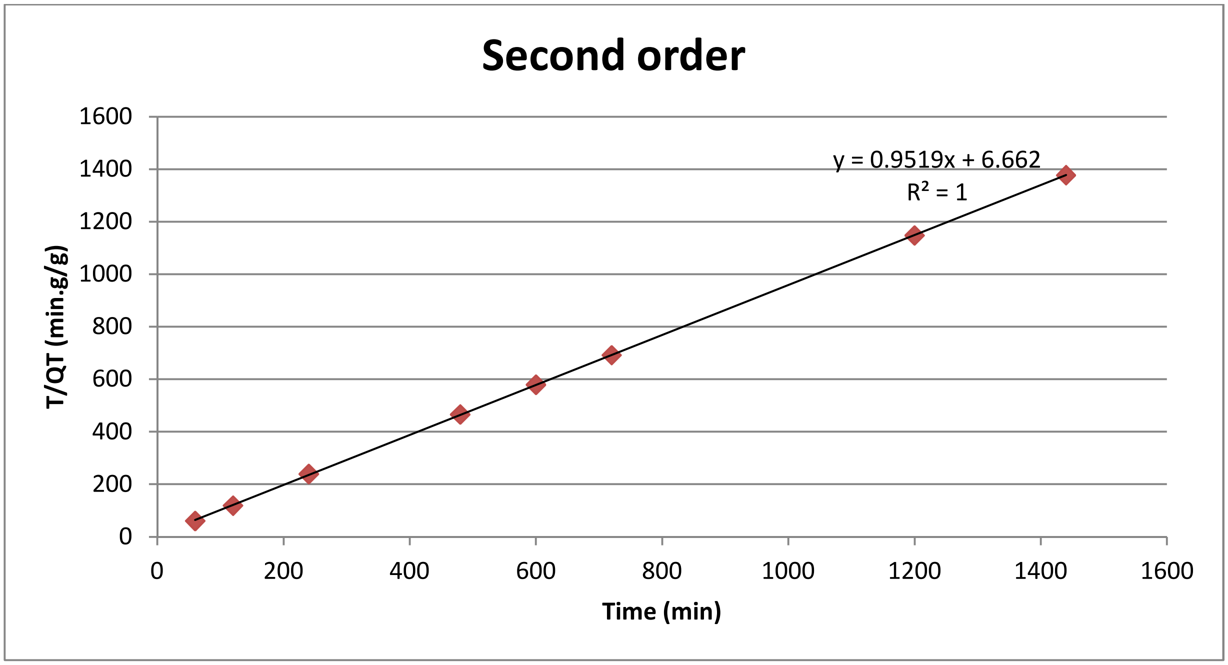

Figure A.3: Pseudo second order plot for Cu

Table A.8: Data for study on kinetics of Pb adsorption

Sample name	Pb un adsorbed (mg/L)	Pb adsorbed (mg/L)	Ce-Ct (mg/L)	Co-Ct (mg/L)	Qt	Qe-Qt	T(minutes)	T/QT
Pb ini	10.8161							
1hr	0.7512	10.0649	0.7404	10.0649	1.0065	0.0740	60.00	59.613
2hr	0.5040	10.3120	0.4933	10.3120	1.0312	0.0493	120.00	116.369
4hr	0.2294	10.5867	0.2186	10.5867	1.0587	0.0219	240.00	226.700
8hr	0.0677	10.7484	0.0569	10.7484	1.0748	0.0057	480.00	446.578
10hr	0.0401	10.7759	0.0294	10.7759	1.0776	0.0029	600.00	556.796
12hr	0.0356	10.7805	0.0248	10.7805	1.0780	0.0025	720.00	667.876
16hr	0.0273	10.7888	0.0165	10.7888	1.0789	0.0016	960.00	889.811
20hr	0.0225	10.7936	0.0117	10.7936	1.0794	0.0012	1200.00	1111.769
24hr	0.0108	10.8053		10.8053	1.0805	0.0000	1440.00	1332.680

