ASSESSMENT OF THE COMPETITIVE ADSORPTION OF SOME HEAVY METAL IONS ONTO SOIL

BY

OPEYEMI ELIZABETH IDOWU
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A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA,
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF
MASTER OF SCIENCE (ANALYTICAL CHEMISTRY)

DEPARTMENT OF CHEMISTRY,
FACULTY OF PHYSICAL SCIENCES,
AHMADU BELLO UNIVERSITY, ZARIA
NIGERIA

FEBRUARY, 2018

DECLARATION

I declare that the work in this Dissertation entitled **"ASSESSMENT OF THE COMPETITIVE ADSORPTION OF SOME HEAVY METAL IONS ONTO SOIL"** has been performed by me in the Department of Chemistry under the supervision of Dr. K. I. Omoniyi and Dr. S. E. Abechi. The information derived from literatures have been duly acknowledged in the text and a list of references provided. No part of this dissertation has been previously presented for another degree or diploma at any University or Institution.

Opeyemi Elizabeth IDOWU	_____	_____
Name of Student	Signature	Date

CERTIFICATION

This Dissertation entitled **"ASSESSMENT OF THE COMPETITIVE ADSORPTION OF SOME HEAVY METAL IONS ONTO SOIL"** by Opeyemi Elizabeth IDOWU meets the regulations governing the award of the degree of Master of Science of the Ahmadu Bello University, Zaria and is approved for its contribution to scientific knowledge and literary presentation.

Dr. K. I. Omoniyi Chairman, Supervisory Committee	_____ Signature	_____ Date
Dr. S. E. Abechi Member, Supervisory committee	_____ Signature	_____ Date
Prof. A. O. Oyewale Head of Department	_____ Signature	_____ Date
Prof. S. Z. Abubakar Dean, School of Postgraduate Studies	_____ Signature	_____ Date

DEDICATION

This dissertation is dedicated to the Almighty God, the Author and Finisher of my faith.

ACKNOWLEDGEMENTS

All glory, honour and praise to the immortal, invisible and the only wise God for giving me His helping hands in all my endeavours.

My profound gratitude goes to my supervisors Dr. K. I. Omoniyi and Dr. S. E. Abechi, for their kind guidance, unwavering support and warm friendship throughout my research period. Their words of encouragement have boosted my faith in myself as a researcher and given me a drive to continue the pursuit of a scientific career. I am truly grateful to them.

My appreciation also goes to the staff of the Multiuser Laboratory, members and staff of the Chemistry Department, Ahmadu Bello University, Zaria and the Federal Ministry of Agriculture, Kaduna.

Credit goes to all my friends and colleagues, for their assistance and support during the course of this research work.

My deepest appreciation goes to my husband who has been my all-round technical and emotional support for the past couple of years.

My heartfelt gratitude goes to my parents and siblings, for without their love and support, I would not have even dreamt of reaching this far.

My last but not the least gratitude goes to all the wonderful people who have immensely contributed to the success of this research work through finance, prayers and valuable inputs.

May God bless you all in Jesus name.

ABSTRACT

This research work assessed the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2} in single-metal and multi-metal ions reaction systems onto a standard reference soil (NIST SRM 2709a). The effect of varying adsorbent dosage, contact time and initial concentration of the metal ions on the soil was examined and for most of the metals, the optimum conditions were attained at 20 mg/dm^3 initial metal ion concentration, 1.0 g adsorbent dose and 2 hrs contact time. The highest percentage adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+}, and Pb^{2+}obtained from their respective solutions were 92.22%, 56.71%, 99.57% and 97.11%. Equilibrium studies showed that the Freundlich isotherm had a better fit for the selected metals than Langmuir isotherm. The kinetics study revealed that all the selected metal ions followed the pseudo-second order model. The results of the experiments confirmed that adsorption from single-metal solution was more effective than adsorption under multi-metal conditions due to competitive effects. Also, the adsorption of the metals decreased with increase in the number of competing ions. Among the metal ions studied in the multi-metal system, Pb^{2+} was most preferably removed because of its high affinity to the soil surface. Metal affinity and capacity for the soil surface were found to increase with metal electronegativity Pb >Cu > Cd > Cr in the competitive systems. The results indicated that high removal efficiency could be achieved by the use of natural standard reference soil.

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LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
Ads	Adsorption
CEC	Cation Exchange Capacity
EDTA	Ethylenediaminetetraacetic acid
EU	European Union
FAAS	Flame Atomic Absorption Spectrometry
ICP-MS	Inductively Coupled Plasma-Mass Spectrometry
NIST	National Institute of Standard and Technology
OM	Organic Matter
pk	Hydrolysis Constant
SRM	Standard Reference Materials
SEM	Scanning Electron Microscope
USEPA	United States Environmental Protection Agency

CHAPTER ONE

1.0 INTRODUCTION

Soil is one of the key elements in the ecosystems. It provides the nutrient-bearing environment for plant life and it is important for degradation of biomass. Soil is a very complex heterogeneous medium, which consists of solid phases (the soil matrix) containing minerals and organic matter and fluid phases (soil water and the soil air); which interact with each other and ions entering the soil system (Brady and Weil, 2002). The ability of soils to adsorb metal ions from aqueous solution is of special interest and has consequences for both agricultural issues (such as soil fertility) and environmental questions such as remediation of polluted soils and waste deposition (Bradl, 2004).

Heavy metals are group of elements between copper and lead on the Periodic Table, having atomic weights between 63.55 and 200.59, high density, precisely greater than 5 gcm^{-3} and specific gravities greater than 4.0 (Hawkes, 1997). Heavy metals in the soil include metals of significant biological toxicity, such as mercury, cadmium, lead and chromium (Ademoroti, 1996).

Environmental pollution with toxic metals is a global phenomenon and the potential effects of metallic contaminants on human health and the environment is on the increase. Therefore, research on the fundamental, applied and health aspects of heavy metals in the environment is also increasing (Yang and Sun, 2009). The coastal regions are some of the most sensitive environments and yet they are subject to growing human pressures because of increasing urbanization, industrial development and recreational activities. Human activities affect the

natural geological and biological redistribution of heavy metals by altering the chemical forms of the metals released to the environment. The main anthropogenic sources of heavy metal contamination are mining, disposal of untreated and partially treated effluents containing heavy metals, as well as metal chelates from different industries and indiscriminate use of fertilizer and pesticides containing heavy metals (Hatje *et al*., 1998).

Heavy metals are non-biodegradable and can accumulate in the human body system, causing damage to the nervous system and other internal organs (Lee *et al.*, 2007). Ni and Cu are tumor promoting factors, whose carcinogenic effect has attracted global concerns (Baryla *et al.*, 2011). Workers who are in close contact with the nickel powder are more likely to suffer from respiratory cancer, and the content of Ni in the environment is positively correlated with nasopharyngeal carcinoma (Chen, 2011).

Aquatic organisms may be adversely affected by heavy metals, slightly elevated metal levels in natural waters may cause the following sublethal effects in aquatic organisms: histological or morphological change in tissues, changes in physiology such as suppression of growth and development, poor swimming performance, changes in circulation, changes in biochemistry such as enzyme activity and blood chemistry, changes in behaviour and reproduction (Cheung *et al.*, 2001).

Conventional methods for removing heavy metals from aqueous solutions include chemical precipitation, ion exchange, adsorption and membrane filtration technologies (Gode and Pelalivan, 2006). In most soil environment, sorption is the dominating speciation process and

thus the largest fraction of heavy metal in a soil is associated with the solid phase of that soil (Basta and Tabatai, 1992).

Adsorption is known as one of the most economical, effective and widely used methods for the removal of heavy metals from aqueous environments. The great advantage of adsorption over others is the low generation of residues, easy metal recovery and the possibility for the reuse of the adsorbent. Several low cost adsorbents such as agricultural/industrial wastes and natural/synthetic soil minerals have been used as effective adsorbents for the removal of heavy metals, organics and radionuclides in water treatment because of their strong ion-exchange and complex formation abilities with the heavy metals (Srivastava *et al*., 2005; Bekkouche *et al*., 2012;). Adsorption of metal ions from aqueous solution onto soil, clay minerals and clays has been a subject of interest in chemistry as well as in other research areas. It is considered that the adsorption of heavy metal ions onto soil occurs as a result of ion exchange, surface complexation, hydrophobic and electrostatic interaction (Jung *et al.*, 1998). This is because the organic components of soils having carboxyl, phenol or amine groups may take part in heavy metal ion retention by complexation (Jung *et al.*, 1998).

1.1 The Chemistry of Metal Ions in Soil

The chemistry of metal ions in soils may be affected by three main factors: specific adsorption to various solid phases, precipitation of sparingly soluble or highly stable compounds and formation of relatively stable complexes or chelates with soil components (Mouni *et al*., 2009). Soil is known to be either positively or negatively charged. Soil with a net positive charge is said to have an anion exchange capacity while a soil is said to have a cation exchange capacity

when the soil particles have a net negative charge and they attract and retain cations (Mouni *et al*., 2009). Soil cations are divided into two categories which are; (i) the base cations which include ammonium, calcium, magnesium, potassium and sodium ions (ii) the acid cations which are aluminum and hydrogen ions. The pH of soil is one of the most important properties involved in understanding how rapidly reactions occur in soil and mostly the pH of soils usually range from 4 to 10 (Brady and Weil, 2002). Soil chemistry may also depend on the presence of organic matter (OM) containing many hydrogen and carbon compounds. The arrangement and formation of these compounds influence soil's ability to handle spilt chemicals and other pollutants (Brady and Weil, 2002).

1.1.1 Soil surface functional groups

Soil surface functional groups consist of the chemically reactive molecular units bound onto the structure of a soil solid phase at its periphery, such that the reactive components of these units are in contact with the solution phase (Bradl, 2004). Soil surfaces display a variety of hydroxyl groups having different reactivity. Alumina surfaces, for example, possess terminal –OH groups which are more likely to accept additional protons in acidic solutions compared to a bridging –OH groups. Goethite (α-FeOOH) possesses four types of surface hydroxyls whose reactivity depends on the coordination environment of the oxygen atom in the Fe– OH group (Bradl, 2004). Alumosilicates (such as clay minerals, micas, zeolites, and most Mn oxides) display both aluminol (≡Al–OH) and silanol (≡Si–OH) edge-surface groups. The deprotonated aluminol group (i.e ≡Al–O−) binds metals in the form of more stable surface complexes (McBride, 1994).

In a natural environment, adsorption by carboxylic groups is more important than adsorption by phenolic groups due to the wide difference between their acidity constants (Wood, 2005). Soil colloidal particles provide large interfaces and specific surface areas which play an important role in regulating the concentrations of many trace elements and heavy metals in natural soils and water systems. Weathering may also produce interlayer hydroxypolymers, interstratification, external-surface organic and inorganic coatings on smectite, as well as organic and iron oxide coatings on kaolinite (Bradl, 2004).

1.2 Sources of Heavy Metals

Metals are natural constituents of rocks, soils, sediments and water. They are released into the environment through volcanism, weathering of rocks and largely by human activities (Qin *et al*., 2008). Heavy metals may enter into an aquatic environment through acid rain, industrial or consumer waste deposition (Stumm and Morgan, 2012). Heavy metals occurring in most rivers are carried by suspended particles and only a fraction is transported in soluble form (Horowithz, 1991). However, heavy metals tend to accumulate more in sediments than in water and aquatic organisms (Lee *et al.,* 2003). In soils, heavy metals can be present in various chemical forms and generally exhibit different physical and chemical behaviour in terms of chemical interaction, mobility, biological availability and potential toxicity (Li *et al.,* 2000).

Heavy metals are persistent in all parts of the environment because they cannot be degraded or destroyed. Living organisms require trace amounts of some heavy metals such as vanadium, chromium, manganese, iron and nickel but excessive levels can be detrimental to the organisms.

Their accumulation over time in the bodies of mammals can cause serious illnesses (Chao *et al.,* 2014).

1.3 Occurrence and Effects of Selected Heavy Metals

1.3.1 Cadmium

Cadmium occurs in a few minerals and in small quantities in other ores, especially zinc ores, from which it is produced as a by - product. Some lead ores also contain small quantities of cadmium and if it is present in sufficient quantity, it is recovered by a cycle of operations similar to that used by zinc smelters (Chronopoulos *et al*., 1997). The concentrations of cadmium in agricultural soils depend upon the amounts present in the parent rocks from which the soil is formed, the amounts added in the form of fertilizers and soil amendments, the amounts deposited onto soils from the atmosphere and the amounts removed by harvested crops and by leaching (Volesky and Holan, 1995). On the average, sedimentary rocks contain greater concentrations of cadmium than either igneous or metamorphic rocks and therefore, recent soils derived from sedimentary rock should contain greater concentrations of cadmium than those derived from igneous or metamorphic rocks (Volesky and Holan, 1995).

In acute cadmium poisoning by ingestion, irritation of the gastrointestinal tract is the major symptom manifesting as nausea, vomiting, diarrhoea and abdominal cramps. Chronic exposure to cadmium by inhalation can damage the nervous system, kidney and liver. Other exposures to cadmium compounds may lead to skin lesions, lung tumour, decrease in heart contraction and damaged blood vessel in humans (Jenne *et al.,* 2011).

1.3.2 Copper

The major portion of copper produced in the world is used by electrical industries, most of which is combined with other metals to form alloy. Important series of alloys in which copper is the chief constituent are brass (copper and zinc) and bronze (copper and tin) (Morse, 1994). Copper resists the action of the atmosphere and sea water on its exposure for a long period of time. This may result in the formation of thin green protective coatings known as patina which is a mixture of hydroxocarbonate, hydrosulphate and small amount of other compounds. Copper is a moderately noble metal, unaffected by oxidizing or complexing dilute acids in the absence of air; it will however, dissolve readily in HNO_3 and in H_2SO_4 in the presence of oxygen (Amin and Khaled, 2010)

Copper is among the heavy metals that are essential to life but could be toxic at elevated levels. It is toxic at high concentration in water and is known to cause brain damage in mammals. Elevated levels of this metal have been found to be toxic (Hukabee *et al.,* 2011). Toxicity of copper in plants through chemical-treated agricultural soil has also been reported (Babula and Adam, 2008). Deposition of metals from industries, dumpsites and power plants that burn fuels have also contributed to the elevated level of copper in the environment (Baryla *et al.,* 2011).

1.3.3 Lead

Lead is present in several minerals but all are of minor significance except the sulphide, PbS (galena), which is the major source of lead production throughout the world. Lead is also found in anglesite ($PbSO_4$) and cerussite ($PbCO_3$). The elimination of lead from insecticides and paint pigments and the use of respirators and other protective devices in areas of exposure have

reduced lead poisoning (Sanborn *et al*, 2002). The recognition that the use of tetraethyl lead [$Pb(C_2H_5)_4$] as an antiknock additive in gasoline was polluting the air and water led to the compound's elimination as a gasoline constituent in the 1980s (Taylor, 1995). The major causes of lead poisoning in humans are: drinking of water carried through lead pipes and ingestion of materials that has lead-based paints. Children who chew painted toys and furnishings or eat paint peelings from walls are most likely to be affected (Sahu *et al*., 2008). Industries in which workers encounter lead-containing solids, dusts or fumes include: the petroleum, mining, smelting, printing, cutlery, plumbing, glass and ammunitions, gas fittings, ceramics and storage-battery manufacturing industries. Other possible sources of lead poisoning include: the agricultural use of insecticides containing lead compounds to spray fruits and vegetables which may eventually affect the workers and the consumers. In the mid-20th century, constant exposure to exhaust fumes of motor vehicles powered by fuel containing tetraethyl lead became a significant cause of lead poisoning, especially in children (Kersten *et al.*, 2003).

Symptoms of lead poisoning may develop gradually or appear suddenly after chronic exposure (Jenne, *et al*., 2011). The poisoning affects the entire body especially the nervous system, the gastrointestinal tract and the blood forming tissues. The victim usually becomes palled, moody irritable and may complain of a metallic taste. Digestion is deranged, the appetite fails and there may be severe abdominal pain, with spasms of the abdominal muscles and constipation. A black line (lead line) may appear at the base of the gums. Other symptoms such as; anaemia headache, dizziness, confusion and visual disturbances may also be observed (Sahu *et al.,* 2008). Peripheral nerve involvement results in a paralysis (lead palsy) that generally first affects the fingers, hands and wrists (wrist drop) (Goyer, 1996). The most serious effects are seen in

children under the age of six, in whose brain and nervous system development is still occurring. In these children, even a small amount of lead can result in permanent damage and loss of function of the affected area of the brain. Complications may occur, such as learning disabilities, slowed growth, blindness, deafness, and, in extreme cases, convulsions and coma ending in death. Brain injury may also occur in adults after massive exposure (Sahu *et al.*, 2008).

1.3.4 Chromium

Chromium is a naturally occurring element present in the earth's crust, with oxidation states (or valence states) ranging from chromium (II) to chromium (VI) (Jacob and Testa, 2005). Chromium enters into various environmental matrices (air, water, and soil) from a wide variety of natural and anthropogenic sources with the largest release coming from industrial establishments. Industries with the largest contribution to chromium release include metal processing, tannery facilities, chromate production, stainless steel welding, and ferrochrome and chrome pigment production (Jacobs and Testa, 2005). The increase in the environmental concentrations of chromium has been linked to air and wastewater release of chromium, mainly from metallurgical, refractory, and chemical industries (Jacobs and Testa, 2005). Chromium is widely used in numerous industrial processes and as a result, it is a contaminant of many environmental systems (Cohen *et al.,* 1993). Commercially chromium compounds are used in industrial welding, chrome plating, dyes and pigments, leather tanning and wood preservation. Chromium is also used as anticorrosive in cooking systems and boilers (Cohen *et al*., 1993). Chromium enhances insulin activity in the body and thus it is essential to the body (Jacobs and Testa, 2005).

However, Chromium (VI) is one of the pronounced toxins; it easily permeates biological membrane due to its oxidizing potential. Occupational and environmental exposure to Cr(VI)-containing compounds is known to cause multiorgan toxicity such as renal damage, allergy, asthma, and cancer of the respiratory tract in humans (Bae *et al.*, 2001).

1.4 Heavy Metals and Environmental Pollution

1.4.1 Effect of heavy metal contamination of soil on water

Heavy metal pollution of surface and underground water sources results in considerable soil pollution and pollution increases when mined ores containing toxic metals are dumped on the ground surface for manual dressing (Duruibe *et al.,* 2007).

Irrigation water may transport dissolved heavy metals to agricultural fields thereby leading to its accumulation in plant roots and possibly throughout the plant (Jaishankar *et al.*, 2014). Consequently, Animals that graze on such contaminated plants or drink from the polluted waters also accumulate such metals in their tissues, and milk (if lactating). Drinking and swimming in contaminated water causes skin rashes and health problems like cancer, reproductive problems, typhoid fever and stomach sickness in humans. Industrial chemicals and agricultural pesticides containing heavy metals that end up in aquatic environments can accumulate in marine lives. Fishes are easily poisoned with metals that are also later consumed by humans (Jaishankar *et al.*, 2014).

1.4.2 Effect of heavy metal contamination of soil on the plants

Plants experience oxidative stress upon exposure to heavy metals that leads to cellular damage and disturbance of cellular ionic homeostasis (Yadav, 2010). High concentration of heavy metals in the soil affects the growth of plants and may lead to the death of the plant if not controlled. Research found that the growth of cabbage and bean seedling under cadmium concentration of 30 μ mol/L was inhibited, decreasing the root length, the plant height and leaf area (Qin *et al.,* 2008). Cadmium may interfere with crop photosynthesis and protein synthesis, and cause membrane damage (Chao *et al.,* 2014). Heavy metals in urban or agricultural soils may either go into the body directly through ingestion, contact with the skin or absorbed and accumulated by crops. Ingesting heavy metals through the soil – crop system is a major way of damaging human health (Aeliona *et al*., 2008).

1.5 Statement of Problem

Heavy metals are non-biodegradable and can accumulate in the human body system, causing damage to the nervous system and other internal organs. Heavy metals are adsorbed either by initial fast reactions (in seconds, minutes or hours) or by slow adsorption reactions and are, thereafter, redistributed into different chemical forms with varying bioavailability, mobility, and toxicity. It is therefore expected that when several heavy metals exist in the water or wastewater stream, some will be more difficult to be removed than others and a competitive environment will be created. Several studies have been carried out to develop more effective and selective adsorbent materials, which are abundant in nature and require minimal processing in order to reduce cost. Many authors have also investigated the adsorption of metals on different soil minerals under different experimental conditions. However, the application of a standard

reference soil for the simultaneous removal of multi-component heavy metal from water and wastewater systems has not been assessed.

1.6 Justification

In order to arrive at an accurate remedial alternative for heavy metal contaminated water, a thorough knowledge of the chemistry of their dissolution, transport, adsorption and selectivity is necessary. Assessing the adsorption capacity of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} on a standard reference soil will aid in modeling a removal scheme for water contaminated with these heavy metals. This study will as well be useful in designing control strategies for the amendments and fixation of heavy metals in water in order to achieve better groundwater protection. Also, the knowledge derived from the competitive assessment of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} will be significant in the design of remediation methods for polluted farmland soil especially when there is multi-elemental interaction between these metals on the soil.

1.7 Aim and Objectives

The aim of this research was to study the competitive adsorption of Cd, Cu, Cr and Pb ions onto a standard reference soil. This aim was achieved through the following objectives:

(i) optimization of the initial metal ion concentrations, adsorbent dosages and contact times for the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} from aqueous solution onto soil

(ii) modeling the adsorption characteristics of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} using Langmuir and Freundlich adsorption isotherms.

(iii) determination of the appropriate kinetic models that best describe the adsorption process.

