UNIVERSITY OF NAIROBI

DEPARTMENT OF CHEMISTRY

ADSORPTION OF HEAVY METALS FROM AQUEOUS SOLUTIONS USING MANGROVES FROM KENYAN COAST

BY:

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DECLARATION

I declare that this thesis is my original work and has not been submitted elsewhere for examination, award of a degree or publication. Where other people's work or my own work has been used, this has properly been acknowledged and referenced in accordance with the University of Nairobi's requirements.

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DEDICATION

To my beloved parents, Dad Salesio, Mom Sabina and My fiancé, Chris.

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ABSTRACT

In this study, adsorption of heavy metals (copper, lead, zinc and cadmium) from aqueous solutions was investigated using mangrove biomass from the Kenyan Coast. The efficacy of mangrove biomass on the removal of divalent metal ions from aqueous solutions was investigated in single state in batch mode. Batch experiments involved the study of the effects of initial pH, temperature, initial concentration of the metal ion, adsorbent dosage and contact time on metal ions adsorption. The roots showed highest ability for the uptake of heavy metals (Cu, Zn, Cd and Pb) from aqueous solutions and were therefore used for all subsequent adsorption studies in this research. The adsorption of the heavy metal ions increased with increase in the ratio of the sample dose of the adsorbent to concentration of the heavy metal ions and decreased with increasing adsorbent particle size. Increase in shaking speed was observed to increase the amount of ions that adsorbed on the adsorbent. However, agitation rate beyond 500 rpm led to a decrease in percentage adsorption. When mangrove roots adsorbent was compared with other adsorbent materials, the results indicate good sorption properties. Langmuir and Freundlich adsorption models were used for mathematical description of adsorption equilibrium. Evaluating the correlation coefficients showed that both Freundlich and Langmuir isotherm described the data appropriately. The adsorption capacities (Q_{max}) from the Langmuir isotherm for Pb (II), Zn (II), Cd (II) and Cu (II) were found to be 13.698 mg/g, 6.211 mg/g, 5.495 mg/g and 11.36mg/g respectively. The effectiveness of mangrove roots in the sorption of the four metals from aqueous system was Pb (II) > Cu (II) > Zn (II) and Cd (II). Kinetic studies showed that a pseudo second order model was more suitable than the pseudo first order model. These results indicated that mangrove roots can be used as low cost adsorbent for the removal of heavy metals from aqueous solutions.

Keywords: *Adsorption, Batch technique, Heavy metal ions, Mangroves and Kinetics.*

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LIST OF ABBREVIATIONS AND SYMBOLS

AAS	Atomic Absorption Spectrophotometer
APANFS	Aminated Polyacrylonitrile Fibres
AW	Atomic weight of the metal (g/mol)
C_e	Equilibrium concentration (mg/L)
Cell-PAN	Cellulose polyacrylonitrile
Cell-PMAN	Cellulose polymethylacrylonitrile
C_o	Adsorbate initial concentration (mg/L) or mg/Kg
DMDHEU	Dimethyloldihydroxy ethylene Urea
DNA	Deoxyribonucleic Acid
ESR	Erythrocyte Sedimentation Rate
FTIR	Fourier Transform Infrared
KBr	Potassium bromide
K_F	Freundlich adsorption capacity constant (mg/g)
MW	Molecular weight of salt used (g/mol)
n	Adsorption intensity
Q_{max}	Adsorption capacity (mg/g)
R^2	Correlation coefficient
ppm	Parts per million equivalent to mg/L
PVC	Polyvinylchloride
q_e	Mass of metal ions adsorbed at equilibrium (mg/g)
q_t	Mass of metal ions adsorbed at time, t (min)
rpm	Rotations per minute
UNDP	United Nations Development Programs
USPHS	United States Public Health Services
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

CHAPTER ONE

1.0 INTRODUCTION

Water pollution by heavy metals has been a major concern for chemists and environmental engineers (Etorki, 2014). Heavy metals are of concern because of their toxicity, bio-accumulating tendency, threat to human life and the environment (Dorris *et al.*, 2000). United States Public Health Service (USPHS) defines polluted water as the presence of any foreign substance (organic, inorganic, radiological or biological) in water which tends to degrade its quality to the extent that it constitute a hazard or impairs the usefulness of water.

Pollutants enter aquatic systems via numerous pathways, including metal finishing, electroplating, painting, dying, photography, surface treatment and printed circuit board manufacture (Papageorgiou *et al.*, 2006). Heavy metals can also enter water bodies via mining activities, agricultural run-off and domestic effluent which lead to increase in metallic species released into the environment (Churong *et al.*, 2013).