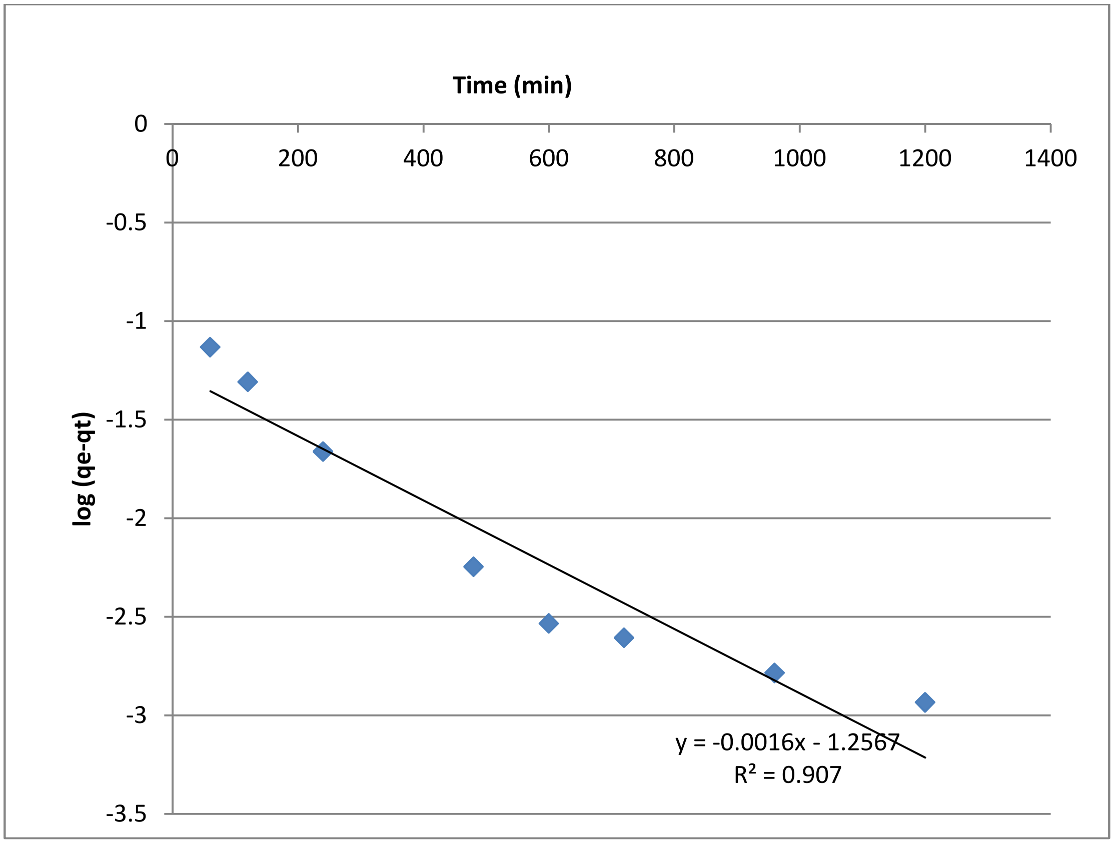

Figure A.4: Pseudo First order plot for Pb

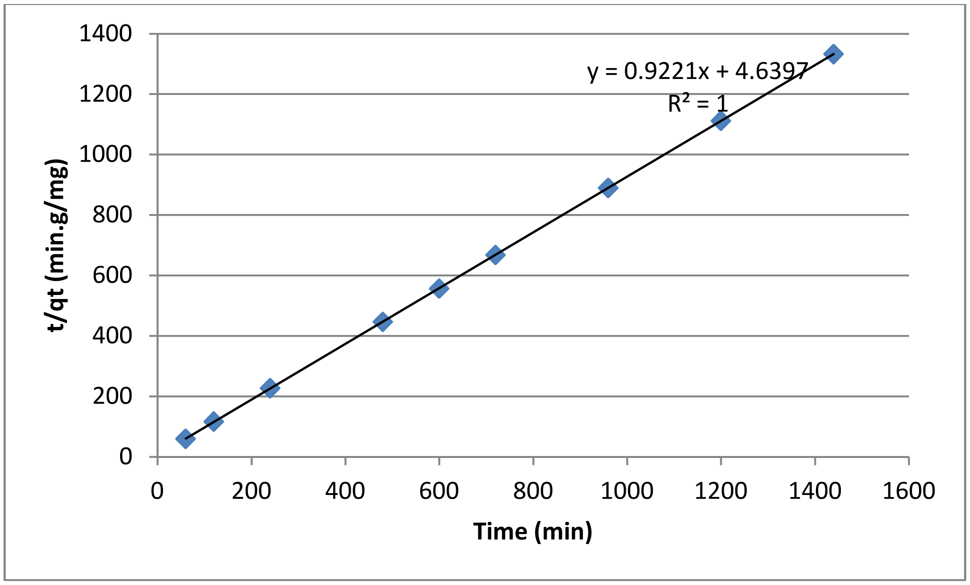

Figure A.5: Pseudo second order Plot for Pb

Table A.9.:Data for slag dose on removal of 10mg/L Pb and Cu

Slag dose	Pb removal	Cu removal
0	0	0
2	38.01896	67.69649
4	85.4683	92.10176
10	99.58441	97.35835
20	99.88422	99.97721
40	99.90014	99.99803