(iv) investigation of the competitive adsorption of the selected metal ions in the binary, ternary and quaternary systems.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Mechanism Adsorption of Heavy Metals onto Soil

Heavy metals adsorption is usually described in terms of two basic mechanisms which are; specific adsorption or surface complexation and non-specific adsorption or ion exchange (Mouni *et al*., 2009). The mechanism of a metal ion adsorption describes the process involved in the binding of the metal ion to an adsorbent and it serves as a basis for quantitative stoichiometric considerations. There are two major processes postulated to be active in adsorption (Mouni *et al*., 2009). They include; (i) Chemisorption (ii) Physical Adsorption

Chemisorption is an irreversible process. It is limited to monolayer coverage of the adsorbent. A covalent bond is usually formed between the adsorbate and the adsorbent in chemisorption. On desorption, the adsorbent undergoes a chemical change (Bhatia, 2006). The binding force involved in this sorption is very strong and the heat liberated during the process is very large. The enthalpy of chemisorption is within the region of 200 kJ/mol (Atkins, 2014). The energy required for a chemisorbed molecule to react with the molecular species may be considerably less than the energy required when the two species react directly in the gas phase (Atkins, 2014).

Physical adsorption also known as the non-specific adsorption is as a result of long range weak van der waal's force between adsorbates and adsorbents. The energy released when a particle is physically adsorbed is of the same order of magnitude as the enthalpy of condensation. The enthalpy of physisorption can be measured by monitoring the rise in temperature of a sample of known heat capacity but mostly, typical values are usually in the region of 20 kJ/mol (Atkins,

2014). The adsorption process is exothermic and heat is liberated depending on the magnitude of the attractive force. Physisorption is usually directly proportional to the amount of solid surface available and the adsorption process is reversible (Dash, 2012).

2.1.1 Ion – exchange mechanism of heavy metals in soil

One of the mechanisms described for the adsorption of metal ions on natural soil material involves ion exchange. In most cases, the adsorption of metals on humic substances results in the release of H^+ and possibly with other exchangeable species such as Ca^{2+}, Mg^{2+}, Na^+ and K^+ (Crist *et al.*, 2004). Ion exchange involves electrostatic interactions between an ion on a charged particle surface and ions in a diffused cloud around the charged particle. It is usually rapid, diffusion-controlled, reversible, stoichiometric, and in most cases there is selectivity of one ion over another by the exchanging surface. Stoichiometry in terms of ion-exchange means that any ion that leaves the adsorbent surface is replaced by an equivalent amount of ion with respect to ionic charge (Sparks, 2003). This same principle applies to the displacement of an adsorbed heavy metal by a more preferred metal ion (Crist *et al.*, 2004).

2.2 Factors Influencing Mobility and Adsorption of Heavy Metal ions in Soil

Heavy metal mobility in soil is affected by some factors which include: particle size distribution, pore structure, pH, temperature, organic matter content, competing ions, humic substances and ionic strength of the soil (Naidu *et al*., 2003).

Particle size distribution and resulting total surface area available for adsorption are important factors in adsorption processes and can affect metal mobility (Hines and Scholes, 2003). Particle

size also affects heavy metal content in soils. Small particles with large surface area to mass ratios can adsorb metal ions more than large particles with small surface area to mass ratios (Ackay *et al.,* 2003). Trace metals have potentials for adsorption onto clay minerals, hydrous oxides and organic matter due to their small particle sizes. The amount of extractable metal usually increases with decreasing particle size (Ackay *et al.,* 2003)

Similarly, reports have shown that soil texture and structure in relation to bulk density or solution flux can play a role in the diffusion of metal ions into and out of soil aggregates. The movement of elements through the soil can also with greater accuracy through the knowledge of flow velocities. Soils with greater macro porosity have higher tendency to enhance the mobility and transport of metal ions (Sherene, 2010).

Soil pH plays a major role in the sorption of heavy metals as it directly controls the solubility of metal hydroxides as well as metal carbonates and phosphates (Appel and Ma, 2002). Most metal hydroxides have very low solubility under high pH conditions in natural water. This is as a result of combination of processes which include; production of carbon(IV)oxide, organic acids and nitrification. In most adsorption processes, the solubility of metal hydroxide minerals increases with decreasing pH. This is because the activity of the hydroxide ion is directly related to the pH. Hence, more dissolved metals become potentially available. Soil pH also affects metal hydrolysis, ion-pair formation, organic matter solubility as well as surface charge iron and aluminum oxides, organic matter and clay edges (McBride, 1994). Soil pH can also influence the trace metal forms, concentration levels, mobility, transformation and accumulation processes in the soil environment (Sherene, 2010). Adsorption, which occurs

when dissolved metals are attached to surfaces of particulate matter (notably iron, manganese and aluminum oxide minerals, clay and organic matter), it is also strongly dependent on pH (Bradl, 2004). Sorption capacities of oxide surfaces generally vary from near 0 to near 100 % over a range of 2 pH units. The adsorption edge and the pH range in which the rapid change in sorption capacity occurs vary among metals. Cadmium and zinc have been proven to have adsorption edges at higher pH than iron and copper and consequently they are likely to be more mobile and more widely dispersed (Xue, 2009).

Temperature exerts an important effect on metal speciation because most chemical reactions are highly sensitive to temperature changes (Davidson, 2006). Temperature may also affect quantities of metal uptake by an organism because biological processes typically double with every 100 ^{o}C increment (Fabrega, 2011). Heavy metals binding forms greatly depend on the different stages of redox processes and flooding (Fabrega, 2011).

Organic matter content is important in determining the chemistry of soils. The reducing condition in soil makes most ion-exchange site to be occupied by hydrogen. Therefore, the cation exchange capacity of the soil is high. Soil organic matter is also a key for adsorbing phase for metals. It is important for the retention of metals by soil solids, thus decreasing mobility and bioavailability. However, because of the complexation of metals by soluble organic matter, the addition of organic matter can result in release of metals from solids to the soil solution (Sauve *et al*., 2000).

In the study "Influence of Electrolyte Composition and pH on Cadmium Sorption in Soil" by Boekhold *et al.*, (1993), it was discovered that the amount of metals adsorbed decreases with increasing ionic strength for minerals with permanent surface charge density. According to Sherene (2010), zinc adsorption was found to be more superior for most diluted $CaCl_2$ solution utilized regardless of pH. The study also showed that the reaction took place on the negative surface of the colloids examined and the reduction of ionic strength made the surface electric potential more negative. Hence the rate of adsorption was increased (Sherene, 2010).

Humic substances present in soil are capable of interacting with metal ions to form metal-organic complexes of different stabilities and characteristics. Oxygen functional groups are involved in the formation of surface complexes with aqueous metal species and ion exchange with the displacement of protons. The capacity of humic and fulvic acids to combine with metals is usually attributed to their high contents of substituents such as carboxyl (COOH), hydroxyl (OH), and carbonyl (C=O) (Xiao and Thomas, 2004).

Competing ions can also have a marked effect on ion sorption by soils. Heavy metal adsorption, and availability does not only depend on soil constituents (inorganic and organic), but also on the nature of metals involved, and on their competition for soil sorption sites. Usually, when competitive sorption of metals is compared with their monometal behaviour, it is found that their adsorption is lower in the competitive systems (Harter, 1992).

2.3 Adsorption of Heavy Metals by Different Soils

The concentration of trace and toxic metals in soil solution has been explained by different authors in terms of adsorption, desorption or precipitation and dissolution reactions in soils. The different amount of metals retained by different soil types may be attributed to the different clay content, mineral composition of the soils, pH, organic matter content, soil composition and the medium of reaction in soils (Naidu *et al*., 2003).

Bradl (2004) reported the adsorption of hexavalent Cr onto various soil materials as a function of pH. The adsorption increased with decreasing pH due to the protonation of the hydroxyl groups. This reaction was described as a surface complexation reaction between the Cr(VI) species and the surface hydroxyl sites. Fe oxides also exhibited the strongest affinity for Cr(VI) followed by Al_2O_3, kaolinite and montmorillonite (Bradl, 2004).

Soils with very high acid solution have been reported to fix Mn and Zn less strongly due to high content of mobile Mn than weakly acid soils (Alvarez *et al.*, 2006). In the adsorption of Cu by different soil constituents as a function of pH (Bradl, 2004), Cu–EDTA was found to be most stable in slightly acidic to neutral soils (pH 6.1–7.3), moderately stable in slightly acidic soils, followed by alkaline and calcareous soils but unstable in acidic soils (pH below 5.7). The adsorption of Hg from solution of humus horizon of a leached chernozem and alluvial horizon of an Alphine-forest soil was reported to occur rapidly, and the Hg compounds in the solid and liquid phases reached equilibrium within 30 minutes at pH between 4.75 and 6.5 (Orhue and Frank, 2011).

The concentration of Hg has also been reported to increase with decreasing diameter of soil particles and the accumulation of Hg in clay and fine-silt fractions was shown to be caused by the stable fixation of the main components of these fractions (Sherene, 2010). In a volcanic and an alluvial soil from Japan studied in the laboratory, it was observed that Cu, Pb, and Ni were the most mobile metals (Orhue and Frank, 2011).

In the study of the removal of organic matter and Fe-oxides from soils (Noppadol and Pongsakorn, 2014), the component of soil was found to influence the retention of clay more effectively onto the organic matter than on Fe-oxides and the consistently greater Cd uptake by soil surface over subsurface was discovered to be due to the differences in the soil organic matter content, but there was no evidence of any strong correlation between Cd uptake and soil cation exchange capacity (Noppadol and Pongsakorn, 2014). Cadmium was discovered to be more readily adsorbed by a positively charged Dothan soil when complexed with EDTA and it was suggested that strong chelation may not necessarily reduce substantial metal adsorption (Domen *et al*., 2008).

Zhu and Alva (1993) found that the adsorption of Fe and Mn increased with increasing clay content of soil and that the rate of adsorption was higher in poorly drained soils than well drained soils. Highly weathered tropical soils have shown to exhibit relatively low affinities for heavy metals as a result of low negative charge densities at common pH values of 4 to 5 (McBride, 1994). Nevertheless, the persistence and mobility of Cd and Pb in some soils are dictated by the extent to which the metals sorb to solid phase which is a function of reactions affecting surface

charge (that is pH and ionic strength) (Naidu *et al.*, 2003). Reports have also shown that Pb sorption was greater than Cd sorption in the same soil sample at an initial metal concentration of > 0.1 mM while other soil sample adsorbed roughly equal amounts of Cd and Pb due in part to their mineralogical properties, as well as higher pH and greater amounts of sorption sites when compared with highly weathered tropical soils (Appel and Ma, 2002).

2.4 Competitive Adsorption of Metal Ions in Soils

It is generally accepted that cations compete with each other for same adsorption site. However, contradictory results have been presented with respect to the importance of competition between cations. Many authors have also noted significant effects of competition on the adsorption of heavy metal ions onto soil while some others found out that there was little effect or even rejected any effect (Jenne, 1998).

Adsorption of heavy metals in soil may result in the release of proton or other metal cations. For instance, according to Doner *et al.*, (1982) the addition of Ni, Cu, and Cd helped in the release of Mn in the soil and the proton release with Ni and Cu sorption accounted for most of the Mn release. More strongly sorbed metals, such as Pb and Cu, could be less affected by competition than mobile metals, such as Cd and Zn as suggested by Zhu and Alva (1993). Also, the presence of Pb can significantly reduce the maximum adsorption of Cd onto soil. There is also a positive correlation existing between Mn and Ni; Ni and Cu; Ni and Fe; Pb and Cu; Pb and Fe; Pb and Mn in soils (Sherene, 2010).

The presence and competitive effect of Cr (III) in a multiple ion mix can greatly reduce the amount of Pb^{2+} adsorbed thereby drastically increasing the mobility and potential for transport to ground water. Similarly, a decrease in Pb adsorption may be related to the abundance of Ca^{2+} ions as well as other cations available in the solution according to Sherene (2010).

In competitive systems, trace elements compete with Ca and Mg for available exchange sites and are retained at higher concentration when in lower pH medium and at lower concentrations in higher pH system (Brady and Weil, 2002). The first solute to arrive the bare soil surface is preferentially adsorbed on the most attractive sites or on positions where their potential energy will be at a minimum. As adsorption proceeds, the less active of the sites become occupied. Therefore, adsorption occurs on sites of progressively decreasing activity (Barrow *et al.*, 1989). By principle, the occupation of adsorption sites proceeds until all available positions are taken. In order for any additional solutes to be adsorbed on the solid surface, some ions may have to be released back into aqueous solution. The displacement of an adsorbed metal can also be associated with the strength of complexation. Metal ions that go into inner-sphere complexes are more stable. A large amount of energy is needed to surpass that of the bonds formed, so it is not easy to dissociate the metal from its complexing ligand. Metals that form outer-sphere complexes but readily exchangeable are expected to be more easily displaced from the adsorbent surface (Sposito, 2008). The formation of chelate structures is also a factor, as it gives added stability to metal adsorption. Thus, the fraction of metals that are adsorbed mainly through electrostatic physical interaction and ion-exchange mechanisms are the ones that are relatively easier to displace from the soil surface.

2.4.1 Adsorption selectivity sequences of heavy metals in soils

Many authors proposed that selectivity sequences should theoretically depend on the characteristics of the metal ions, and it has been assumed that the tendency of the metals to form covalent bonds is related to their ionic radii and ionization potentials and proposed a selective sequence of Pb > Cd > Cu > Co > Ni > Zn (Sposito, 2008). According to McBride (1994), the electronegativity should be the determining factor of chemisorption. Based on this, he proposed the selectivity sequence: Cu > Ni > Co > Pb > Cd > Zn > Mg > Sr. This same author indicated that if chemisorption of metals depends only on the electrostatic force of attraction, the strongest bond would be formed by the metal with the highest charge-to-radius ratio, giving rise to the sequence: Ni > Mg > Cu > Co > Zn > Cd > Sr > Pb. It has been shown that specific adsorption increased when hydrolysis constant (pK) values decreased (Cu = Pb < Zn < Ni < Cr < Cd). The pK values of the reaction $M^{n+} + H_2O \rightarrow (MOH)^{+(n-1)} + H^+$ determine the adsorption behaviour of different metals (Emma *et al*., 2004). In the case of similar values of pK, as occurs with hydrolysis of Pb^{2+} and Cu^{2+}, Pb^{2+} is more strongly adsorbed, because it has the larger ionic radius.

In the study "The Selectivity Sequence and Competitive Adsorption of Heavy Metals by Soils" (Gomes *et al*., 2001, it was reported that the Misono softness parameter of the studied heavy-metals influenced their selectivity sequences in the competitive adsorption systems. The Misono softness parameter according to Sposito, (2008) was defined as the ability of a metal to form strong complexes by covalent bonding.

2.5 Standard Reference Soil

The NIST SRM 2709a San Joaquin soil is a suitable standard reference soil for direct use as a sorbent for determining the bias of procedure ASTM C1733. The as-received dried soil can be used in testing without further preparation (washing or sizing). This soil has been certified by the National Institute of Standards and Technology (NIST) and it has been made available and accessible for research. The composition of the soil is well- known and its physical characteristics acceptably uniform (Mackey, 2010).

Beginning in 1992, the National Institute of Standards and Technology (NIST) provided three soil types known as "Standard Reference Materials (SRM) intended for use in method development, method validation, and routine quality assurance in the analysis of element content of soils. The three materials include; SRM 2709 San Joaquin Soil, SRM 2710 Montana Soil I, and SRM 2711 Montana Soil II which represented a baseline agricultural soil, a highly contaminated soil, and a moderately contaminated soil respectively. They were developed to provide representative agricultural soils with certified mass fraction values for the elements of interest. (McElhiney, 1992). The original SRM soils were each provided with certified and information values for approximately 50 elements. These three SRMs were also analyzed by several collaborating laboratories to determine the acid-extractable element content based on U.S. Environmental Protection Agency (USEPA) Methods. These values expressed both as mass fraction values and as percent recoveries (calculated based on comparison with NIST certified values) were included as addenda to the Certificates of Analysis for each SRM (Mackey, 2010).

2.6 Applications of Adsorption of Metal Ions from Solution

Adsorption from solution is an important process in natural systems, and has also been exploited for use in analytical chemistry and engineering processes. It finds applications in electro-analytical chemistry, ion-exchange, froth flotation, coagulation and collection of trace contaminants. Adsorption reactions are common processes in waste water treatment and in the transport of chemical species in the aquatic environment. Isotherm adsorption models are useful in waste stream treatment to predict the ability of an adsorbent to remove a pollutant down to a specific discharge value (Veglio and Beolchini, 1997).

2.7 Principle of Atomic Absorption Spectrophotometry (AAS)

Flame atomic absorption spectrometry (FAAS) was first proposed and developed by Walsh in 1955. Atomic absorption spectra are formed by the absorption of radiation of certain wavelengths by atoms whose electrons are in the ground state. On absorbing this energy, the atoms become excited. The extent of absorption is dependent on the number of atoms in the ground state in the path of radiation beam at any one time and can thus be used as quantitative method of determining this number (Elwell, 2013). In practice, air is blown through a venturi, and the sample solution is drawn into the throat of the venturi and into the air stream as a spray of fine droplets. A large fraction (~ 90%) of the drops falls out of the air stream in the cloud chamber but the very small ones remain suspended. In the flame the sample vaporizes and forms a cloud of atoms in the gaseous state. Radiation of a characteristic wavelength corresponding to the radiation (energy) required to raise the atoms of the particular element being analysed from their ground state to an excited state from a hollow cathode discharge lamp is passed through the flame. The decrease in intensity is measured, using a monochromator and detector system

(Elwell, 2013). This decrease is related to the concentration of the element in the sample solution. The number of atoms capable of absorbing any transmitted light of appropriate wavelength is proportional to the product of the concentration of these atoms in the flame and the length of the light path through the flame.

Atomic absorption follows Beer's law namely:

log I/lo = **abc**

I is the intensity of the light before passing through the flame while Io represents the intensity of the light after passing through the flame. a is the absorption coefficient, b is the path length of the flame and c is the concentration (Volesky and Holan, 1995).

2.8 Adsorption Isotherm

Adsorption isotherms are important criteria in optimizing the use of adsorbents materials because they describe the nature of the interaction between sorbate and adsorbent. Thus, analysis of experimentally obtained equilibrium data by either theoretical or empirical equations is useful for practical design and operation of adsorption systems. Adsorption is usually described through isotherms, that is, functions which connect the amount of adsorbate on the adsorbent. Distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as Langmuir and Freundlich.

2.8.1 Langmuir adsorption model

The Langmuir isotherm is often used to estimate the maximum adsorption capacity corresponding to complete monolayer coverage on the adsorbent surface and it is expressed by the equation 2.1 below;

$$\frac{Ce}{q_e} = \frac{Ce}{q_{max}} + \frac{1}{b\, q_{max}} \quad (2.1)$$

Where q_e (mg/g) is the amount of adsorbate adsorbed per gramme of adsorbent at equilibrium. q_{max} (mg/g) is a constant relating to the ultimate monolayer adsorption capacity which is the maximum amount of adsorbate ion bound to the adsorbent, b is Langmuir constant, adsorption coefficient or the adsorption affinity for binding adsorbate on the adsorbent sites and C_e (mg/dm^3) is the equilibrium (residual) adsorbate concentration in solution after adsorption (Gupta and Rastogi, 2007). The values of q_{max} and b can be obtained from the intercept $\left(\frac{1}{bq_{max}}\right)$ and slope $\left(\frac{Ce}{q_{max}}\right)$ respectively when $\frac{Ce}{q_e}$ is plotted against Ce (Ademiluyi and Ujile, 2013).

2.8.2 Freundlich adsorption model

The Freundlich isotherm assumes a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Thus the Freundlich model describes the adsorption on an energetically heterogeneous surface on which the adsorbed molecules are interactive. The linearized form of the freundlich equation is expressed by equation 2.2 below;

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2.2)$$

Where $\log q_e$ is the amount of adsorbate adsorbed per unit weight of adsorbent, K_f is Freundlich constant measuring adsorption capacity, C_e is the equilibrium concentration of the adsorbate in solution, n is a constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent. Also, the value of $\frac{1}{n}$ indicates the affinity of the adsorbate towards the adsorbent (Raghavaro *et al*., 2009). The experimental data is usually fitted into the equation (2.2) by plotting $\log q_e$ against $\log C_e$; and the values of $\frac{1}{n}$ and $\log K_f$ could be determined from the slopes and intercepts of the plots respectively.

2.9 Adsorption Kinetics

Equilibrium analysis is fundamental in order to evaluate the affinity or capacity of an adsorbent. Kinetic models are useful in assessing how adsorption rates vary with aqueous free metal concentrations, and how rates are affected by adsorption capacity or by the sorbent character in terms of their kinetics. Adsorption kinetics may be controlled by several independent processes such as transport from the bulk to the surface and chemical binding reactions of the adsorbate (Gupta and Rastogi, 2007).

2.9.1 Pseudo - first order model

The pseudo-first order equation is usually expressed by the equation 2.3 given below (McKay and Ho, 1999);

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \qquad (2.3)$$

Where q_e and q_t are the amount of adsorbate adsorbed on an adsorbent at equilibrium (mg/g) and time t respectively, k_1 is the rate constant of pseudo-first order adsorption. The plot of log ($q_e - q_t$) versus t would give a straight line and the values of k_1 and q_e (calculated) can be obtained from the slope and intercept of the graph respectively (Gupta and Rastogi, 2007).

2.9.2 Pseudo - second order model

The pseudo-second order kinetic model is expressed as

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (2.4)$$

Where k_2 is the pseudo-second order rate constant of adsorption. The plot "$\frac{t}{q_t}$ versus t" would give a linear relationship with $\frac{1}{q_e}$ and $\frac{1}{k_2\, q_e^2}$ as slope and intercept respectively. The values of q_e and k_2 can be determined from the slope and intercept (Gupta and Rastogi, 2007).

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Apparatus and Equipment

Volumetric flasks (1000 cm^3), measuring cylinders (50 cm^3 and 10 cm^3), conical flasks (250 cm^3), polypropylene sample bottles (120 cm^3), beakers (250 cm^3), petri-dish, watch glass, refrigerator, wash bottles, funnels, glass rod, Whatman No1 filter papers, Analytical balance (A and D instrument GR-200EC model), mechanical shaker (Gallenkamp BKS-300-010F model), pH meter (Jenway), deionizer (Elgacan C115 model) and atomic adsorption spectrophotometer (AA240FS Varian).

3.1.1 Reagents

All reagents used were of analytical grade and they include: Cadmium nitrate tetrahydrate ($Cd(NO_3)_2.4H_2O$), potassium chromate($K_2Cr_2O_4$), copper nitrate trihydrate ($Cu(NO_3)_2.3H_2O$), lead nitrate($Pb(NO_3)_2$), tetraoxosulphate (VI) acid (H_2SO_4), sodium hydroxide (NaOH) and deionised water.