Heavy metals are non-biodegradable and extremely toxic because as ions or in certain compounds, they are soluble in water. They may be ingested and absorbed in the body where they tend to combine with proteins and inhibit the functioning of particular enzymes (Kobya *et al.*, 2005).

Heavy metals are associated with myriad adverse health effects, including allergic reactions (e.g., beryllium, chromium), neurotoxicity (e.g., lead), nephrotoxicity (e.g. mercury, cadmium), and cancer (e.g., arsenic and hexavalent chromium). Therefore metals are of special concern because of their persistency and toxicity due to their ability to bind with proteins and prevent DNA replication (Das *et al.*, 2007).

There are several methods for treatment of metal contaminated effluents such as chemical precipitation (Wingenfelder *et al.*, 2005), coagulation–flocculation (Semerjian and Ayoub, 2003; Ayoub *et al.,* 2001), reverse osmosis (Metcalf and Eddy, 2003), ultra-filtration (Semerjian and Ayoub, 2003), electro-dialysis (Metcalf and Eddy, 2003) and ion exchange (Ayoub *et al.*, 2001). These methods have their inherent advantages and limitations in application.

Chemical precipitation, reverse osmosis, ultra-filtration, electrochemical and deposition become inefficient when contaminants are present in trace concentration, and do not seem to be economically feasible for relevant industries because of their relative high costs. Activated carbon is most widely used adsorbent, as it has good capacity for adsorption of carcinogenic metals. However, high cost of activated carbon, readily solubility under extreme pH conditions and 10-15% loss during the regeneration, has deterrents in the utilization of activated carbon in developing countries (Sharma and Foster, 1996).

There is increasing research interest in using alternative low-cost adsorbents. Many materials have been investigated, including microbial biomass, compost, peat, coal, leaf mould, palm press fiber, sugarcane bagasse, straw, wool fiber and by products of rice milling, cotton seeds hulls and soybeans. Coal and straw, are inexpensive but ineffective while ion exchange resins are totally effective but expensive. Peat moss has been found as very effective in adsorbing heavy metals. Quek *et al*. (1999) used sago processing waste, which is both a waste and a pollutant, to adsorb lead and copper ions from solution. Mahavi *et al*. (2005) used tea waste as an adsorbent for the removal of heavy metals from industrial wastewater.

Among all these methods, adsorption process is preferred well than other methods because of convenience, easy operation and simplicity of design (Gupta and Babua, 2006). In addition, adsorption has gained a lot of credibility because of its eco- friendly nature, excellent performance and cost effectiveness (Amboga *et al*., 2014). Further, this process can remove different types of pollutants and thus have wider applicability in water pollution control.

A fundamentally important characteristic of good adsorbents is their high porosity and consequent larger surface area with more specific adsorption sites (Bhatnagar and Sillanpaa, 2010). Adsorption was one of the alternatives for above mentioned techniques and is an effective purification and separation technique used in industry especially in water and wastewater treatments. Adsorption is the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. Adsorption has advantages over other methods. The design is simple, selective for some metal ions and sludge-free and can involve low investment in terms of both the initial costs of materials and land (Hashem, 2007).

Adsorption utilizes the ability of certain materials to accumulate nuisance pollutants from aqueous solutions by either metabolically mediated or physico-chemical pathways of uptake. Sathish *et al.* (2014) recently reported on the efficacy of mangrove leaf powder (MLP) for bioremediation of chromium (VI) from aqueous solutions. The study found out that adsorption was affected by parameters like, particle size, solution pH, initial concentration of Cr (VI) ion and adsorbent dose.

1.1 STATEMENT OF THE PROBLEM

Discharge of pollutants containing heavy metals into water systems is one of the most serious environmental problems globally (Das *et al*., 2007; Ibrahim *et al*., 2010). With the rapid industrialization in developing and developed countries, large volumes of wastes containing heavy metals are generated and directly or indirectly discharged into water ecosystems thus posing significant danger to human health.

Throughout history, human progress has depended on access to clean water and on the ability of societies to harness the potential of water as a productive resource (UNDP, 2006). Water for life in the household and water for livelihoods through production are two of the foundations for human. Therefore there is a growing concern that the world is facing a crisis of shortage of clean water that if left unchecked, will derail progress towards the Millennium Development Goals and hold back human development.