Table A.10.Data for slag dose on 100mg/L Pb

Sample Label	Slag dose (g/L)	Pb in solution (mg/L)	Adsorption efficiency (%)
Pb 100 initial	0	100	0
Pb 0.5g 10 hrs	10	45.47267	54.5273
Pb 1g 10 hours	20	28.43133	71.56866
Pb 2g 10 hrs	40	1.00275	98.99725
Pb 3 g 10hrs	60	0.014453	99.98554

Table A.11.Data for slag dose on 100mg/L Cu

Sample label	Cu in soln (mg/L)	Slag dose (g/L)	Adsorption efficiency (%)
Cu 100 ini 10	100	0	0
Cu 100 0.5g 10hrs	32.28633	10	67.71367
Cu 100 1g 10hrs	6.882467	20	93.11753

Cu 100 2g 10hrs	3.5962	40	96.4038
Cu 100 3g 10hrs	0.600123	60	99.39988

Table A.12: Data on multimetal removal with slag dose

Label	Cf of Cd (mg/L)	Cd (%)removed	Cf of Cu	Cu % removed	Cf of Ni	Ni % remov	Cf of Pb	Pb% remov	Cf of Zn	Zn % removed
Com ini (mg/L)	7.4548		10.78		11.759		11.675		11.731	
Com 10g/L ose	7.2987	2.0944	0.45	95.829	12.72	-8.172	0.5695	95.122	7.8565	33.03
Com 20g/L dose	7.024	5.7797	0.208	98.072	13.437	-14.27	0.0542	99.536	4.4605	61.98
Com 40g/L dose	3.8653	48.15	0.004	99.966	10.7215	8.823	0.0132	99.887	0.1513	98.71
Com 60g/L dose	0.5228	92.986	0	100	3.2415	72.434	0.0137	99.883	0.0103	99.91
Com 80g/L dose	0.0329	99.558	0	100	0.03039	99.742	0	100	0.0033	99.97

Table A.13: Data on study of particle size with 10mg/L Pb removal

Mesh size	Particle size (µm)	Pb in soln (mg/L)	std dev	std error	Adsorption efficiency (%)
Pb ini 10		10.2015			
40	425	8.561375	0.213929	0.123512	16.07729
60	338	8.302675	0.104447	0.060302	18.61319
100	200	7.890475	0.236268	0.136409	22.65378
140	128	3.965925	0.525926	0.303643	61.1241
200	91	1.77655	0.394858	0.227971	82.5854
pan	75	0.00063	0	0	99.99382

Table A.14: Data on study of particle size with 10mg/L Cu removal

Mesh size	Particle size (µm)	Cu in soln (mg/L)	Adsorption efficiency (%)
Cu initial 10		9.853	
40 m	425	8.8919	9.75439
60 m	250	8.755433	11.13942
100 m	150	7.074567	28.19886
140 m	106	2.635533	73.25146
200 m	75	0.87651	91.10413
pan	75	0	100

Table A.15: Data for study on adsorption of Pb over 5 cycles

sample label	Cf of Pb(mg/L)	Adsorption efficiency (%)	Pb adsorbed (mg/L)
Pb ini cyc1	10.4975		
Pb adsorb cycle 1	0.11271	98.92632	10.38479
Pb adsorb ini cyc 2	9.8297		
Pb adsorb cyc 2	6.522275	33.64726	3.307425
Pb adsorb ini cyc3	9.96745		
Pb adsorb cyc 3	5.4745	45.07622	4.49295
Pb adsorb ini cyc4	10.3075		
Pb ads cyc 4	6.508225	36.85933	3.799275
Pb adsorb ini cyc 5	10.3935		
Pb adsorb cyc 5	5.623125	45.89768	4.770375

Table A.16: Data on adsorption of Cu over 5 cycles

sample	cu in soln (mg/L)	Cu adsorbed (mg/L)	Adsorption efficiency (%)
Cu ini	9.415667		
Cu adsorb1	0.74829	8.667377	92.05271
Cu adsorb 2	7.905617	1.514383	16.07626
Cu adsorb 3	7.320867	2.099133	22.28379
Cu adsorb 4	7.455583	1.964417	20.85368
Cu adsorb 5	7.656083	1.763917	18.72523