3.2 Collection of Soil Sample

The Soil standard reference materials (NIST SRM 2709a) were obtained from the Soil Laboratory of the Federal Ministry of Agriculture, Kaduna, Nigeria.

3.2.1 Preparation of soil sample

The Standard reference soil has been well-characterized, its physical characteristics are acceptably uniform and can be used in experiments without further preparation (washing or

sizing). The collected soil samples were passed through a 500-mm sieve to obtain a suitable particle size for analysis (Barbagelata andMallanno, 2013).

3.3 Determination of Soil pH

The pH meter was calibrated using pH 7 buffer solution. 5 g of soil sample was weighed and transferred into 50 cm^3 beaker, 20 cm^3 distilled water was added and stirred well with a glass rod. This was allowed to stand for 30 minutes. The electrode was immersed and pH value was determined from the automatic display on the pH meter (Kalra, 1995).

3.4 Preparation of Stock Solutions

3.4.1 Cadmium solution

The solution was prepared by dissolving 2.744 g $Cd(NO_3)_2.4H_2O$ in distilled water and the solution was made up to 1000 cm^3 in a volumetric flask to obtain 1000 mg/dm^3 cadmium solution (APHA, 1995).

3.4.2 Copper solution

This was prepared by dissolving 3.803 g of $Cu(NO_3)_2.3H_2O$ in distilled water and the solution was made up to 1000 cm^3 in a volumetric flask to obtain 1000 mg/dm^3 copper solution (APHA, 1995).

3.4.3 Lead solution

This was prepared by dissolving 1.599 g $Pb(NO_3)_2$ in distilled water and made up to 1000 cm^3 in a volumetric flask to obtain 1000 mg/dm^3 lead solution (APHA, 1995).

3.4.4 Chromium solution

Chromium stock solution was prepared by dissolving 2.862 g $K_2Cr_2O_4$ in distilled water and made up to 1000 cm^3 in a volumetric flask to obtain 1000 mg/dm^3chromium solution.

3.4.5 Preparation of binary solutions

Six different stock solutions of 1000 mg/dm^3binary systems (Cd-Cr, Cd-Pb, Cr-Cu, Cr-Pb, Cu-Pb and Cd-Cu) were prepared by dissolving varying amounts (2.744 g, 3.803 g, 2.862 g, 1.599 g) of $Cd(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$, $K_2Cr_2O_4$ and $Pb(NO_3)_2$ in distilled water and made up to 1000 cm^3 in a volumetric flask (Futalan *et al*., 2012).

3.4.6 Preparation of ternary solutions

Three different stock solutions of 1000 mg/dm^3ternary systems (Cr-Cu-Pb, Cd-Cr-Pb and Cd-Cr-Cu) were prepared by dissolving varying amount (2.744 g, 3.803 g, 2.862 g and 1.599 g) of $Cd(NO_3)_2.4H_2O$, $Cu(NO_3)_2.3H_2O$, $K_2Cr_2O_4$ and $Pb(NO_3)_2$ in distilled water and made up to 1000 cm^3 in a volumetric flask (Futalan *et al*., 2012).

3.4.7 Preparation of quaternary solutions

The stock solution of 1000 mg/dm^3 quaternary system (Cd-Cr-Cu-Pb) was prepared by dissolving 2.744 g $Cd(NO_3)_2.4H_2O$, 3.803 g $Cu(NO_3)_2.3H_2O$, 2.862 g $K_2Cr_2O_4$ and 1.599 g $Pb(NO_3)_2$) in distilled water and made up to 1000 cm^3 in a volumetric flask (Futalan *et al*., 2012).

3.5 Standard Working Solution of Metal Ions

The working solutions concentration of 10 mg/dm^3, 20 mg/dm^3, 30 mg/dm^3 and 40 mg/dm^3 were prepared from the 1000 mg/dm^3 stock solution by serial dilution (Jimoh *et al.*, 2012).

$$\text{Vssr} = \frac{\text{Csws} \times \text{Vsws}}{\text{Css}}$$

Where Vssr represents the volume of stock solution required in cm^3, Csws is the concentration of the standard working solution in mg/dm^3, Vsws is the volume of the standard working solution in cm^3 (the volume used was 100 cm^3) and Css is the concentration of the stock solution (1000 mg/dm^3).

3.6 Adsorption Experiments

Optimization of the adsorption of the selected metal ions (Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}) was carried out in a batch of experiment. Exactly 50 cm^3 of the working solution was transferred into a series of 250 cm^3 Erlenmeyer flask and 0.5 g, 1.0 g, 1.5 g and 2.0 varying dosages of the soil sample was added to each solution containing a particular metal ion. The solutions were placed on a shaker maintained at room temperature for 1 hr, 2 hrs, and 3 hrs varying amount of contact time. Aliquots were retrieved and filtered through membrane filters and then analysed for the residual concentration of their respective metal ions. The filtrates were analyzed for the heavy metal ion concentrations using the conventional method of atomic absorption spectrophotometer (AAS). The amount of the metal adsorbed was calculated using the equation below:

$$\text{Qe} = \frac{(\text{Co}-\text{Ce})\text{V}}{\text{M}} \qquad (3.1)$$

The % of metal ion removal from aqueous solution at a given time was determined by the following equation;

$$(\%) \text{ of metal ion adsorbed} = \frac{(Co - Ce)}{Co} \times 100 \quad (3.2)$$

Where Q_e = the amount of metal ion adsorbed in milligram per gram (mg/g) of the adsorbent

V = volume of the metal ion solution in the batch flask

C_o = the initial concentration of the metal ion before adsorption process

C_e = the equilibrium concentration of the metal ion in the filtrate after adsorption

M = mass of adsorbent in grammess (Odoemelam *et al.*, 2015).

3.6.1 Effects of initial concentrations on the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

The effects of initial metal ion concentrations of each metal ion were studied by varying the metal ion concentrations used for the adsorption. The metal ion concentrations used were 10 mg/dm^3, 20 mg/dm^3, 30 mg/dm^3 and 40 mg/dm^3. The experiment was carried out by adding a known metal ion concentration to 250 cm^3 Erlenmeyer flask containing 1.5 g adsorbent dose. The flask was agitated for 1 hr at room temperature. The mixture was then filtered through a Whatman no. l filter paper into a 120 cm^3 polyethylene bottle. The concentration of the residual metal ions remaining in the filtrate was determined by using AAS (Odoemelam *et al.*, 2015).

3.6.2 Effects of adsorbent dose on the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

The effects of adsorbent dose on the adsorption of each metal ion were studied by varying the adsorbent doses used for adsorption. The dosages of interest in grammes used were 0.5, 1.0, 1.5 and 2.0 respectively. The experiment was carried out by adding a known adsorbent dose to a 250 cm^3 Erlenmeyer flask containing 50 cm^3 of 20 mg/dm^3 initial metal ion concentration. The flask was agitated for 1 hr at room temperature. The mixture was then filtered through a

Whatman no. l filter paper into a polyethylene bottle. The concentration of the residual metal ions remaining in the filtrate was determined using AAS (Odoemelam *et al.*, 2015).

3.6.3 Effects of contact time on the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

The effects of contact time on the adsorption of each metal ion were studied by varying the contact time used for the adsorption. The contact time of interest in hrs used was 1, 2 and 3. The experiment was carried out by adding 50 cm^3 of 20 mg/dm^3 initial metal ion concentration to 250 cm^3 Erlenmeyer flask containing 1.0 `g adsorbent dose. The flask was agitated for 1 hr, 2 hrs and 3 hrs at room temperature. The mixture was then filtered through a Whatman no. l filter paper into a 120 cm^3 polyethylene bottle. The concentration of the residual metal ions remaining in the filtrate was determined using AAS (Odoemelam *et al.*, 2015).

3.7 Modeling Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

Equilibrium adsorption experiment was carried out to evaluate the adsorption capacity of the adsorbent. The batch equilibrium for the adsorption was performed in a set of 250 cm^3 Erlenmeyer flask. About 50 cm^3 solution of each metal ion with varying initial metal ion concentration of 10, 20, 30 and 40 mg/dm^3 were placed in these flasks. Equal mass (1.5 g) of the soil sample was added to each metal solution. The resulting solution was then placed on a shaker for 1 hr at room temperature. Thereafter, the different supernatants were filtered and the concentration remaining in the filtrates were determined using the atomic absorption spectrophotometer. The rates of adsorption of the various samples were determined from the uptake level of the selected heavy metals in their aqueous solution. The adsorption process was described using Langmuir and Freundlich models (Ademiluyi and Ujile, 2013).

3.8 Adsorption Kinetics of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

Kinetics studies were carried out at a fixed initial metal ion concentration of 20 mg/dm^3. The batch equilibrium for the adsorption was performed in a set of 250 cm^3 Erlenmeyer flasks. About 50 cm^3 solution of each metal ion were measured into these flasks. Equal mass (1.0 g) of the soil sample was added to each metal solution. The resulting solution was then placed on a shaker at room temperature, varying the contact times for 1 hr, 2 hrs and 3 hrs. Thereafter, the different supernatants were filtered and the concentrations remaining in the filtrates were determined using the atomic absorption spectrophotometer. The rates of adsorption of the various samples were determined from the uptake levels of the selected heavy metals in their aqueous solutions (Ademiluyi and Ujile, 2013).

3.9 Competitive Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

The competitive adsorption of the selected metal ions was investigated in a group of experiments at fixed parameters which are: initial metal ion concentration of 20 mg/dm^3, 1.0 g dose of soil sample, 2 hrs contact time and pH 5.5. In this group of experiments, the amount of metal uptake by the soil for each metal was examined in the binary, ternary and quaternary systems (Selim and Zhang, 2013).

3.9.1 Adsorption studies on the binary systems

Six different combinations (Cd-Cr, Cd-Pb, Cr-Cu, Cr-Pb, Cu-Pb and Cd-Cu) of binary systems involving the four metals were subjected to batch equilibration. Each combination in the binary system involved two metal ions considered at a time to compete for the adsorption sites. 50 cm^3 of each of the equilibrating solution in all the binary systems was added to 1 g of soil in a set of

Erlenmeyer flasks (250 cm^3). These were shaken at room temperature for 2 hrs and the resulting supernatants were filtered. The concentrations remaining in the filtrates were determined using the atomic absorption spectrophotometer. The respective metal adsorbed was calculated as the difference between the initial amount of metal ion in the solution before equilibrium and the amount of metal ion remaining in solution after equilibrium (Selim and Zhang, 2013).

3.9.2 Adsorption studies on the ternary systems

Three different combinations (Cr-Cu-Pb, Cd-Cr-Pb and Cd-Cr-Cu) of ternary systems involving the four metals were subjected to batch equilibration. Each combination in the ternary system involved three metal ions considered at a time to compete for the adsorption sites. 50 cm^3 of the equilibrating solution containing each ration in all the ternary systems was added to 1 g of soil in a set of Erlenmeyer flasks (250 cm^3). These were shaken at room temperature for 2 hrs and the resulting supernatants were filtered. The concentrations remaining in the filtrates were determined using the atomic absorption spectrophotometer. The respective metal adsorbed was calculated as the difference between that in the solution initially and that remaining after equilibrium (Selim and Zhang, 2013).

3.9.3 Adsorption studies on the quaternary system

The quaternary system involved the combination of four metal ions (Cd-Cr-Cu-Pb) considered at a time to compete for the adsorption sites. The system was subjected to batch equilibration. 50 cm^3 of the equilibrating solution was added to 1 g of soil in a set of Erlenmeyer flask (250 cm^3). This was shaken at room temperature for 2 h and the resulting supernatant was filtered. The concentration remaining in the filtrate was determined using the atomic absorption

spectrophotometer. The respective metal adsorbed was calculated as the difference between that in the solution initially and that remaining after equilibrium (Selim and Zhang, 2013).

3.10 Statistical Analysis

Statistical analyses were performed using the statistical functions of Microsoft Excel version Office XP. Mean values of the metals in each of the systems were compared using the two-way ANOVA with replicate at 95 % confident limit, α is 0.05.

Null hypothesis (Ho); the mean of adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} among the systems are not equal i.e μ_{single} system $\neq \mu_{binary}$ systems $\neq \mu_{ternary\ systems} \neq \mu_{quaternary}$ systems.

Alternative hypothesis (Ho); the mean of adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} among the systems are equal i.e $\mu_{single\ system} = \mu_{binary}$ systems $= \mu_{ternary}$ systems$= \mu_{quaternary}$ systems.

CHAPTER FOUR

4.0 RESULTS

4.1 Scanning Electron Microscope (SEM) Analysis

The SEM micrographs for the standard reference soil before and after analysis are shown in Figures 4.1 and 4.2 below. The Scanning Electron Micrograph shown in Figures 4.1 and 4.2 clearly reveals the surface texture of the soil before and after adsorption at 1000x magnifications. It was observed that the surface of the soil sample before adsorption was rough, fused together alongside with large particles, but after adsorption, it is evident from the Figure 4.2 displayed that the surface morphology of the soil had undergone remarkable physical disintegration due to adsorption of metal ions.

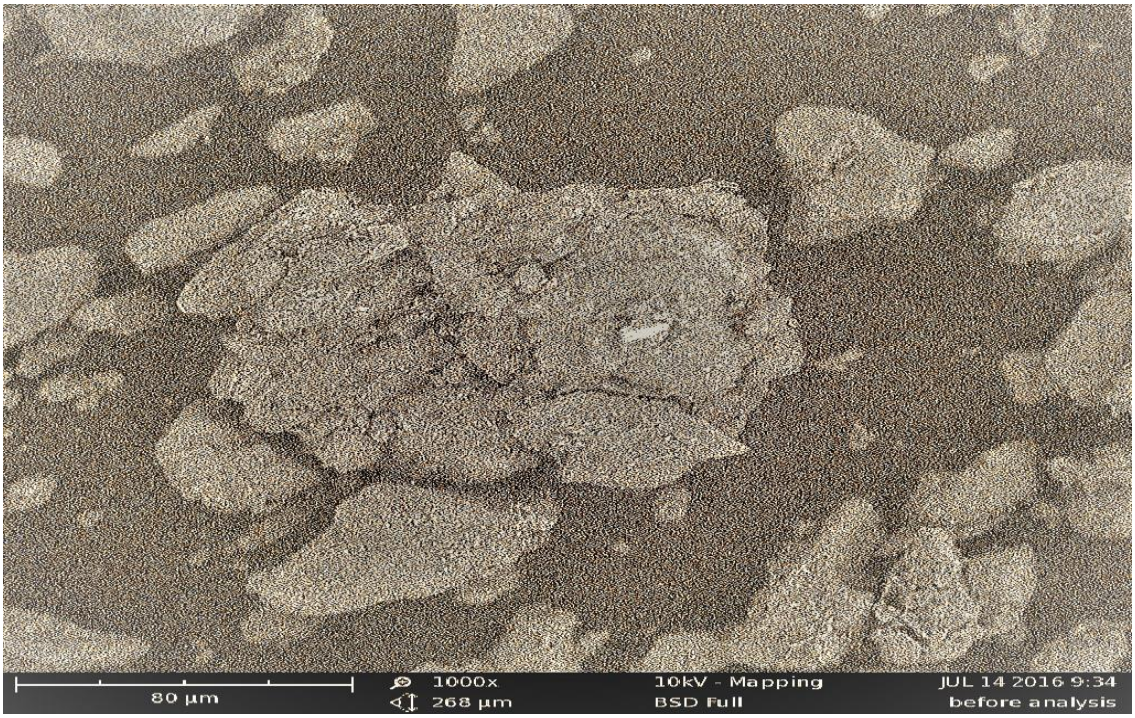

Figure 4.1: SEM Micrograph of Soil Before Adsorption

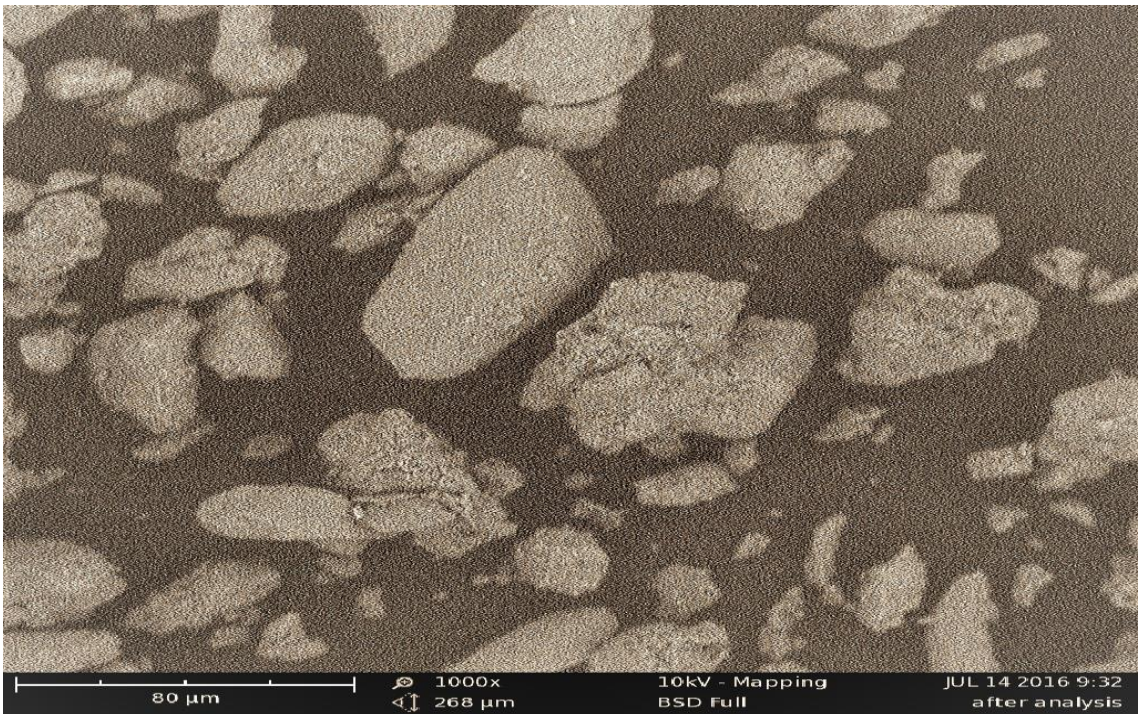

Figure 4.2: SEM Micrograph of Soil After Adsorption

4.2 Adsorption of Selected Metal Ions

4.2.1 Effects of Initial Metal Ions Concentrations on Adsorption of Selected Metal Ions

The effect of initial metal ion concentration on the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} in the single system is presented in Figure 4.3 below. The highest percentage (%) adsorption for Cd^{2+}, Cr^{6+} and Cu^{2+} obtained at 20 mg/dm^3 were: 97.78, 38.29 and 98.78; while their approximate values for the amount of metal uptake (q_e) in mg/g were: 0.65, 0.26 and 0.66 respectively. Pb^{2+} on the other hand had its highest percentage adsorption (97.11 %) at 40 mg/dm^3 with the amount of metal uptake as approximately 1.30 mg/g.

4.2.2 Effects of adsorbent dose on the adsorption of Selected Metal Ions

The effects of adsorbent doses on the adsorption Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} is presented in Figure 4.4. The highest percentage (%) adsorption for Cr^{6+}, Cu^{2+} and Pb^{2+} obtained at 1.0 g were: 40.90, 99.57 and 97.07; while their approximate values for the amount of metal uptake (q_e) in mg/g were: 0.41, 1.00 and 0.97 respectively. Cd^{2+} on the other hand, had its highest percentage adsorption (99.22 %) at 1.5 g with the amount of metal uptake as approximately 0.66 mg/g.

4.2.3 Effects of contact time on the adsorption of Selected Metal Ions

The relationship between percentage adsorption and contact time was plotted and presented in Figure 4.5. The highest percentage (%) adsorption for Cr^{6+}, Cu^{2+} and Pb^{2+} obtained at 2 hrs were: 56.71, 98.95 and 94.94; while their approximate values for the amount of metal uptake (q_e) in mg/g were: 0.0.57, 0.99 and 0.95 respectively. Cd^{2+} on the other hand, had its highest percentage adsorption (98.43 %) at 3 hrs with the amount of metal uptake as approximately 0.98 mg/g.

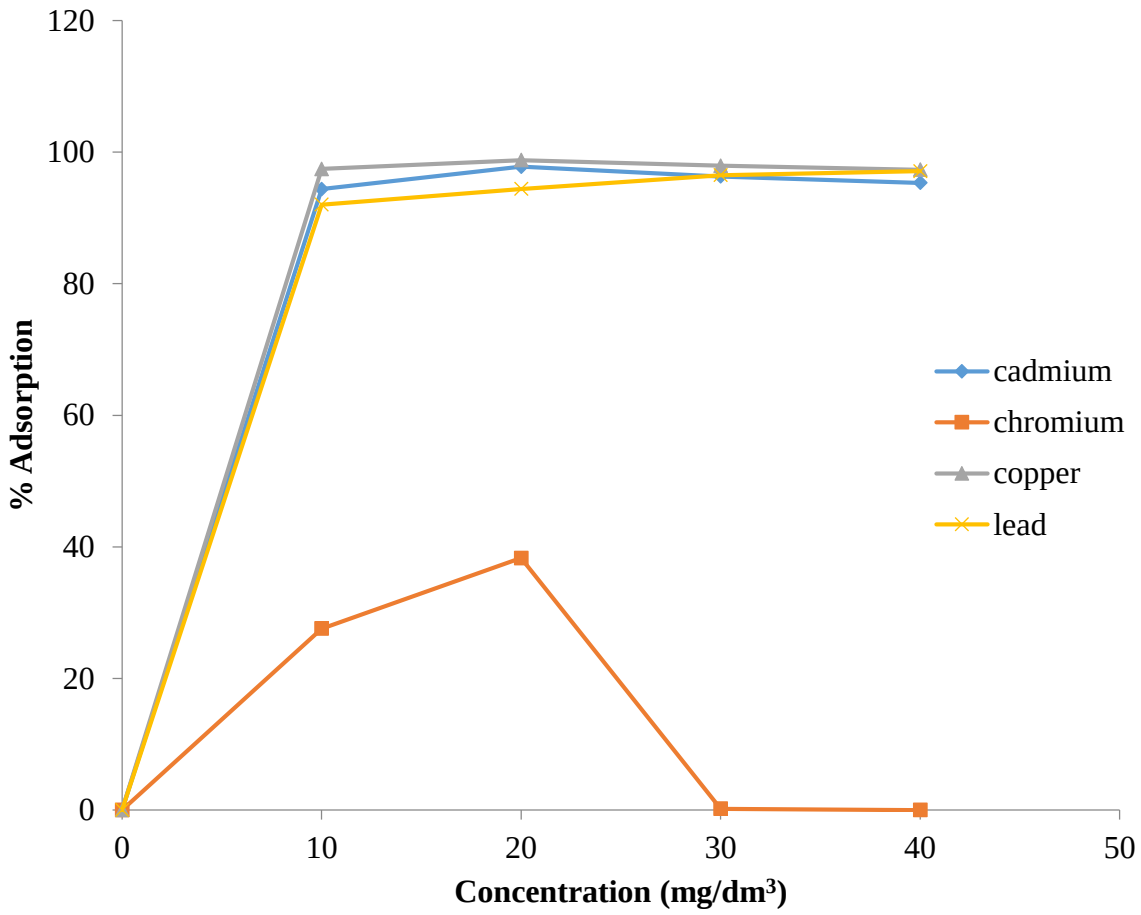

Figure 4.3: Effects of Initial Metal Ion Concentrations on the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and pb^{2+}.