Heavy metals are of concern because once they get into the environment, they bio-accumulate and bio-magnify as they go through the tropic levels of the food chain. Furthermore, metals being inorganic, they are non-biodegradable. It is therefore important that they are excluded from circulation in the ecosystem due to various neurological, reproductive and systemic impacts on humans and negative impacts on other animals especially the aquatic species.

Conventional physicochemical methods for metals remediation include chemical precipitation, filtration, coagulation, evaporation, ion exchange, membrane separation and solvent extraction. However, application of such processes is always expensive and ineffective in terms of energy and chemical products consumption, especially at low metal concentrations of 1–100 mg/L (Wang and Chen, 2009).

Therefore, there is a great need for an alternative technique, which is both economical and efficient. Adsorption has been shown as the most appealing as an economic and environmental friendly procedure to remove heavy metals in wastewater (Ahmad *et al.*, 2009). Activated carbon is the most popular material used as an adsorbent. However, it is quite expensive. The search for alternative adsorbents to replace the costly activated carbon is highly encouraged. Adsorption, based on live or dead adsorbent, has been regarded as a cost-effective biotechnology for the treatment of complex wastewater containing heavy metals at high volume and low concentration (Amboga *et al.*, 2014).

The present work investigated the usage of a low- cost adsorbent obtained from untreated mangroves for heavy metal removal from aqueous solutions in batch systems since the adsorbent material is abundant, locally available and relatively cheap. The parameters influencing adsorption phenomenon such as the initial metal ions, biomass dosage, contact time, particle part, particle size, temperature, shaking speed and pH were also investigated.

1.2 OBJECTIVES

1.2.1 Overall Objective

To establish the potential of mangroves as an adsorbent material for the removal of heavy metals from aqueous solutions.

1.2.2 Specific Objectives

1. To determine the effects of pH, contact time, temperature and adsorbent dose, initial concentration of selected metal ions (Cu, Pb, Cd and Zn), shaking speed and particle sample part on the removal of selected metal ions from aqueous solution.
2. To investigate the equilibrium removal of selected metal ions in terms of adsorption isotherms. Langmuir and Freundlich adsorption isotherm modeling to fit the experimental data obtained.
3. To determine the sorption capacity of the mangroves for selected metal ions removal.
4. To investigate the kinetics of selected metal ions removal from aqueous solutions by fitting the experimental data with the pseudo first order and pseudo second order reactions.

1.3 JUSTIFICATION AND SIGNIFICANCE OF THE STUDY

Industrial activities release about 300 to 400 million tons of heavy metals, solvents, toxic sludge and other waste into the world waters each year (UNDP, 2006). Coupled with the increasingly and rapidly growing population, this has created serious water quality challenges and consequently most of the water sources are unfit for human consumption.

Research has shown that many of the technologies for the removal of heavy metals from wastewater such as reverse osmosis and filtration are very expensive for a developing country like Kenya and some produce sludge whose disposal also raises concern. It is because of this that technologies involving use of low cost adsorbent material for heavy metals removal is being sought across the globe.

This research is part of that process of developing an alternative technology for utilizing cheap effective and available mangroves for the adsorptive removal of heavy metals from aqueous solutions.

CHAPTER TWO

2.0 LITERATURE REVIEW

Heavy metals, is a term used to describe elements that are metallic or metalloids and have a relatively high density (ranging between 63.546 and 200.590) and are toxic or poisonous at low concentrations (Thakur and Parmar, 2013). Examples of heavy metals include copper (Cu), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb).

As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning (Mataka *et al*., 2006). Heavy metal poisoning could result, for instance, from drinking-water contaminated with heavy metal (e.g. lead pipes), high ambient air concentrations near emission sources or intake via the food chain. Heavy metals are dangerous because they tend to bio-accumulate. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted (Ahmad *et al*., 2009).

Water bodies can be polluted by heavy metals through different natural and artificial activities (Mataka *et al*., 2006). The major sources and methods of water pollution include:

Petroleum products: These include spillage from ships, trunk tanker, pipelines and underground spillage. Sometimes improper refinery process which lead to production of toxic by-products which find their way to the water systems.

Synthetic agricultural chemicals: Chemicals like fungicides, insecticides and herbicides accumulate in plants and animals (Buajan and Pumijumnong, 2010). When these plants and animals die, the chemicals do not decompose but instead they are washed to the water bodies by rainfall and this increases toxicity of water.

Hazardous wastes: These results from improper treatment of radioactive, reactive and ignitable materials .They become toxic when they get to water systems.