Table A.17: Data on adsorption of multiple metals over 5 cycles

Sample label	Cd	cd removal (%)	Cu	Cu removal (%)	Ni	Ni removal (%)	Pb	Pb removal (%)	Zn	Zn removal (%)
All adsorb ini cy 1	6.589		9.48		10.245		10.79		10.43	
All adsorb cyc1	0.007	99.89	0.00	100.0	0.028	99.725	0.00	100.0	0.00	100.00
All adsorb ini cycle 2	6.970		9.99		10.809		10.98		10.84	
All adsorb cycle 2	6.359	8.77	6.67	33.3	13.259	-22.670	0.57	94.8	10.03	7.47
All adsorb ini cycle 3	7.064		10.23		10.899		11.09		10.91	
All adsorb cycle 3	6.693	5.24	4.99	51.2	13.336	-22.363	0.47	95.8	10.62	2.67
All adsorb ini cycle4	7.065		10.08		10.847		11.14		10.88	
All adsorb cycle 4	6.316	10.61	4.23	58.1	12.523	-15.451	0.34	97.0	9.93	8.71
All adsorb ini cycle 5	7.125		10.23		11.024		11.34		11.00	
All adsb cycle 5	6.464	9.27	5.13	49.8	12.553	-13.870	0.80	93.0	10.22	7.04

Table A.18: Data used for Pb Isotherms

Ce (mg/L)	qe (mg/g)	Ce (mg/L)	Ce/Qe (g/L)	log Ce	log qe
0.010774	0.9989226	0.010774	0.01078562	-1.967623029	-0.000468161
0.040051	1.638128	0.040051	0.024449249	-1.397386636	0.214347834
5.687322222	2.831267778	5.687322222	2.008754617	0.754907834	0.451980946
19.09633	3.1074	19.09633	6.145436699	1.280949911	0.492397161
37.92233	3.708333	37.92233	10.22624721	1.578895013	0.569178726
44.88578	4.199256	44.88578	10.68898395	1.652108777	0.623172351

TableA.19: Data used for Cu isotherms

Co (mg/L)	Ce (mg/L)	Ce/Qe (g/L)	Qe (mg/g)	Log Ce	log qe
10.5735	0.116075	0.228071	1.045743	-0.93526	0.019425
20.557	4.8218	3.06434	1.57352	0.683209	0.196872
43.351	16.937	6.41213	2.6414	1.228836	0.421834
65.671	36.669	12.64361	2.9002	1.564299	0.462428
92.6675	58.6425	17.23512	3.4025	1.768212	0.531798
101.97	63.915	16.79543	3.8055	1.805603	0.580412

Table A.20: Results from Cd modelling with Visual MINTEQ

pH	Cd+2	Cd(OH)2 (aq)	Cd(OH)3-	Cd(OH)4-2	Cd2OH+3	CdOH+		OH-		Cd(OH)2(s)	H+1
	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration		Concentration		Saturation index	Saturation index
2	1E-16	3.705E-33	3.9582E-44	5.1524E-56	4.337E-40	6.3169E-25	1E-16	1.09E-12		-25.781	0
3	1E-16	4.581E-31	4.6374E-41	5.152E-52	4.114E-39	7.401E-24	1E-16	1.03E-11		-23.689	0
4	1E-16	4.916E-29	4.889E-38	5.1523E-48	4.042E-38	7.8022E-23	1E-16	1.02E-10		-21.658	0
5	1E-16	5.028E-27	4.9725E-35	5.1523E-44	4.019E-37	7.9355E-22	1E-16	1.01E-09		-19.649	0
6	1E-16	5.064E-25	4.9989E-32	5.1519E-40	4.011E-36	7.9777E-21	1E-16	1.01E-08		-17.645	0
7	9.99E-17	5.07E-23	5.0023E-29	5.1482E-36	4.004E-35	7.983E-20	1E-16	1.01E-07		-15.645	0
8	9.92E-17	5.024E-21	4.9595E-26	5.1113E-32	3.948E-34	7.9147E-19	1E-16	1.01E-06		-13.649	0
9	9.22E-17	4.637E-19	4.5855E-23	4.7514E-28	3.418E-33	7.3179E-18	1E-16	1.01E-05		-11.684	0
1	4.4E-	2.163E	2.1515	2.2675	7.829E	3.4335	1E-	0.0001		-10.015	0

0	17	-17	E-20	E-24	-33	E-17	16	02			
11	1.83E-18	8.379E-17	8.482E-19	9.4259E-22	1.377E-34	1.3536E-17	1E-16	0.001033		-9.427	0