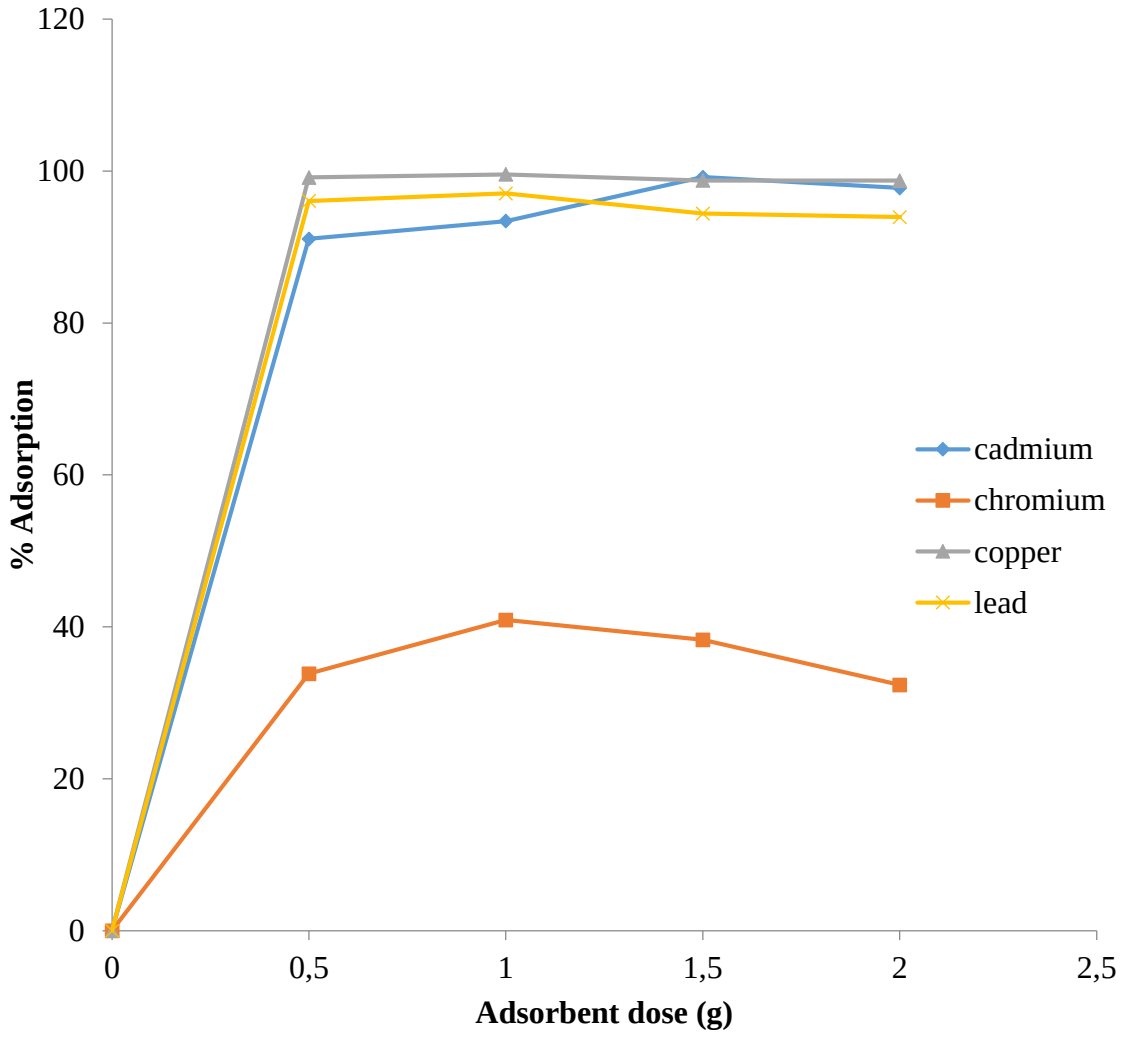

Figure 4.4: Effects of Adsorbent Doses on Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}.

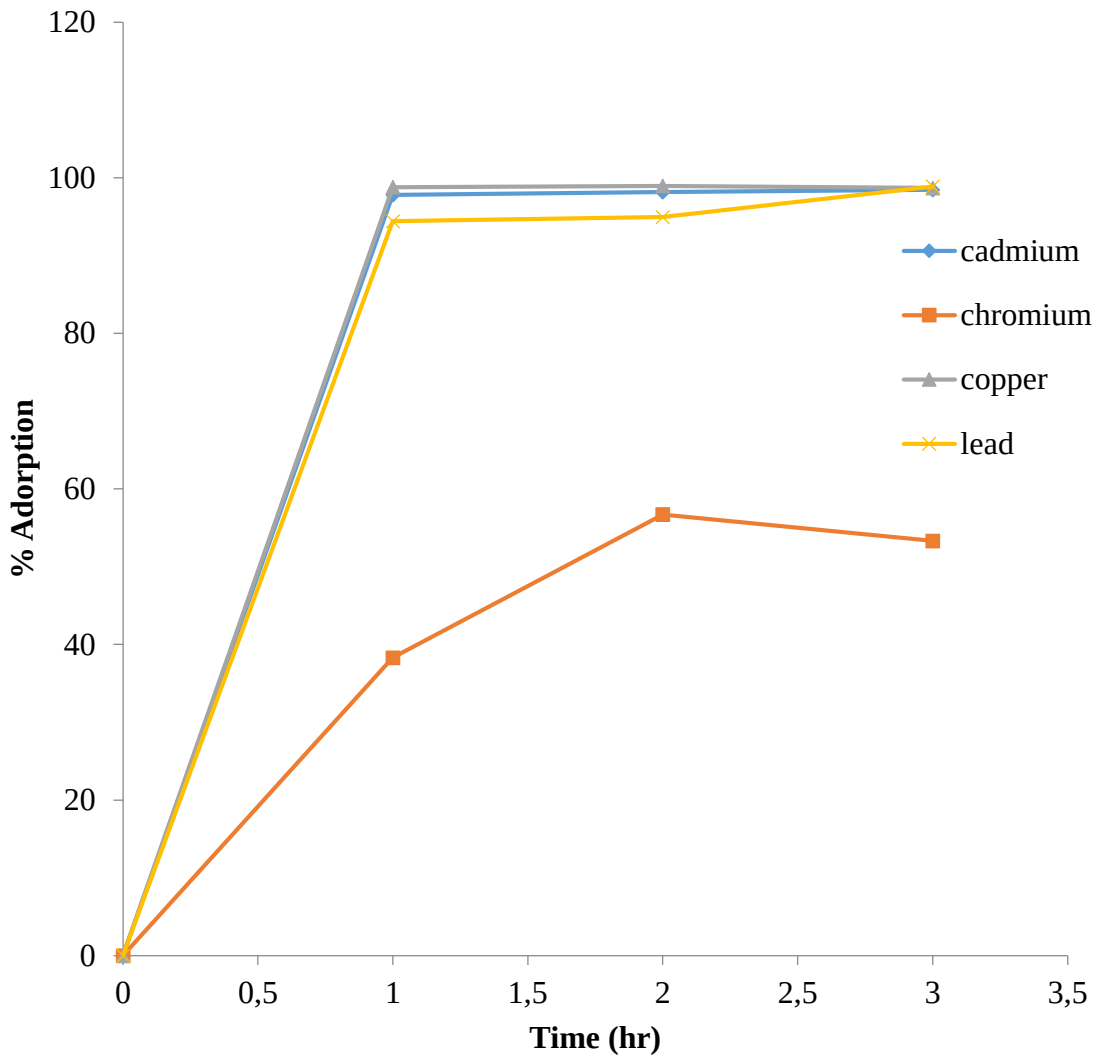

Figure: 4.5: Effect of Contact time on the Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

4.3 Adsorption Modeling

The extent of adsorption of selected metal ions was determined using Langmuir and Freundlich Isotherms Models as shown in Figures 4.6 to 4.13 respectively. Table 4.4 presents the Langmuir and Freundlich isotherm parameters for the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} at room temperature. The plots C_e/q_e against C_e on Figures 4.6 to 4.9 describes the Langmuir isotherm; showing the relationship between the amount of metal uptake by the soil and the metal ion concentrations. This corresponds to complete monolayer adsorption on the soil surface. The data obtained from these plots were used to estimate the maximum adsorption capacity of each of the metal ion. Also, Figures 4.10 to 4.13 are Freundlich plots (log q_e against log C_e) which show the relationship between the amount of metal uptake by the soil and the metal ion concentrations. Thus, describing the adsorption of the metal ions on an energetically heterogeneous surface. The metal ion concentration of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} for both isotherms ranges from 10 to 40 mg/dm^3. According to the graphs in Figures 4.6 to 4.13, the R^2 represents the correlation coefficient value of the metal ion. The equation y= mx + c is equivalent to $\frac{Ce}{q_e} = \frac{Ce}{q_{max}} + \frac{1}{b\, q_{max}}$ and $\log q_e = \log K_F + \frac{1}{n}\log C_e$ for the langmuir and freundlich plots respectively.

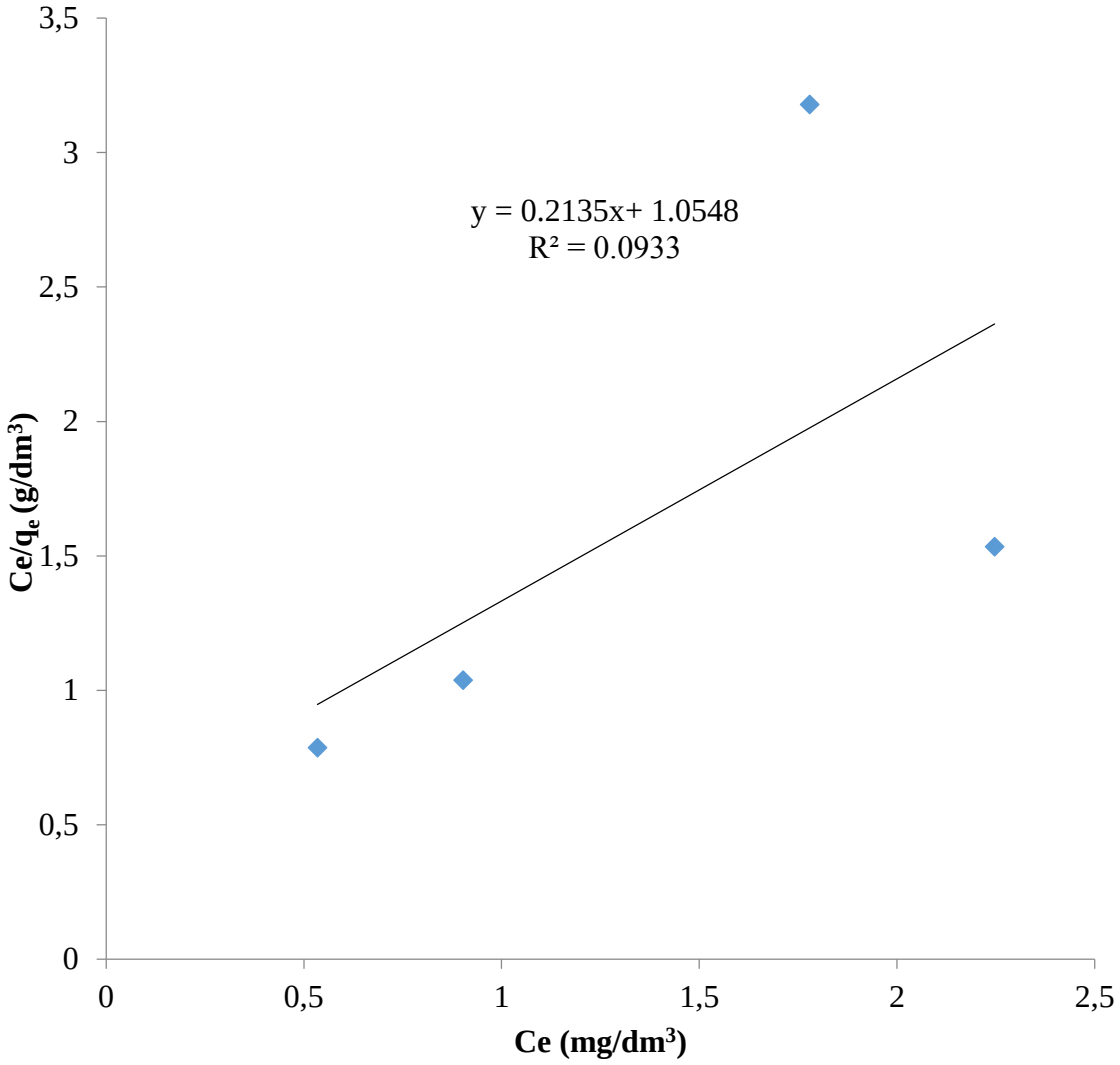

Figure 4.6: Langmuir Adsorption Isotherm for Cd^{2+}

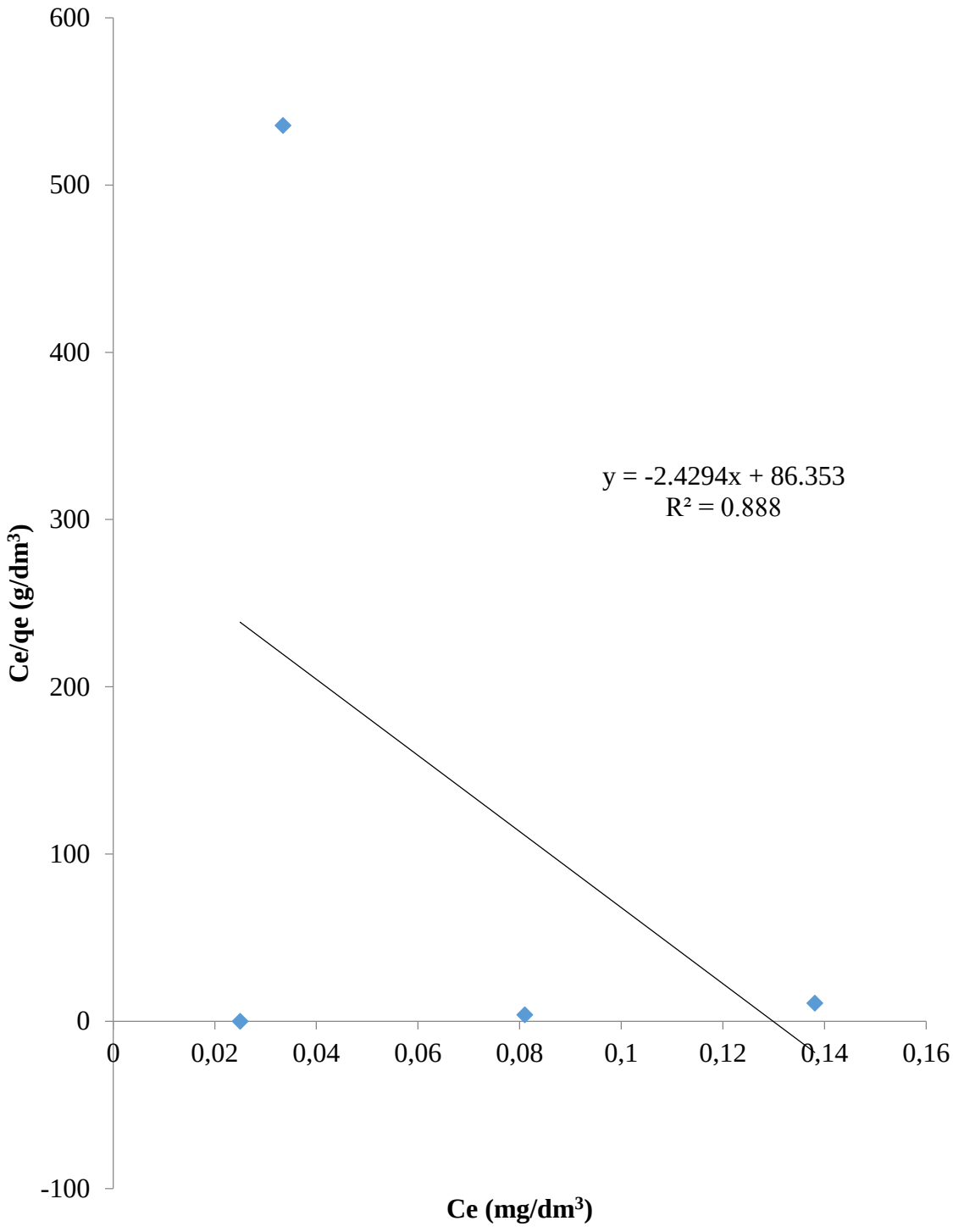

Figure 4.7: Langmuir Adsorption Isotherm for Cr^{6+}

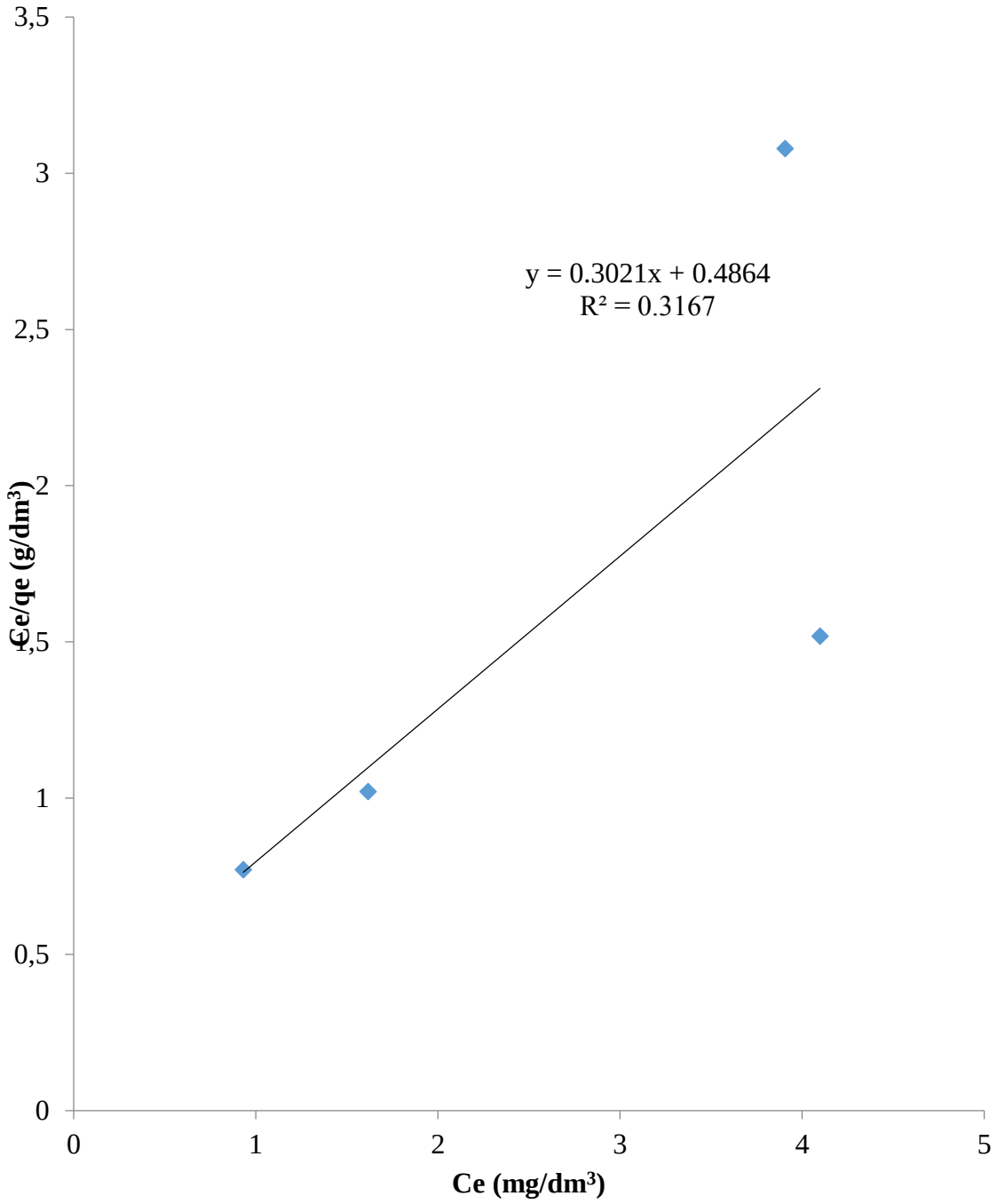

Figure 4.8: Langmuir Adsorption Isotherm for Cu^{2+}

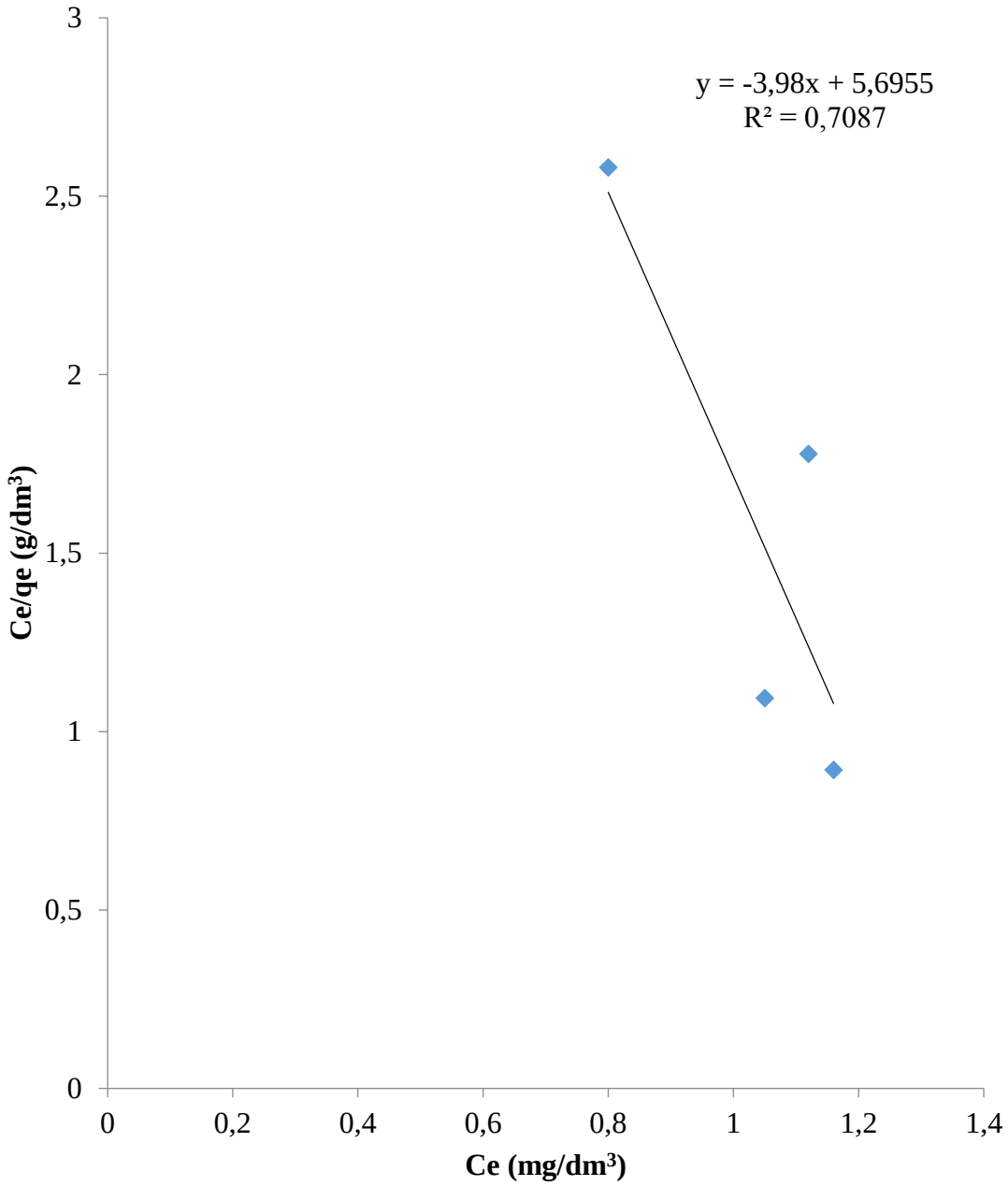

Figure 4.9: Langmuir Adsorption Isotherm for Pb^{2+}

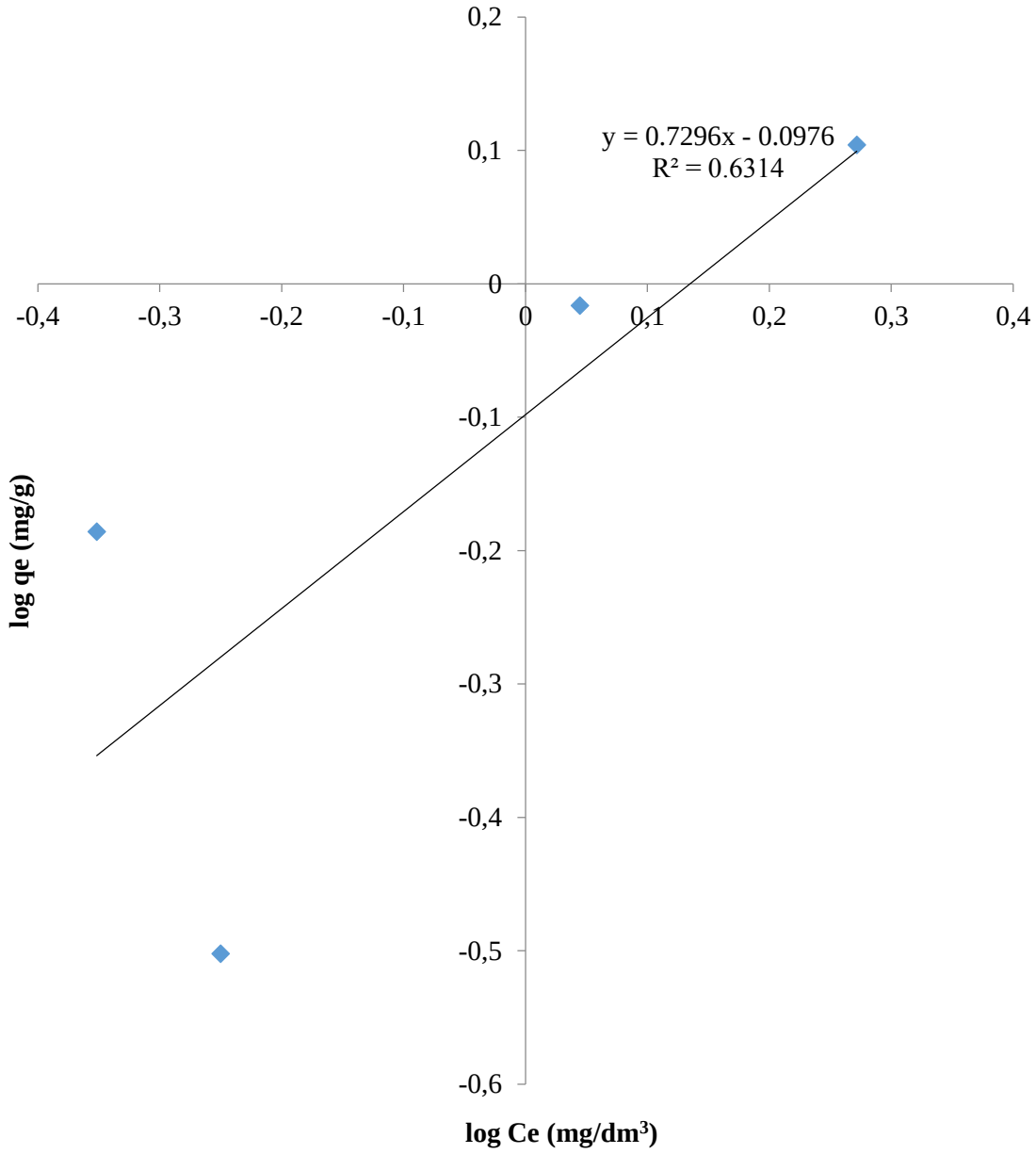

Figure 4.10: Freundlich Adsorption Isotherm for Cd^{2+}

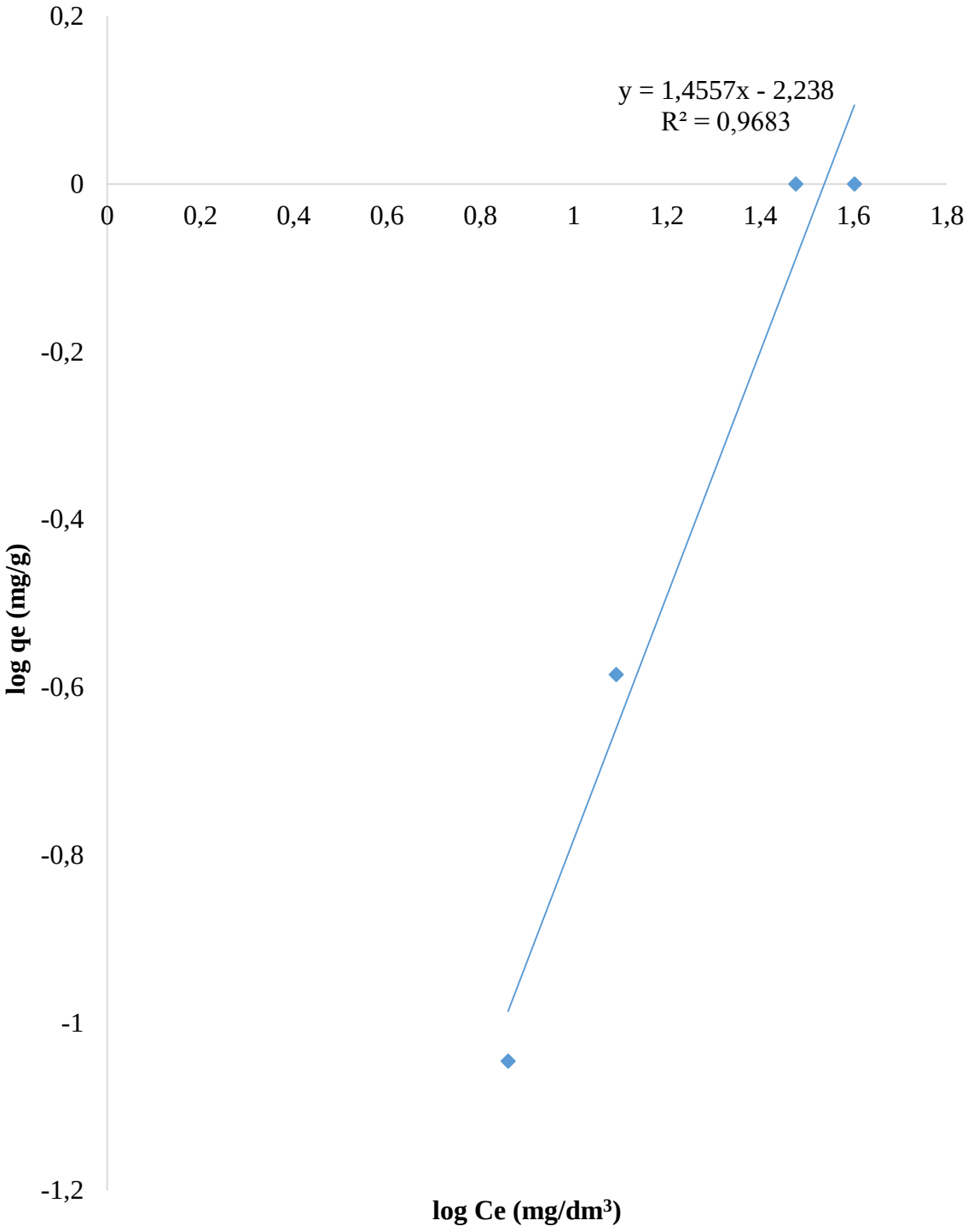

Figure 4.11: Freundlich Adsorption Isotherm for Cr^{6+}

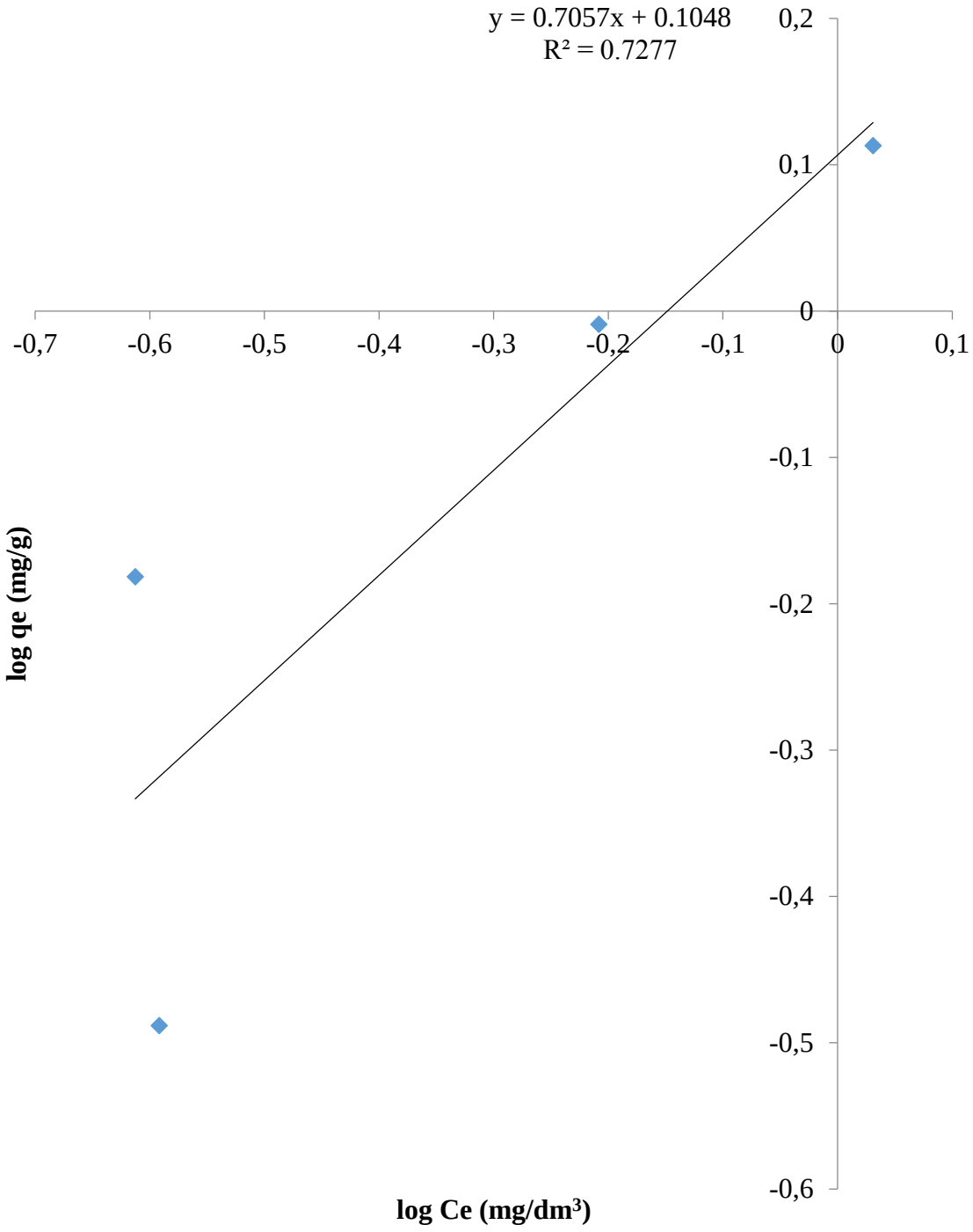

Figure 4.12: Freundlich Adsorption Isotherm for Cu^{2+}

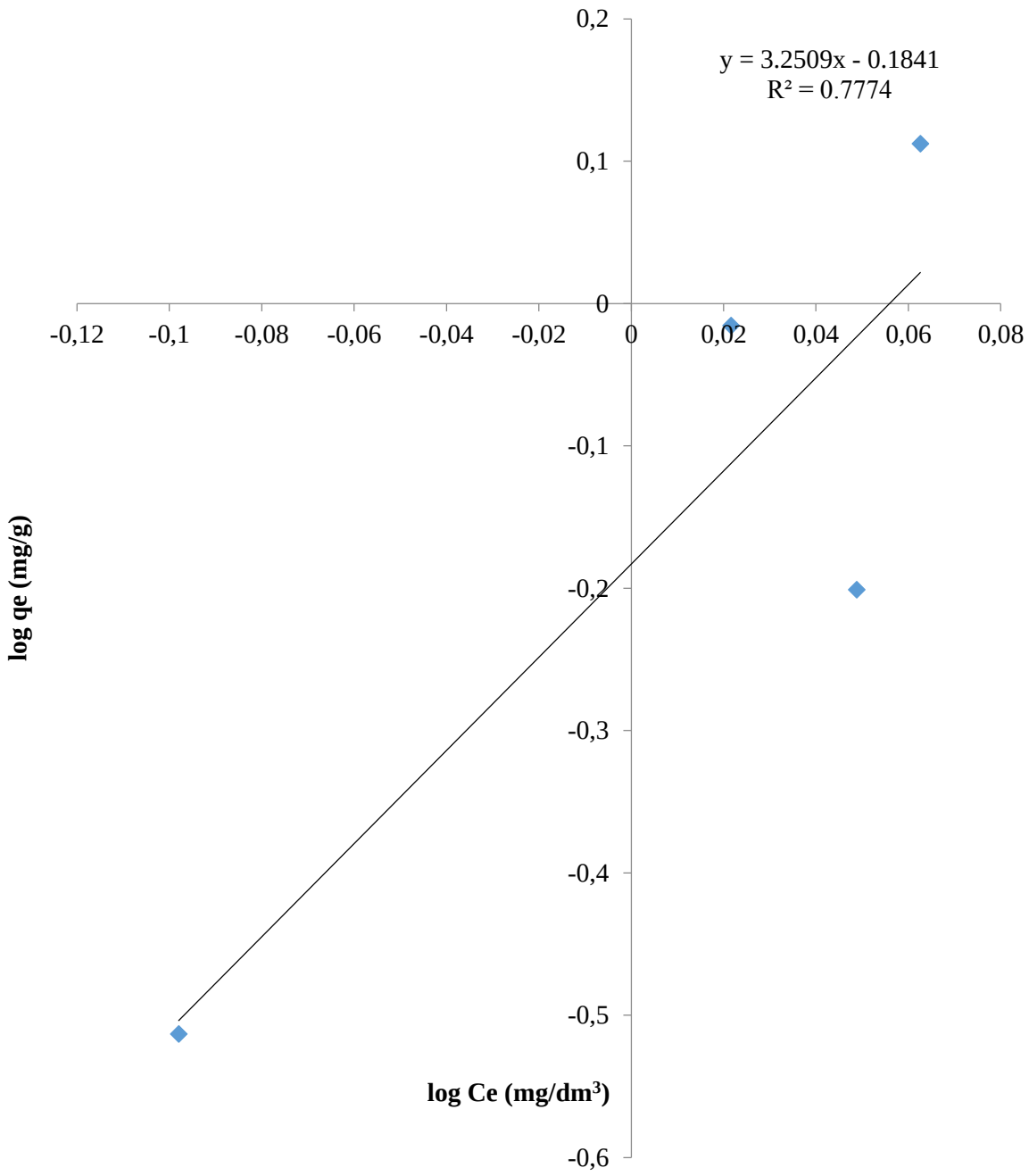

Figure 4.13: Freundlich Adsorption Isotherm for Pb^{2+}

Table 4.1: Langmuir and Freundlich Isotherm Constants for the Adsorption of all the Selected Metal Ions

Metals	Langmuir Constant			Freundlich Constant		
	q_{max} (mg/g)	b (dm^3/mg)	R^2	1/n	K_f (dm^3/mg)	R^2
Cadmium	4.684	0.202	0.093	0.730	0.798	0.631
Chromium	-0.412	-0.028	0.888	1.456	0.006	0.968
Copper	3.310	0.621	0.317	0.706	1.273	0.728
Lead	-0.251	-0.700	0.709	3.251	0.654	0.777

(q_{max} is the maximum metal uptake (mg/g), K_F is the Freundlich constant measuring adsorption capacity(dm^3/mg), while n is the constant related to the intensity of adsorption and b is energy of adsorption)

4.4 Adsorption Kinetics

Figures 4.14 – 4.21 represents the pseudo- first and pseudo-second order kinetics modeling of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} adsorption. Table 4.2 shows comparison between adsorption rate constants, the metal uptake ($q_{e)}$ estimated and correlation coefficient (R^2) associated to the pseudo-first and pseudo-second order adsorption of all the metals at varying contact time ranging from 1hr to 3 hrs. The plots log (q_e- q_t) against t (h) on Figures 4.14 to 4.17 describes the pseudo- first order kinetics; showing the relationship between the amount of metal uptake by the soil and the contact time. The R^2 values of the pseudo- first order model for Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} are: 0.623, 0.249, 0.004 and 0.086 respectively. Figures 4.18 to 4.21 are the pseudo-second order plots (t/q_t against t) also showing the relationship between the amount of metal uptake by the soil and the varying contact time. These plots describe the chemical process of adsorption that involves the rate limiting step reaction for each of the metal ion. The R^2 values as given in the graphs (Figures 4.18 to 4.21) are: 1.00, 0.95, 1.00 and 1.00 for Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} respectively. The equation y= mx + c is equivalent to $\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$ or $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$ for the pseudo- first order or the pseudo-second order plots respectively.