Table A.21: Results from Pb modelling with Visual MINTEQ

pH	H+1	Pb+2	OH-	Pb(OH)2 (aq)	Pb(OH)3-	Pb2OH+3	Pb3(OH)4+2	Pb4(OH)4+4	PbOH+	Litharge	Massicot	Pb(OH)2(s)	Pb2O(OH)2(s)
	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Saturation index	Saturation index	Saturation index	Saturation index
2	0.0108	5E-05	1E-12	3E-18	0	1E-13	8E-30	7E-31	1E-10	-13.144	-13.34	-8.604	-27.1
3	0.001	5E-05	1E-11	3E-16	0	9.6E-13	1E-25	7E-27	1E-09	-11.055	-11.26	-6.515	-22.92
4	0.0001	5E-05	1E-10	4E-14	0	9.5E-12	1E-21	7E-23	1E-08	-9.031	-9.231	-4.491	-18.87
5	1E-05	5E-05	1E-09	4E-12	0	9.4E-11	1E-17	7E-19	1E-07	-7.028	-7.228	-2.488	-14.87
6	1E-06	5E-05	1E-08	4E-10	0	9E-10	1E-13	6E-15	1E-06	-5.037	-5.237	-0.497	-10.88
7	1E-07	4E-05	1E-07	3E-08	0	6.1E-09	7E-10	3E-11	9E-06	-3.12	-3.32	1.42	-7.051
8	1E-08	1E-05	1E-06	1E-06	0	7.2E-09	3E-07	4E-09	3E-05	-1.578	-1.778	2.962	-3.966

9	1E-09	1E-06	1E-05	1E-05	0	6.1E-10	2E-06	3E-09	3E-05	-0.612	-0.812	3.928	-2.034
10	1E-10	4E-08	0.0001	3E-05	0	6.9E-12	9E-07	4E-11	1E-05	-0.088	-0.288	4.452	-0.987
11	1E-11	3E-10	0.001	2E-05	0	4.3E-15	4E-09	1E-15	8E-07	-0.228	-0.428	4.312	-1.265

A.22: Results on Cu modelling with Visual MINTEQ

pH	Cu+2	H+1	Cu(OH)2 (aq)	Cu(OH)3-	Cu(OH)4-2	Cu2(OH)2+2	Cu2OH+3	Cu3(OH)4+2	CuOH+	OH-	Cu(OH)2(s)	Tenorite(am)	Tenorite(c)
	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Concentration	Saturation index	Saturation index	Saturation index
2	0.000157	0.010841	6.7E-17	2.83E-25	2.93E-36	5.75E-15	5.24E-13	3.33E-25	3.93E-10	1.09E-12	-9.233	-8.433	-7.583
3	0.000157	0.001033	8.13E-15	3.27E-22	2.93E-32	6.97E-13	4.99E-12	4.89E-21	4.54E-09	1.04E-11	-7.15	-6.35	-5.5
4	0.000157	0.000102	8.48E-13	3.37E-19	2.93E-28	7.27E-11	4.93E-11	5.32E-17	4.69E-08	1.03E-10	-5.131	-4.331	-3.481
5	0.000157	1.02E-05	8.51E-11	3.38E-16	2.92E-24	7.27E-09	4.9E-10	5.34E-13	4.7E-07	1.03E-09	-3.13	-2.33	-1.48
6	0.000151	1.02E-06	8.23E-09	3.27E-13	2.82E-20	6.78E-07	4.56E-09	4.82E-09	4.54E-06	1.03E-08	-1.145	-0.345	0.505
7	7.75	1.02	4.27	1.69	1.44	1.8E	1.19	6.63	2.35	1.02	0.57	1.37	2.22

	E-05	E-07	E-07	E-10	E-16	-05	E-08	E-06	E-05	E-07			
8	6.2E-06	1.01E-08	3.47E-06	1.37E-08	1.15E-13	1.17E-05	7.58E-10	3.51E-05	1.9E-05	1.02E-06	1.48	2.28	3.13
9	3.03E-07	1.01E-09	1.71E-05	6.71E-07	5.65E-11	2.82E-06	1.82E-11	4.15E-05	9.33E-06	1.02E-05	2.172	2.972	3.822
10	1.13E-08	1.01E-10	6.35E-05	2.5E-05	2.11E-08	3.92E-07	2.53E-13	2.15E-05	3.48E-06	0.000102	2.743	3.543	4.393
11	5.92E-11	1.03E-11	3.12E-05	0.000125	1.1E-06	1.01E-09	7.02E-17	2.71E-08	1.73E-07	0.0001035	2.434	3.234	4.084

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