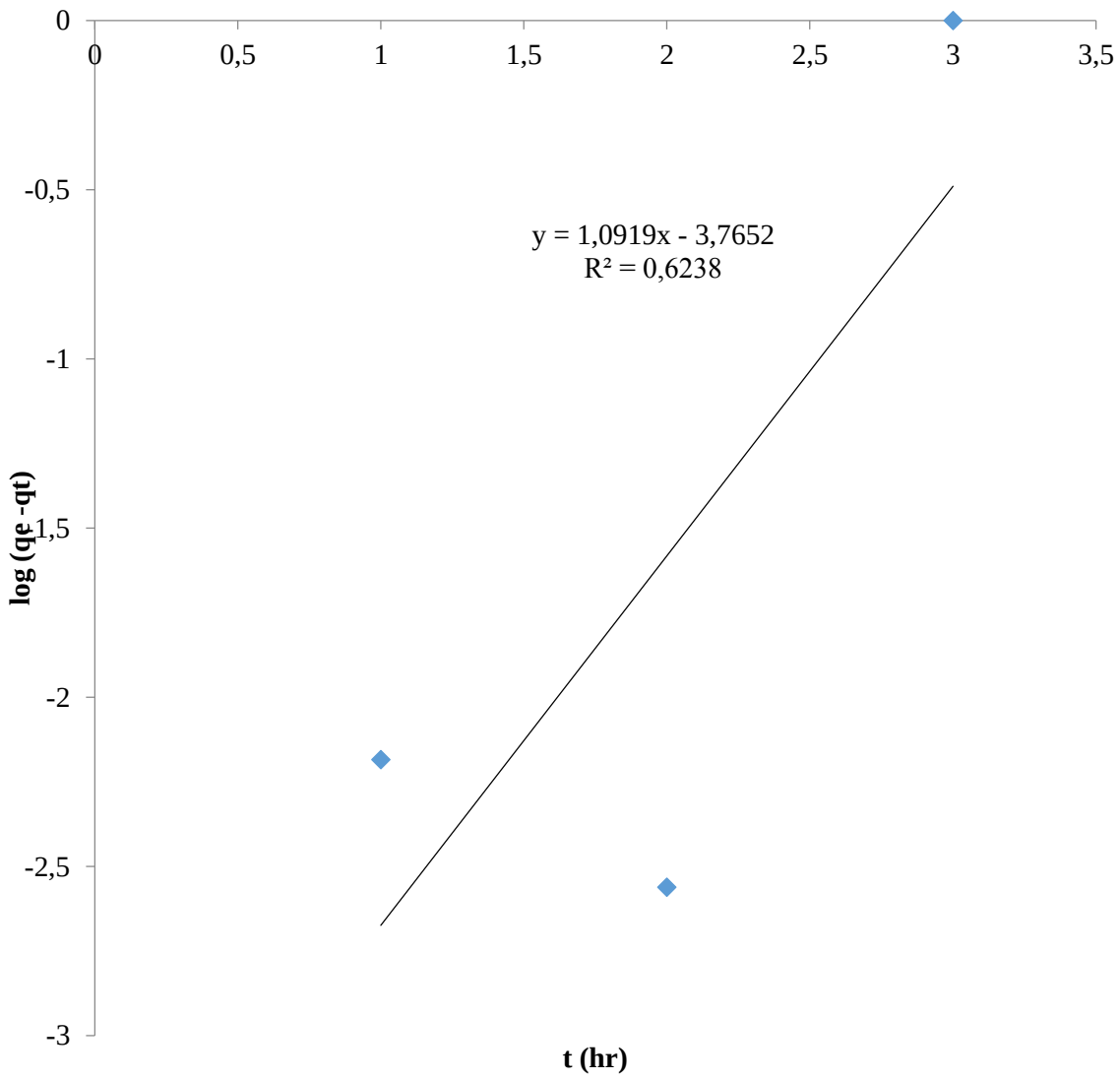

Figure 4.14: Pseudo- First Order Model for the Adsorption of Cd^{2+}

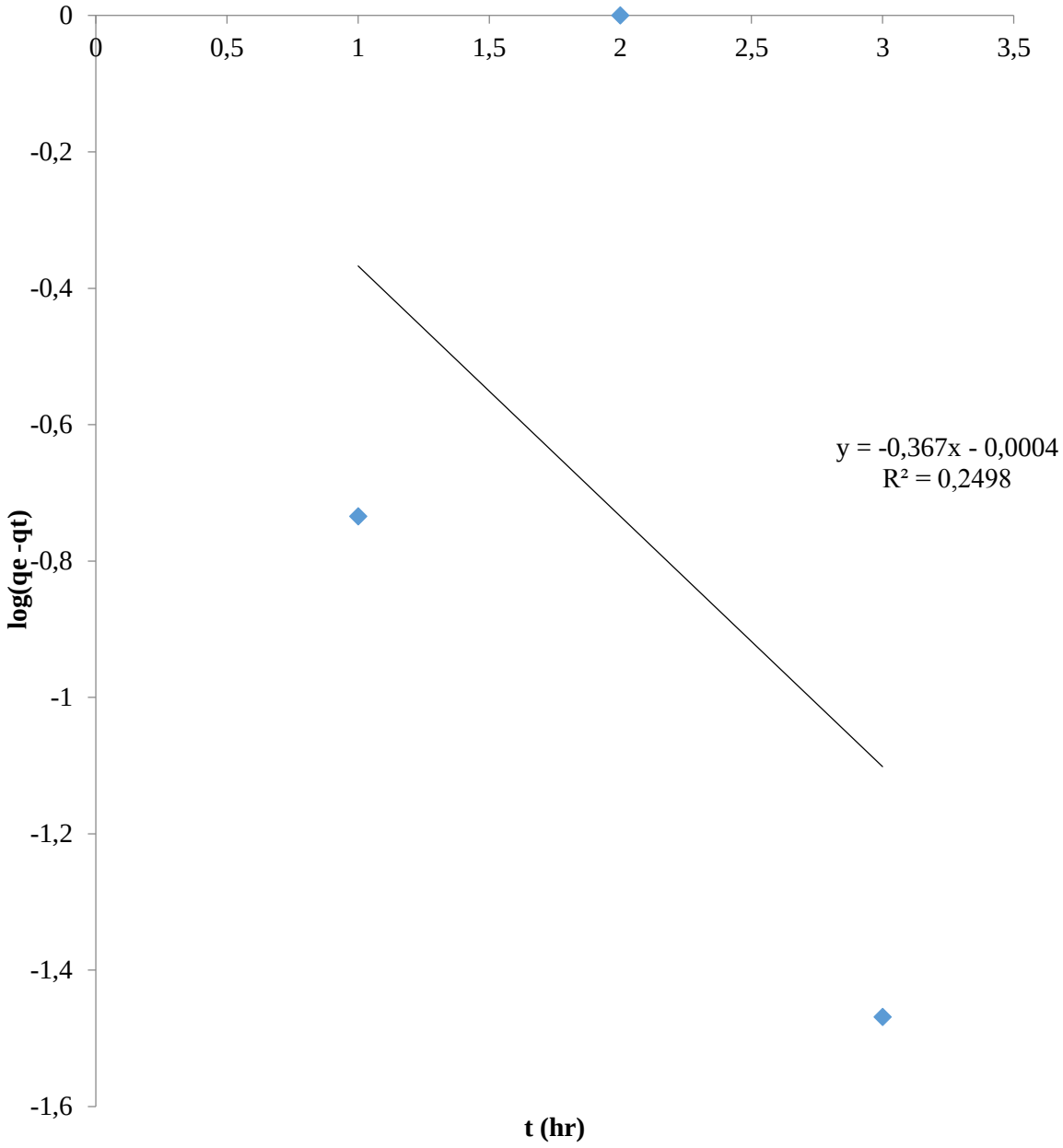

Figure 4.15: Pseudo- First Order Model for the Adsorption of Cr^{6+}

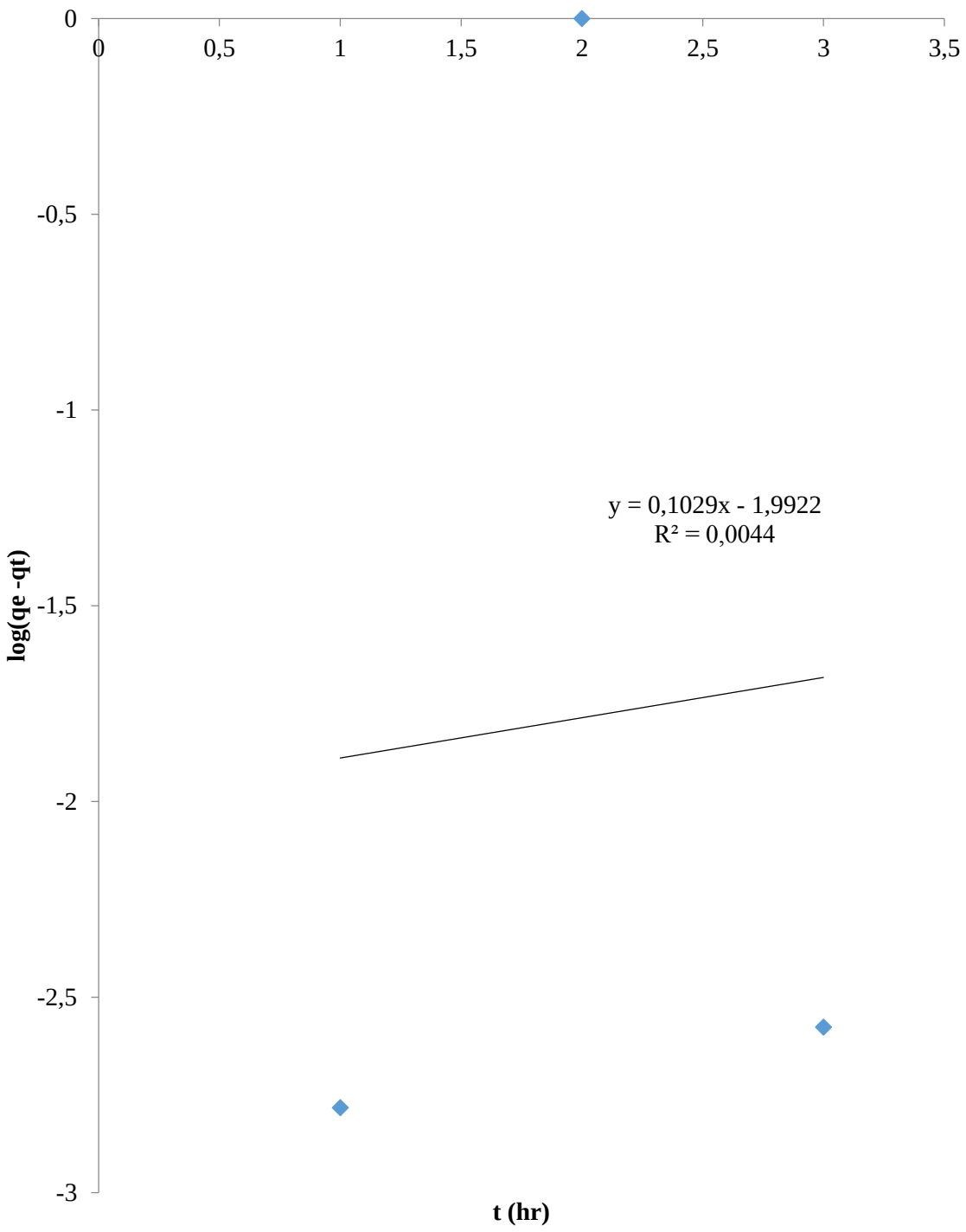

Figure 4.16: Pseudo- First Order Model for the Adsorption of Cu^{2+}

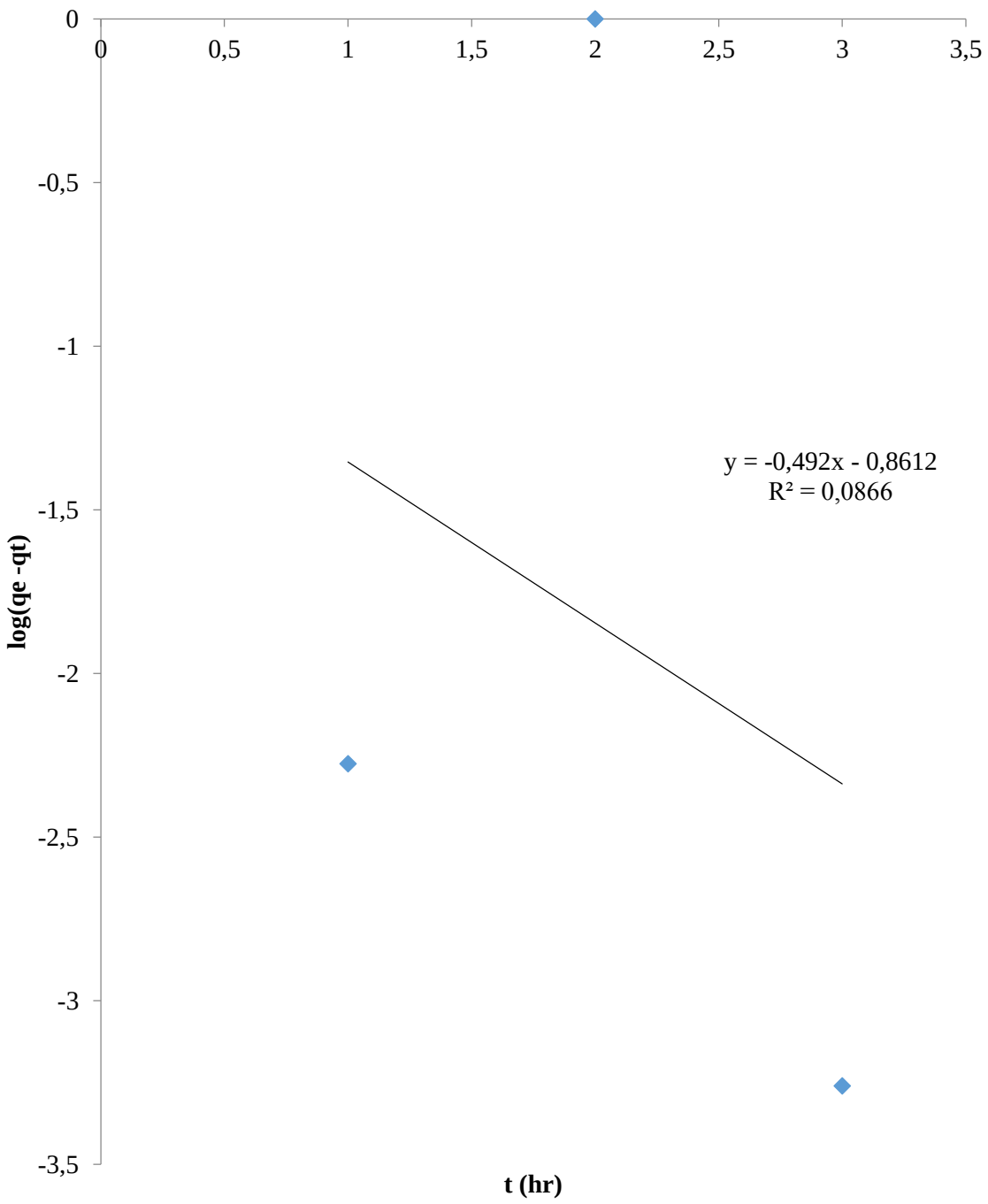

Figure 4.17: Pseudo- First Order Model for the Adsorption of Pb^{2+}

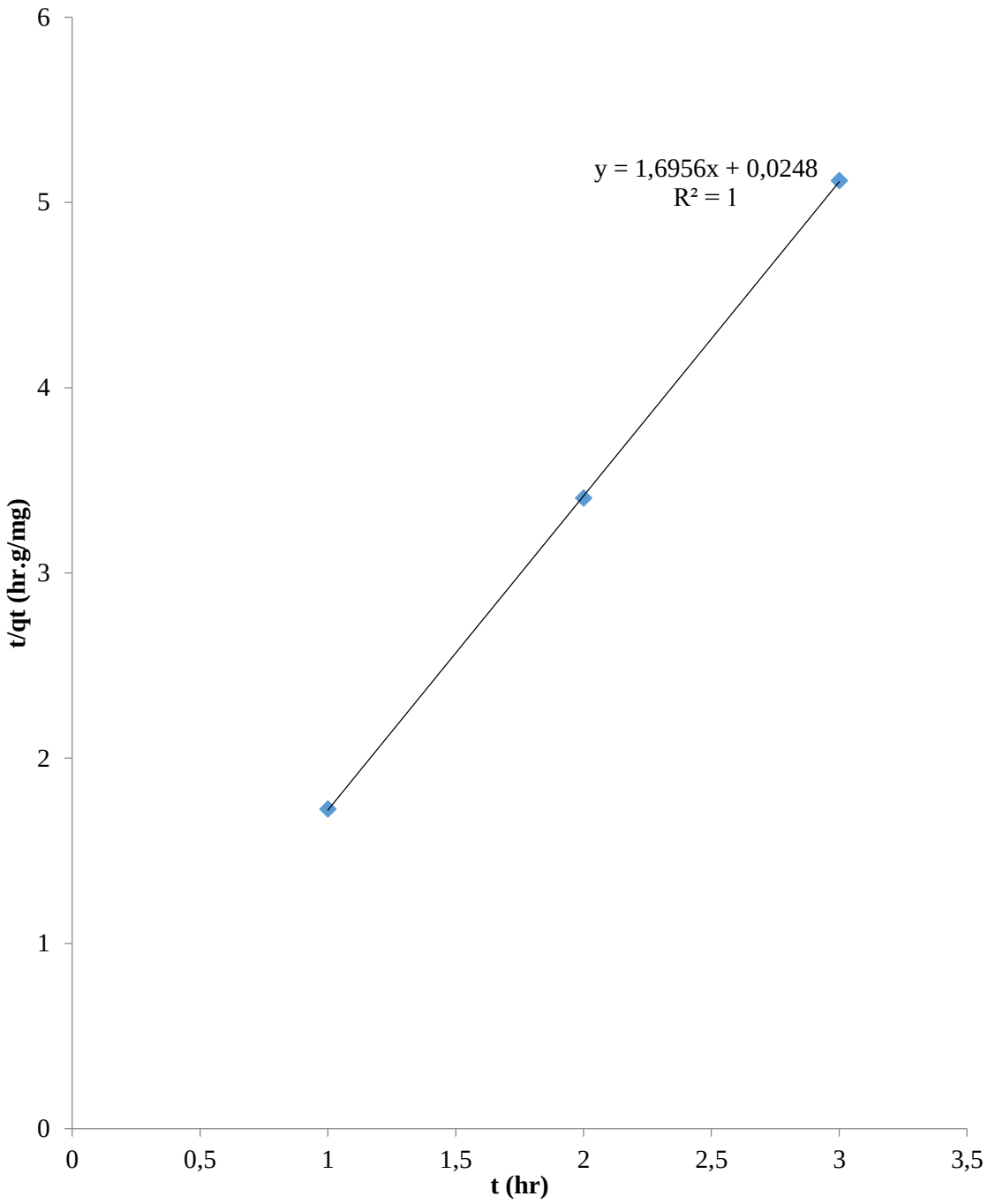

Figure 4.18: Pseudo- Second Order Model for the Adsorption of Cd^{2+}

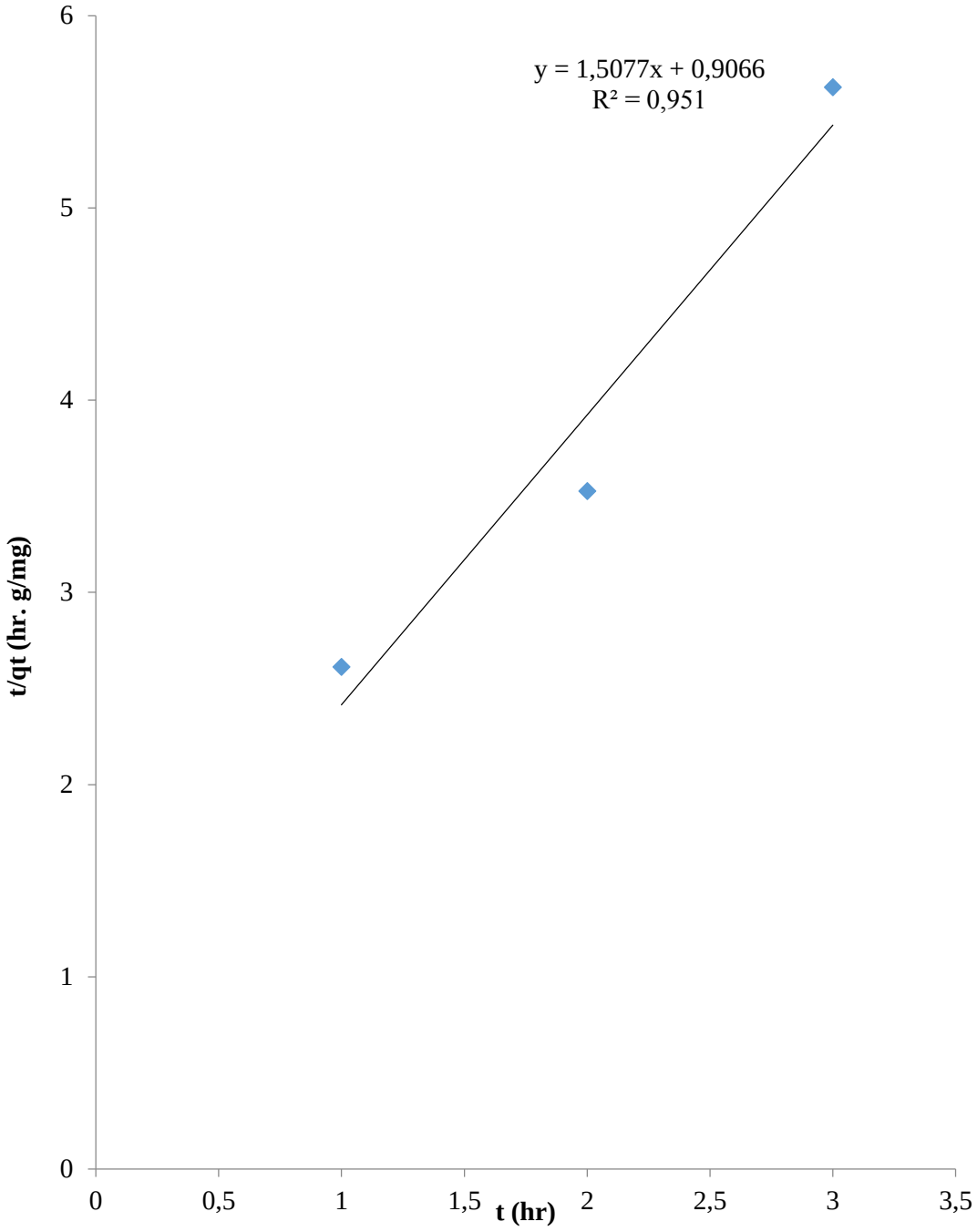

Figure 4.19: Pseudo- Second Order Model for the Adsorption of Cr^{6+}

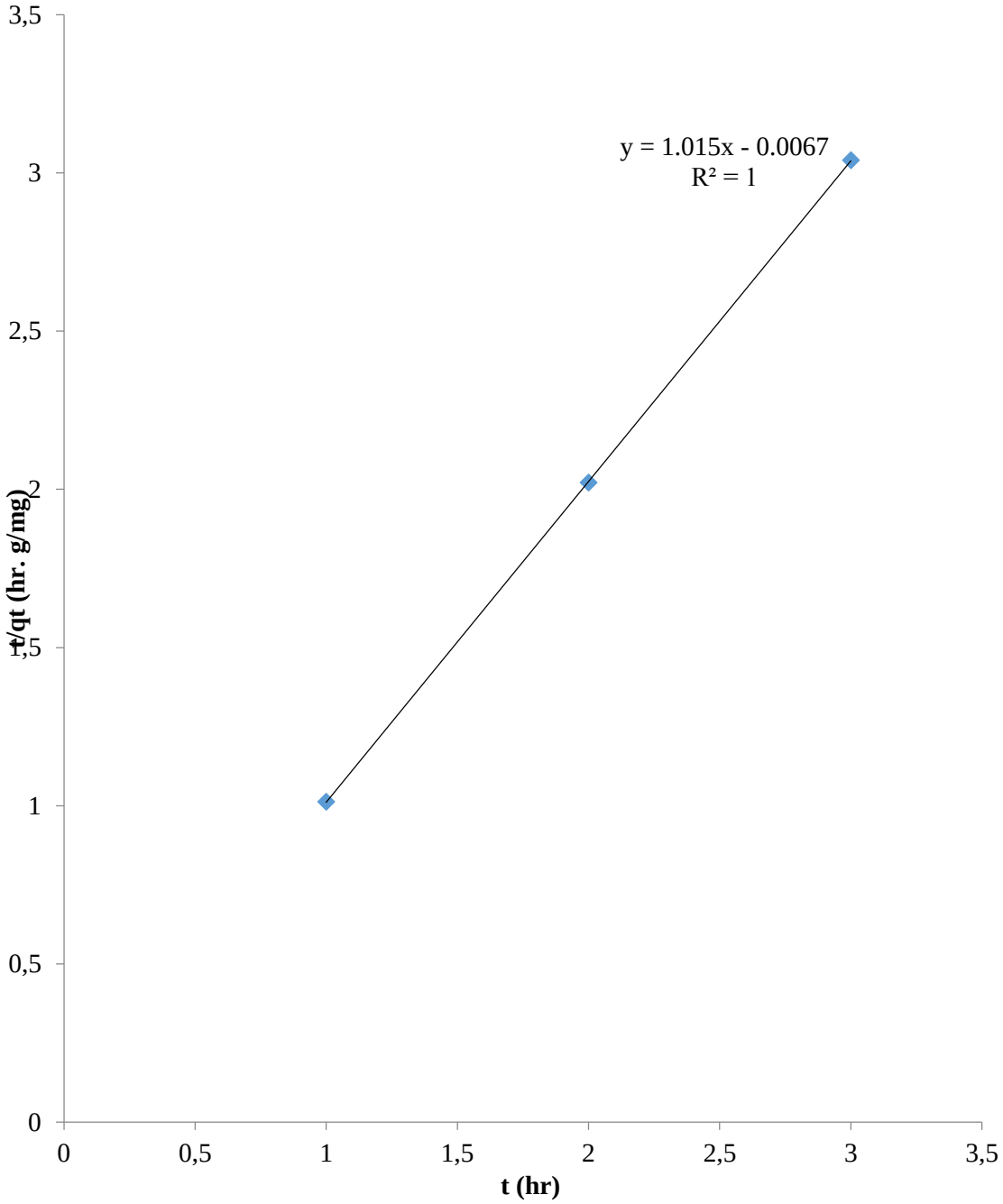

Figure 4.20: Pseudo- Second Order Model for the Adsorption of Cu^{2+}

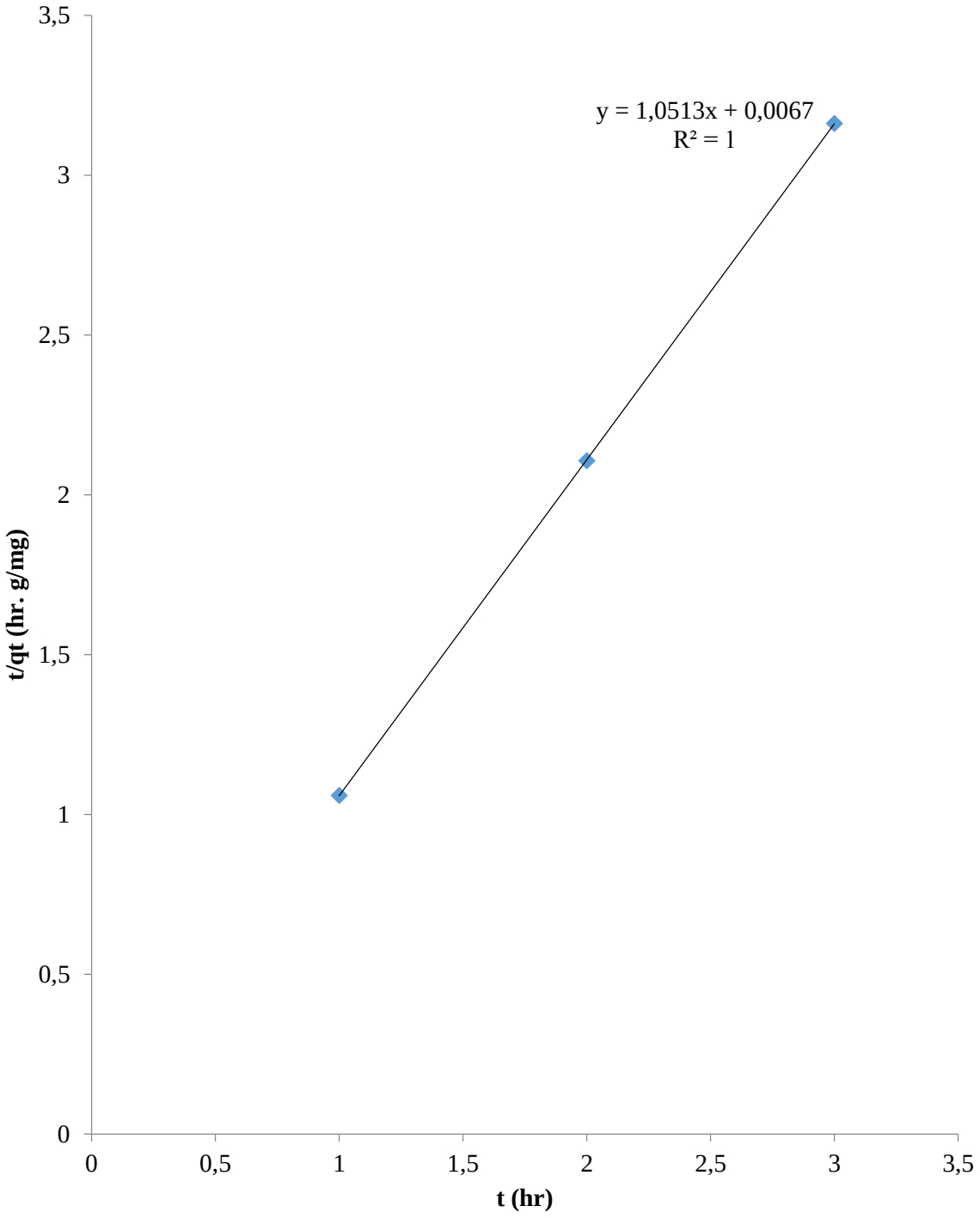

Figure 4.21: Pseudo-Second Order Model for the Adsorption Pb^{2+}

Table 4.2: Comparison between Adsorption Rate Constants, q_e Estimated and Correlation Coefficients Associated with Pseudo- First and Pseudo- Second Order Adsorptions

Metal ion	$q_{e\,(exp)}$ (mg/g)	Pseudo- First Order Model			Pseudo- Second Order Model		
		$q_{e\,(calc)}$ (mg/g)	K_1 (hr^{-1})	R^2	$q_{e\,(calc)}$ (mg/g)	K_2 ($gmg^{-1}hr^{-1}$)	R^2
Cadmium	0.9843	0.0002	2.51	0.623	0.9881	93.104	1.000
Chromium	0.5671	1.0000	-0.85	0.249	0.6636	2.507	0.951
Copper	0.9895	0.0101	0.23	0.004	0.9872	-97.066	1.000
Lead	0.9494	0.1377	-1.13	0.086	0.9515	184.100	1.000

(k_1 is the rate constant for pseudo- first order adsorption, k_2 is the pseudo-second order rate constant of adsorption, $q_{e(calc)}$ is metal uptake calculated using pseudo- first and pseudo-second order equations, $q_{e(exp)}$ is metal uptake obtained experimentally during the adsorption of the metal ions).

4.5 Competitive Adsorption of Selected Metal Ions

The approximate mean values of the amount (in mg/dm^3) and percentage adsorptions of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} in the single and mixed systems are presented in the table 4.3 below. Cd^{2+}, Cu^{2+} and Pb^{2+} had percentage adsorptions of 91.21 %, 97.17 % and 99.71 % respectively in the single system which decreases down the mixed systems. Their percentage adsorptions from the binary systems ranged from 44.63 to 49.26 %, 49.34 to 49.78% and 49.91 to 50.00 %; respectively. However, Cr^{6+} had a percentage adsorption of 21.87 % in the single system and increased in the mixed systems ranging from 35.84 to 38.18 % and 22.21 to 27.99 % in the binary and ternary systems respectively. In the quaternary systems the percentage adsorptions of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} are 23.93%, 21.20 %, 25.00 % and 25.00 % respectively.

4.5.1 Comparison between the adsorption of selected metal ions in the single and mixed systems using statistical analysis

The means of adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} in the single and mixed systems were compared using the 2-way ANOVA with replicate statistical tool. The result is presented in table 4.4 below. At 95 % confidence limit ($\alpha = 0.05$), the p values were 8.4×10^{-80}, 2.2×10^{-38}, and 5.2×10^{-83} which represents the respective variations in the sample, columns and interactions.

Table 4.3: Amounts and Percentages of Selected Metal Ions Adsorbed in the Single and Mixed Systems

System	Cd^{2+}		Cr^{6+}		Cu^{2+}		Pb^{2+}	
	(mg/dm^3)	% ads	(mg/dm^3)	% ads	(mg/dm^3)	% ads	(mg/dm^3)	% ads
Single	18.24	91.21	4.37	21.87	19.43	97.17	19.94	99.71
Binary(Cd + Cr)	9.85	49.26	7.17	35.84	-		-	
Binary(Cd + Pb)	9.50	47.54	-		-		9.98	49.91
Binary (Cr + Cu)	-		7.64	38.18	9.87	49.34	-	
Binary(Cr + Pb)	-		7.56	37.79	-		10.00	50.00
Binary (Cu + Pb)	-		-		9.98	49.90	10.00	50.00
Binary(Cd + Cu)	8.93	44.63	-		9.96	49.78	-	
Ternary (Cr+Cu+Pb)	-		5.60	27.99	6.67	33.34	6.67	33.34
Ternary (Cd+Cr+Pb)	6.48	32.40	5.23	26.13	-		6.67	33.34
Ternary (Cd+Cr+Cu)	6.38	31.89	4.44	22.21	6.59	32.97	-	
Quaternary (Cd+Cr+Cu+Pb)	4.79	23.93	4.24	21.20	5.00	25.00	5.00	25.00

(All the values are means of three replicates at 95% confidence limit ($\alpha \leq 0.05$). Initial metal ion concentration is 20 mg/dm^3, adsorbent dose = 1.0 g, time = 2 hrs at room temperature, pH is 5.5).

Table 4.4: Comparison between the Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} in the Single and Mixed Systems

ANOVA						
Source of Variation	SS	Df	MS	F	P-value	F crit
Sample	3.1663	10	0.3166	717.9171	8.42E-80	1.9400
Columns	0.2522	3	0.0841	190.5853	2.25E-38	2.7081
Interaction	5.8299	30	0.1943	440.6153	1.16E-83	1.5888
Within	0.0388	88	0.0004			
Total	9.2871	131				

All the values are means of three replicates at 95% confidence limit ($\alpha \leq 0.05$).

CHAPTER FIVE

5.0 DISCUSSION

5.1 Scanning Electron Microscope (SEM) Analysis

The Scanning Electron Micrograph shown in Figures 4.1 and 4.2 clearly reveals the surface texture of the soil before and after adsorption at 1000x magnifications. It was observed that the surface of the soil sample before adsorption was rough, fused together alongside with large particles, but after adsorption, it is evident from the Figure 4.2 displayed that the surface morphology of the soil had undergone remarkable physical disintegration. The roughness correlates with the specific surface area. Increasing roughness and porosity produces a greater specific surface area, which makes an adsorbent have a higher adsorption capacity (Noppadol and Pongsakorn, 2014). The disintegration of the soil after adsorption resulted in high surface interaction between metal ion and the binding sites on the surface of the soil. Similar SEM observations have been reported according to Noppadol and Pongsakorn, (2014) and Shakirullah *et al.*, (2006).

5.2 Soil pH

The pH of the soil plays a major role in the adsorption of heavy metals and mostly the pH of soils usually ranges from 4 to 10 (Brady and Weil, 2002). Soil pH influences the concentration levels, mobility and the retention of heavy metals in the soil (McBride, 1994). The pH of the soil assessed in this study was found to be 5.5. This means that the soil is moderately acidic (Brady and Weil, 2002). Some heavy metals have been reported to be more stable in slightly or moderately acidic soils to neutral soil (pH 5.5 – 7.3) rather than highly acidic soils (Mouni et al., 2009). Also, according to Fonseca *et al*., (2011), in the study “Mobility of Cr, Pb, Cd, Cu

and Zn in a loamy sand soil", soils with pH 5.5 were found to have heavy metal ions concentrations below the national legislated limit for soils. It can therefore be inferred that the soil can serve as a good adsorbent for the adsorption of metal ions from aqueous solutions.

5.3 Effects of Initial Metal Ions Concentrations on the Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

The efficiency of metal uptake by an adsorbent is highly dependent on the initial metal ion concentration of the solution (Gimba *et al.,* 2009). Figure 4.3 presents a graphical representation of the effect of initial metal ion concentration on the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}. It can be deduced that the percentage adsorption of Pb^{2+} increases as the initial concentration increases up to 40 mg/dm^3. This might be due to increase in the ratio of initial number of moles of Pb^{2+} to the available surface area of the soil, because at higher initial solute concentrations, the ratio of initial amount of solute to the available surface area is usually high (Mataka *et al.*, 2010). Similar works from different studies supported this assertion (Adelaja *et al.,* 2011). The maximum Pb^{2+} adsorption of the adsorbent was obtained at an initial concentration of 40 mg/dm^3. According to Bhatti *et al.* (2006) higher initial concentration increases the driving force to overcome all mass transfer resistance of metals between aqueous and solid phase thereby accelerating the probable collision between metal ion and sorbents which can result into higher metal uptake. This implies that surface saturation is dependent on the initial metal ion concentration (Bhatti *et al.,* 2006).

On the other hand, the adsorption efficiency of Cd^{2+}, Cr^{6+} and Cu^{2+} on the soil increased initially up to 10 mg/L, and then equilibrated at 20 mg/L and beyond. The increase in the adsorption capacity during the first stage may be attributed to increased active sites and binding surface

area (Ahalya *et al.,* 2003) Also, for a fixed dose of adsorbent, the total available binding sites are limited. At the saturation stage, screening effects on the dense layer of the adsorbent may occur due to accumulation and coagulation of adsorbent, thus limiting the adsorption process (Xiangliang *et al*., 2005). A similar trend was reported by Al-Omair and El- Sharkawy, 2007; Hussain *et al*., 2009 and Ahalya *et al.,* 2003).

5.4 Effect of Adsorbent Dose on the Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

The efficiency of metal removal is significantly influenced by the amount of adsorbent used (Gupta and Rastogi, 2007). Figure 4.4 presents the effects of adsorbent doses on the adsorption of each of these metal ions, Cd^{2+}, Cr^{6+} Cu^{2+} or Pb^{2+} onto the standard reference soil sample. An increment in adsorption capacity was observed from 0.5 to 1.5 g for cadmium after which further increment of adsorbent resulted in a decline in adsorption capacity. Similarly, for Cr^{6+}, Cu^{2+} and Pb^{2+}, there were significant increments in the percentage adsorption up to 1.0 g after which they began to decrease gradually with increasing masses of the adsorbent. The initial increment in adsorption capacity with increase in adsorbent dosage was expected, since the number of adsorbent particles increased and thus more surface area was available for metal attachment. Same trend was reported by Dakiky *et al*. (2002) and Acharya *et al.* (2009).

On the other hand, it is plausible to suggest that with higher dosage of adsorbent there would be greater availability of exchangeable sites for metal ions (Babel and Kurniawan, 2004; Najua *et al*., 2008) but further increment in the adsorbent dose beyond maximum adsorption capacity resulted in a decline in adsorption efficiency as shown in Figure 4.4. The reduction in adsorption efficiency may be attributed to overlapping resulting from overcrowding of dosage which in

turn imposed a screening effect on the adsorbent and shielding of binding site (Pons and Fuste, 1993). Saradhi *et al*. (2010) also explained that decrease in metal uptake with increase in adsorbent dose could be associated with interference of inter – particle cohesive forces, desorption due to abrasion and turbulence.

Hence, from the study as depicted by Figure 4.4, the maximum percentages of the Cu^{2+}, Cd^{2+}, Pb^{2+} and Cr^{6+} adsorbed onto the standard reference soil samples as a function of the dosage of soil sample used are: 99.57 %, 97.07 %, 99.22 %, 40.90 % respectively. This implies that the soil has high tendency to adsorb about 90 % of Cd^{2+}, Cu^{2+} and Pb^{2+} at low adsorbent dose of about 0.5 g (Appendix II). This could be attributing to high affinity of these metals towards the soil (Alumaa *et al*., 2001). It is therefore of environmental concern, especially for cadmium and lead that have toxicological consequences when bio-accumulated by plants and animals on the long run.

5.5 Effect of Contact Time on the Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}

The relationship between the amount of adsorbed Cd^{2+}, Cr^{6+} Cu^{2+} or Pb^{2+} onto the soil sample with contact time is presented in Figure 4.5. All metal ions (except cadmium) showed similar trend, adsorption approached equilibrium within 2 hrs. Thereafter the rate of adsorption decreased as the time increased from 2 hrs to 3 hrs. This may be attributed to large number of vacant active binding sites available at the first phase of the experiment leading to a rapid bounding of large amount of metal ions on the soil at the initial stage (Drake *et al.,* 1996). The binding site shortly became limited and the remaining vacant sites were difficult to be occupied by metal ions due to the formation of repulsive forces between the metal ions on the solid surface

and the liquid phase (Okuo and Ozioka, 2001; Anwar *et al*., 2010). However, in the case of cadmium, there was an increase in the amount of adsorbed ions as the time increased such that the optimum time was attained at 3 hrs. The pattern of the curves established from the results therefore shows that adsorption capacity is proportionally related to time before equilibrium and adsorption is time dependent (Volesky and Holan, 1995).

Following the result presented in Figure 4.5, chromium had the least amount of ions adsorbed onto the soil sample with time being: 38.29 % at 1 hr, 56. 71 % at 2 hrs and a decline to 53.31 % at 3 hrs while Pb^{2+}, Cd^{2+} and Cu^{2+} ranged from 94.41 to 98.78% at 1 hr contact time. Therefore, this study shows that the soil has high tendency to adsorb about 94 – 98 % of Pb^{2+}, Cd^{2+} and Cu^{2+} at 1 hr contact with wastewater containing any of these ions. This is relevant in designing a remedial option for the removal of these ions that have efficient adsorption for soil in a short-term range of 1 hr.

5.6 The Langmuir and Freundlich Isotherms Modeling for Metals Uptake

The evaluation of the adsorption capacity of the soil for each of the metal ions studied using the optimum conditions of adsorbate concentration, adsorbent dose and contact time adsorbent was further carried out by analyzing the isotherm data using Langmuir (Figure 4.6 - 4.9) and Freundlich adsorption (Figure 4.10 - 4.13) isotherms modeling. The data obtained from the isotherm parameters summarized in Table 4.1 shows that the Langmuir isotherm does not provide an accurate description of the adsorption process for Cd^{2+}, Cr^{6+} Cu^{2+} or Pb^{2+} over the range of concentrations studied. The R^2 values ranged from 0.093 for Cd^{2+} to 0.888 for Cr^{6+}. This behaviour halted the linearization procedure and the determination of the maximum

adsorption capacity. The non-linearization of the Langmuir isotherm could be attributed to the exceedingly high percentage adsorption of the metals onto the soil. These findings are in agreement with the reports of Silvera *et al*. (2002). Moreira and Alleoni, (2010) also studied the adsorption of some metals in tropical soils and reported that isotherms could not be fitted into experimental data for soils with high metal adsorption because isotherms that have similar equilibrium concentration for the studied metals might have had metal precipitation during experiments (Brummer *et al*., 1983). Harter (1992) also proposed that errors in the estimation of maximum adsorption may reach 50% due to precipitation of metal during experiments. Nevertheless, the values of b according to the Langmuir isotherm for Cd^{2+} and Cu^{2+} was found to be > 1 (signifying favorable adsorption) with Qmax of 4.68 and 3.31 respectively. The higher value of Cd^{2+} above Cu^{2+} is as result of its higher ionization energy, atomic and ionic radii. The small maximum adsorption capacity (MAC) of the selected metals may be due to the sandy nature of the soil (Moreira and Alleoni, 2010).

The amount (q_e in mg/g) of Cd, Cu, and Pb was found to increase as the concentration of the metals increased (Appendix II), almost all the amount of metals added were adsorbed in the soil as can be seen by the steep isotherms (Figures 4.6 - 4.10). This behaviour demonstrated the high affinity of metals by the adsorption site of the soil. Similar results were reported by Alumaa *et al*. (2001) for highly-weathered tropical soils.

Although, the linear plots obtained (Figures 4.10 – 4.13) also showed low fitting of the Freundlich isotherm to the experimental adsorption data in relation to the of the R^2 values (<0.97) the Freundlich model had a better fitness as compared to the Langmuir model. The

adsorption coefficient 'K_f' (in dm^3/mg) of the Freundlich parameter which represents the adsorption affinity of the soil and the quantity of metal ion adsorbed onto the soil for a unit equilibrium concentration decreased in the order $Cu^{2+} > Cd^{2+} > Pb^{2+} > Cr^{6+}$ with values 1.276, 0.798, 0.656 and 0.006 respectively. This order may be due to their charge-to-radius ratio. The strongest bond is usually formed by the metal with the highest charge-to-radius ratio, giving rise to the sequence Ni > Mg > Cu > Co > Zn > Cd > Sr > Pb (McBride, 1994). The values of 1/n for Cd^{2+} and Cu^{2+} were found to be less than unity (1/n <1.0) which corresponds to favourable adsorption equilibria. The slope 1/n is a measure of adsorption intensity or surface heterogeneity and adsorption becomes more intense or heterogeneous as its value gets closer to zero (Mataka *et al*., 2010). It implies that for Cd^{2+} and Cu^{2+}, significant adsorption actually took place even at low concentrations. Therefore, this data is significant in the design of metal remediation methods for polluted farmland soil by Cd and Cu that are of much environmental concern than the other metals studied, and also calls for study of Cd and Cu when there is multi-elemental interaction on farmland soil.

5.7 Kinetics Modeling of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} Adsorption

The rate of adsorption was evaluated through the experimental data obtained from the effects of contact time by using Lagergren's pseudo-first order and pseudo-second order as given in table 4.5. The experimental adsorption capacities ($q_{e\,(exp)}$ in mg/g) for Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} were 0.9843, 0.5671, 0.9895 and 0.9494 respectively. The calculated adsorption capacities for Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} by the pseudo-second order model were very close to their respective experimentally determined adsorption capacities (0.9881, 0.6636, 0.9872 and 0.9515) but there was a large difference between the experimental and calculated adsorption capacities of the

metal ions by the pseudo-first order model (0.0002, 1.0000, 0.0101 and 0.1377). Additionally, the correlation coefficients, R^2 values of the pseudo - second order model are higher (≥ 0.951) than that of pseudo- first order model (≤ 0.004). Hence, the Pseudo-second order adsorption model is more suitable to describe the adsorption kinetics of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} on the standard reference soil. This supports the assumption which states that kinetic behavior and chemical process of adsorption involve the rate-limiting step reaction (Gupta and Rastogi, 2007). This implies that the adsorption of the studied metals is enhanced by electrostatic force of attraction. According to McBride (1994) chemisorption of metals depends only on the electrostatic force of attraction.

In the experimental data obtained for the Pseudo-second order adsorption model, the rate constant (K2) which represents the affinity of the metals by the adsorption site of the soil increased in the order Cr < Cd < Cu < Pb. This is related to the difference in their electronegativity values. The electronegativity series for these metals according to Allen's series follows a similar order; Pb > Cu > Cd > Cr (Sabry, et al., 2012). The more electronegative metals should form the strongest covalent bond on any particular mineral surface as assumed by McBride (1994). Hence, this kinetic information establishes that ion exchange is the mechanism of the adsorption in this study. This conclusion is in agreement with those obtained by others (Mataka *et al,*. 2010; Yue-ming *et al*., 2013).

5.8 Competitive Adsorption of Heavy Metal Ions

Competitive adsorption experiments were conducted to assess the effects of competing ions on the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} onto the soil. The two-way ANOVA replicate

statistical tool was employed in order to determine the significant adsorption of each of the selected metal ions and to make comparison among the systems. The result obtained from the mean amount of metal uptake by the soil samples (mg/dm^3) for Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}in the single, binary, ternary and quaternary systems are presented in Table 4.3, and was also used to assess the geochemical behaviour of the four metals.

Qin *et al.* (2006) suggested that when two or more metal ions are present together in a reaction system, the adsorption capacity of the metal of interest may increase, decrease or not change. The adsorption capacities of the selected metals were observed to decrease as the number of competing ion(s) increases such that the least adsorption capacity was recorded in the quaternary system. This may be due to interference of other metal ions in the reaction system limiting the adsorption process. The interfering metal ion(s) may also create a suppressive effect on the metal of interest as the ions competed for sorption sites (Serrano *et al.,* 2005).

For cadmium as presented in Table 4.3, competition decreased the adsorption of the metal. The percentages of cadmium adsorbed were found to be 49.26 %, 47.54 % and 44.63 % in the (Cd + Cr), (Cd + Pb) and (Cd + Cu) systems respectively. However, in the single medium the percentage of Cd adsorbed was 91.21 %. The lowest percentage of adsorbed Cd was obtained as 31.89 % in the presence of Cr and Pb (in the ternary system).

ANOVA (Table 4.4) indicated that the percentage of Cd adsorbed onto the soil samples decreased significantly as a result of competition in the binary, ternary and quaternary media. This implies that in situations of wastewater contamination (usually multi-elemental) of soil,

the percentage of the metal adsorbed by soil will be drastically less than indicated by the single elemental medium.

Cadmium adsorption is known to be strongly influenced by the presence of competing cations. These cations compete with Cd for sorption sites in soils and are able to desorb Cd from the soils (Bradl, 2004). It is probable that cadmium was easily affected by the other metal ions in the competitive media as a result of its smaller ionic radius, low density and lower electronegativity. The competitive adsorption of Cd and Pb onto acid soils was studied by Serrano *et al*. (2005) and it was noted that the co-existence of Pb and Cd reduces their tendency to be adsorbed onto the soil solid phases, thereby affecting the adsorption capacity of Cd to a greater extent than Pb.

The competitive adsorption of chromium with other metals in the binary, ternary and quaternary media is presented in Table 4.3; the table revealed that competition had no significant effect on the adsorption of chromium onto the soil surface. The percentages of chromium adsorbed were found to be 35.846 %, 38.18 % and 37.79 % in the (Cd + Cr), (Cr + Cu) and (Cr + Pb) systems respectively; but in the single medium, the percentage of Cr^{6+} adsorbed was 21.87 %; indicating an enhancement in the amount adsorbed in the binary systems. The ternary and quaternary media resulted to lowered percentage of adsorbed chromium than the binary system (Table 4.3). The ternary media containing Cr^{6+} had the range of adsorbed chromium as 22.21 - 27.99 %. The quaternary medium (Cd + Cr + Cu +Pb) had the percentage of adsorbed Cr as 21.20 %.

ANOVA (Table 4.4) indicated that the percentage of Cr adsorbed onto the soil samples did not significantly change as a result of competition in the binary, ternary and quaternary media.

Also, Chromium was the least adsorbed in all the systems. This may be attributed to low electronegativity and small ionization potential. The pH value (5.5) maintained during the adsorption experiments in this study might have also contributed to the low adsorption of Cr in the reaction systems. Cr^{6+} has been noted to be more adsorbed in lower pH media (Bradl, 2004). The adsorption of Cr^{6+} increases with decreasing pH due to the protonation of the hydroxyl groups (Bradl, 2004). At low pH values, Cr^{6+} exists mainly as an oxyanion, which is adsorbed at positively charged sites indicating the degree of protonation of the soil surface (Fonseca *et al*., 2011). Furthermore, oxyanions are "soft" bases and according to the Pearson concept, can react strongly with Lewis acid sites created by inner-sphere surface complexation (Banks *et al.*, 2006).

The competitive adsorption of Cu onto the soil is presented in Table 4.3, competition decreased the adsorption of the metal. The percentage of copper adsorbed was found to be in the range 49.34 - 49.90 % in the binary systems containing copper ion. However, in the single medium the percentage of Cu adsorbed was 97.17 %. Also, the percentages of copper adsorbed were found to be in the range 32.97 - 33.34 % in the ternary systems containing copper ion. The least percentage of adsorbed Cu was obtained as 25.00 % in the quaternary system.

ANOVA (Table 4.4) indicated that the percentage of Cu adsorbed onto the soil samples decreased significantly as a result of competition in the binary, ternary and quaternary media

compared to the single medium. And implies that in situations of wastewater contamination (usually multi-elemental) of soil, the percentage of the metal adsorbed by soil will be drastically less than indicated by the single medium containing only copper.

Copper was favourably adsorbed over Cd in all the multi-metal systems. This may be due to the fact that Cu possesses a larger density, higher charge to radius ratio and greater hydrolysis constant than Cd (Emma *et al*., 2004). Cu greatly competed with Pb having close range values of percentage adsorption in the mixed systems. This is attributed to their Hydrolysis constant i.e the Pk of Cu =Pb (Emma *et al*., 2004). Fontes and Gomes (2003) evaluated the competitive adsorption of metals in samples of tropical soils and observed that Cu and Pb kept the high affinity for soil solid surfaces, while Cd was displaced from the adsorbing surfaces. Cd is more affected by electrostatic interactions with the surface exchange sites, while Cu is more affected by covalent binding to mineral surfaces (McBride, 1994). Such ideas are in agreement with the findings of Gomes *et al.* (2001) and Fontes and Gomes (2003).

The competitive adsorption of Pb onto the soil is presented in Table 4.3; competition decreased the adsorption of the metal. Lead adsorbed onto the soil in the single medium was 99.71%. The percentages of lead ion adsorbed onto the soil sample in the binary systems containing lead were found to be in the range 49.91 - 50.00%. However, the percentage of lead adsorbed was found to be 33.34% in the ternary system containing lead ion. The least percentage of adsorbed Cu was obtained as 25.00% in the quaternary system.

ANOVA (Table 4.4) indicated that the percentage of Pb adsorbed onto the soil samples decreased significantly as a result of competition in the binary, ternary and quaternary media compared to the single medium. This implies that accidental discharge of wastewater containing Pb to soil will lead to the percentage of the metal adsorbed onto soil being drastically less than that adsorbed from single medium containing only lead.

The experimental data given in Appendix IV shows from the mean values that the amount of Pb adsorbed by the soil is more than that of Cu in all the mixed systems. This means that Pb was preferably adsorbed over Cu. The overall preference of Pb on Cu could be attributed to the postulation by Emma *et al*., (2004), that in the case of similar Pk values, like that of Pb and Cu it is probable that more preference would be given to Pb because of its larger ionic radius (Gomes *et al*., 2001). Additionally, the prevalence of Pb over Cu may be due to Pb's larger density and higher electronegativity. This is in agreement with the report by Chen *et al*. (2010). Hence, the general affinity sequence of the four metals to the standard reference soil from the various systems examined could be deduced as $Pb^{2+} > Cu^{2+} > Cd^{2+} > Cr^{6+}$. This agrees with the sequence obtained by the pseudo-second order rate constant of adsorption (K_2) in the single adsorption system. This implies that the adsorption and selectivity of the metal ions in this study is highly influenced by their hydrolysis constants and electronegativities which according to Allen's series follows the same order; Pb> Cu > Cd > Cr (Sabry, *et al.,* 2012).

Al-Degs *et al*. (2006) mentioned that based on conventional theory, metals with higher electronegativities should adsorb more readily; and so it was in the case of the studied metals. This same theory suggests that metals of higher hydrolysis constants have better adsorption

capacities (Appel and Ma, 2002). Since the chemisorption of metals also depends on the electrostatic force of attraction as proposed by McBride (1994), it clearly suggests that the adsorption of the selected metal ions on the standard reference soil in this study is through electrostatic interactions. Similar reports have been given by McKay and Porter, (1997) and Serrano *et al.* (2005).

5.7.1 Comparison of the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} in the single and mixed systems

The two-way ANOVA replicate statistical tool was employed in order to make comparison in the adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} in all the systems as shown in Table 4.4. According to the table, at 95 % confidence limit ($\alpha = 0.05$), the p values; 8.4×10^{-80}, 2.2×10^{-38}, and 5.2×10^{-83} representing the respective variations in the sample, columns and interactions show that $p < 0.05$. This therefore implies that at $p \leq \alpha$ there is a significant difference in the means of adsorption of Cd, Cr, Cu and Pb in each of the systems. Hence, it is evident that the metals actually competed for the same binding sites with one another. This agrees with the reports by Chen *et al*. (2010) and Sabry *et al*. (2012).

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

The aim of this research was to assess the competitive adsorption of Cd, Cu, Cr and Pb ions onto a standard reference soil. This research showed that soil is an efficient adsorbent for the sorption of the metal ions studied. The effects of varying parameters: concentration (10 to 40 mg/dm^3), adsorbent dosage (0.5 to 2.0 g), contact time (1 - 3 hrs), at room temperature and pH 5.5 of the soil were investigated. The overall percentage adsorption for all the metal ions in the batch experiments except for Cr^{6+} ($\leq$ 32.34%) ranged between 91.08 and 99.57 %. The SEM results showed a remarkable physical disintegration on the soil surface after adsorption of the metal ions. The percentage adsorption of Pb^{2+} increased as the initial concentration increased up to 40 mg/dm^3 while the adsorption of Cd^{2+}, Cr^{6+} and Cu^{2+} increased with initial concentration up to 20 mg/dm^3, and then gradually decreased as the initial metal ion concentration increased.

Increments in adsorption were observed at adsorbent dosages of 0.5 g to 1.5 g for Cd^{2+} and 0.5 g to 1.0 g for Pb^{2+}, Cu^{2+} and Cr^{6+} after which further increment of adsorbent resulted in a decline in adsorption capacity. The adsorption of all the metals (except cadmium at 3 hrs) reached equilibrium within 2 hrs. Freundlich isotherm gave a better fitting than Langmuir isotherm for all the metals in terms of R^2 values. Cd had the greatest sorption capacity as estimated by the maximum sorption parameter (q_{max}) of the Langmuir equation. The ranked affinity of the selected metals for the soil was Cu > Cd > Pb > Cr according to the Freundlich parameter K_f. The kinetic studies carried out showed that the R^2 values of the pseudo second order model were higher ($\geq$0.951) than that of the pseudo- first order model ($\leq$0.004) and the calculated adsorption

capacities of all the metals by pseudo- second order model were closer to their respective experimentally determined adsorption capacities than those from the pseudo- first order model. Hence, adsorption of these metal ions on the soil can be said to have occurred as a result of electrostatic reactions.

In the competitive experiment, the results showed that the adsorption capacity of the metals decreased as the number of competing ion(s) increased such that the least adsorption capacity was recorded in the quaternary system. Apparently due to Pb's chemical characteristics such as relatively high electronegativity, lower pK_H, small hydrated radius and electronic structure, this metal was the strongest adsorbed than other studied metals. Additionally, statistical results showed that at 95 % confidence limit ($\alpha = 0.05$), there were significant differences in the means of adsorption of Cd, Cr, Cu and Pb among the groups of systems examined. The lowest percentage of adsorbed Cd was obtained as 31.89 % in the presence of Cr and Pb (in the ternary system). Competition significantly decreased the adsorption of Cd, Cu and Pb onto the soil surface.

6.2 Conclusion

These studies showed that the standard reference soil material has a high capacity to adsorb metal ions especially those of Cd, Cr, Cu and Pb. Based on the results obtained from this research, the following conclusions can be deduced:

The adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} by the standard reference soil is dependent on the initial metal ions concentrations of the solution, the mass of soil used and the contact time of the adsorption process.

The pseudo- second order adsorption model is more suitable to describe the adsorption kinetics of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} by the standard reference soil. This implies that the adsorption process is by chemical sorption**.**

The presence of competing ions led to a significant reduction in the adsorption of Cd^{2+}**,** Cu^{2+} and Pb^{2+} onto the soil.

The selectivity of the metal ions (Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}) onto the standard reference soil in the competitive system is highly influenced by the difference in their electronegativity and hydrolysis constant parameters.

6.3 Recommendation for Further Studies

(i) The composition of the standard reference soil has been well-known, its physical characteristics are acceptably uniform and can be used in experiments without further preparation (washing or sizing). However, it is recommended that a single source be used by participants in inter-laboratory studies to mitigate the effects of any differences in the experimental processes.

(ii) The application of the soil standard reference material as a model or reference standard for subsequent research on adsorption by other soil materials is also suggested.

(iii) Further work on the removal of other heavy metals by this soil considering the effects of other parameters such as temperature, pH, ionic strength and agitation speed with appropriate modifications may be investigated. Similarly, the analysis of metal pairs using mole ratios instead of mass loading may be useful in understanding the stoichiometry involved in the adsorption reactions.

(iv) It is also advisable to try working at higher initial concentrations above 40 mg/dm^3 for selected metal systems, as adsorption behaviour may be different from that at low concentrations.

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APPENDICES

Appendix I: The Base Trace Metals Concentrations in the Standard Reference Soil

Element	Concentration ± SD
Aluminium	5.95 ± 0.05 %
Antimony	1.55 ± 0.06 mg/kg
Arsenic	10.50 ± 0.30 mg/kg
Barium	730.00 ± 15.00 mg/kg
Boron	20.00 mg/kg
Cadmium	0.37 mg/kg
Calcium	0.97 ± 0.05 %
Chromium	23.00 ± 6.00 mg/kg
Cobalt	5.99 ± 0.14 mg/kg
Copper	33.90 ± 0.50 mg/kg
Iron	3.36 ± 0.07 %
Lead	0.00173 ± 0.00001 %
Magnesium	1.46 ± 0.02 %
Manganese	529.00 ± 18.00 mg/kg
Mercury	0.90 ± 0.20 mg/kg
Nickel	8.00 ± 1.00 mg/kg
Phosphorus	0.07 %
Potassium	2.11 ± 0.06%
Selenium	1.50 mg/kg
Silicon	30.30 ± 0.40 %

Sodium	1.22 ± 0.03 %
Uranium	3.15 ± 0.05 mg/kg
Zinc	103.00 ± 4.00 mg/kg
Zirconium	195.00 ± 46.00 mg/kg

Appendix II: **Effects of Initial Metal ion Concentrations, Adsorbent Dose and Contact time on the Adsorption of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+}**

Initial Conc (mg/L)	Cadmium		Chromium		Copper		lead	
	q_e(mg/g)	% Ads	q_e(mg/g)	% Ads	q_e(mg/g)	% Ads	q_e(mg/g)	% Ads
10	0.31	94.38	0.092	27.58	0.325	97.44	0.307	92.02
20	0.65	97.78	0.255	38.29	0.659	98.78	0.629	94.41
30	0.96	96.31	0.002	0.19	0.979	97.94	0.965	96.50
40	1.27	95.33	0.000	0.00	1.298	97.32	1.295	97.11
Adsorbent dose(g)								
0.5	1.822	91.08	0.676	33.82	1.983	99.18	1.921	96.07
1.0	0.934	93.41	0.409	40.90	0.996	99.57	0.971	97.07
1.5	0.661	99.22	0.255	38.29	0.659	98.78	0.629	94.41
2.0	0.489	97.78	0.161	32.34	0.494	98.74	0.470	93.95
Time (hr)								
1	0.978	97.78	0.383	38.29	0.988	98.78	0.944	94.41
2	0.982	98.16	0.567	56.71	0.990	98.95	0.949	94.94
3	0.984	98.43	0.533	53.31	0.987	98.68	0.949	94.88

Appendix III: Equilibrium Data for Plotting Langmuir and Freundlich Isotherms of the Selected Heavy Metals

Ce (mg/ dm^3)	q_e (mg/g)	Log qe (mg/g)	Log Ce (mg/ dm^3)	1/Ce (dm^3/mg)	1/qe (g/mg)
Cadmium					
0.56	0.32	-0.50	-0.25	1.78	3.18
0.45	0.65	-0.19	-0.35	2.25	1.53
1.11	0.96	-0.02	0.05	0.90	1.04
1.87	1.27	0.10	0.27	0.53	0.79
Chromium					
7.242	0.09	-1.04	0.86	0.14	10.88
12.34	0.26	-0.59	1.09	0.08	3.92
29.94	0.00	-2.73	1.48	0.03	535.71
40.00	0.00	0.00	1.60	0.03	0.00
Copper					
0.26	0.33	-0.49	-0.59	3.91	3.08
0.24	0.66	-0.18	-0.61	4.10	1.52
0.62	0.98	-0.01	-0.21	1.62	1.02
1.07	1.30	0.11	0.03	0.93	0.77
Lead					
0.80	0.31	-0.51	-0.10	1.25	3.26
1.12	0.63	-0.20	0.05	0.90	1.59
1.05	0.96	-0.02	0.02	0.95	1.04
1.16	1.30	0.11	0.06	0.87	0.77

Appendix IV: Equilibrium Data for Plotting the Kinetics Model for the Selected Metals

Ce (mg/dm^3)	q_t (mg/g)	q_e (expt (mg/g)	qe– qt (mg/g)	log(qe -qt (mg/g)	t/qt (hr)
Cadmium					
0.45	0.98	0.98	0.01	-2.18	1.02
0.37	0.98	0.98	0.00	-2.56	2.04
0.31	0.98	0.98	0.00	0.00	3.05
Chromium					
12.34	0.38	0.57	0.18	-0.73	2.61
8.66	0.57	0.57	0.00	0.00	3.53
9.34	0.53	0.57	0.03	-1.47	5.63
Copper					
0.244	0.99	0.99	0.00	-2.79	1.01
0.211	0.99	0.99	0.00	0.00	2.02
0.264	0.97	0.99	0.00	-2.58	3.04
Lead					
1.119	0.94	0.95	0.01	-2.28	1.06
1.013	0.95	0.95	0.00	0.00	2.11
1.024	0.95	0.95	0.00	-3.26	3.16

Appendix V: Amounts of Cd^{2+}, Cr^{6+}, Cu^{2+} and Pb^{2+} Adsorbed (in mg/g) in the Single and mixed system

	Amount of metal adsorbed (mg/g)			
System	Cadmium	Chromium	Copper	Lead
Single	0.938	0.152	0.983	0.997
Binary(Cd + Cr)	0.493	0.358	-	-
Binary(Cd + Pb)	0.475	-	-	0.499
Binary (Cr + Cu)	-	0.382	0.493	-
Binary(Cr + Pb)	-	0.378	-	0.500
Binary (Cu + Pb)	-	-	0.499	0.500
Binary(Cd + Cu)	0.446	-	0.498	-
Ternary (Cr+Cu+Pb)		0.280	0.333	0.333
Ternary (Cd+Cr+Pb)	0.324	0.261	-	0.333
Ternary (Cd+Cr+Cu)	0.319	0.222	0.330	-
Quaternary(Cd+Cr+Cu+Pb)	0.239	0.212	0.250	0.250
Total average mean	0.294	0.204	0.308	0.310