Excess organic matter: Chemical fertilizers, sewage sludge and animal wastes on entering the water source encourage excessive algal growth and during decomposition of dead algae a lot of dissolved oxygen are used up and as a result there is increase in mortality of flora and fauna (Mataka *et al*., 2006). At the same time decaying materials turns water murky.

Sediments: Soil particles washed by storms and floods from unprotected soils enter water bodies. Accumulation of sediments in water makes it murky. Mass accumulation of mud in water systems interferes with water clarity (Buajan and Pumijumnong, 2010).

Thermal pollution: Warm water from power plants changes the species makeup of aquatic ecosystem which in turn alters the composition of water.

2.1 SOURCES, USES AND TOXICITIES OF SELECTED HEAVY METALS

2.1.1 Lead

Lead accounts for most cases of pediatric heavy metal poisoning. It is a very soft metal and is used in pipes, drains and soldering materials. About 80-90% of lead emissions into the atmosphere are caused by the combustion of alkyl Pb additives in motor fuel but their degree of pollution varies from country to country (Ziemacki *et al*., 1989). Most of this lead is used for batteries and the remainder is used for cable coverings, plumbing ammunition and fuel additives. Lead targets the bones, brain, blood, kidneys and thyroid gland. Symptoms include abdominal pain, convulsions, hypertension and kidney dysfunction, loss of appetite, fatigue, and sleeplessness (Gupta and Ali, 2004). In addition to symptoms found in acute lead exposure, symptoms of chronic lead exposure could include allergies, arthritis, autism, colic, hyperactivity, mood swings, nausea and numbness, lack of concentration, seizures and weight loss.

Chronic exposure to lead may result in birth defects, mental retardation, autism, psychosis, allergies, dyslexia, hyperactivity, weight loss, shaky hands, muscular weakness and paralysis (Mataka *et al*., 2006). Children who are particularly sensitive to lead, are prone to ingesting it because they chew on painted surfaces and eat products not intended for human consumption (e.g., hobby paints, cosmetics, hair colorings with lead-based pigments and playground dirt).

2.1.2 Cadmium

Cadmium is a byproduct of mining and smelting of lead and zinc. Zinc production constitutes the largest source of cadmium supply (Ziemacki *et al*., 1989). Cadmium is used in nickel-cadmium batteries, PVC plastics and paint pigments. Lesser known sources of exposure are dental alloys, electroplating, motor oil and exhaust. Inhalation accounts for 15-50% of absorption through the respiratory system; 2-7% of ingested cadmium is absorbed in the gastrointestinal system. Cadmium targets the liver, placenta, kidneys, lungs, brain and bones (Feng *et al*., 2011). Symptoms of chronic exposure could include alopecia, anemia, arthritis, learning disorders, migraines, growth impairment, emphysema, osteoporosis, loss of taste and smell, poor appetite and cardiovascular disease (Sathish *et al.*, 2014).

2.1.3 Copper

Copper is a reddish metal with a face-centered cubic crystalline structure. Copper is used for electrical equipment (60%); roofing, plumbing and other construction applications (20%), industrial machinery such as heat exchangers (15%) and alloys (5%). Copper is ideal for electrical wiring because it is easily worked, can be drawn into fine wire and has a high electrical conductivity (Churong *et al*., 2013). Copper can be found in many kinds of food, in drinking water and in air. Because of that, we absorb significant quantities of copper each day by eating, drinking and breathing. The absorption of copper is necessary, because copper is a trace element that is essential for human health. Although humans can handle proportionally large concentrations of copper, too much copper can still cause eminent health problems (Sharma *et al*., 2004). Copper concentrations in air are usually quite low, such that exposure to copper through breathing is negligible. Occupational exposure to copper often occurs in the work place environment. Copper contagion is caused by oversensitivity leading to a flu-like condition known as metal fever.

Long-term exposure to copper can cause nose, mouth and eyes irritation, headaches, stomachaches, dizziness, vomiting and diarrhea (Odell and Campbell, 1971). Chronic copper poisoning results in Wilson’s disease which characterized by a hepatic cirrhosis, brain damage, demyelization, renal disease and copper deposition in the cornea. Recommended daily intake of copper is 2mg (UNEP, 2008).

2.1.4 Zinc

Zinc is a transition metal whose atomic number is 65.38. In 1978, the United States Environmental Protection Agency (USEPA) published a list of organic and inorganic pollutants which are found in waste water and constitute serious health hazards. The list included zinc which is essential in lower concentrations. In higher concentrations (100-500 mg/day), it has serious effects including depression, lethargy, neurologic signs such as seizures and ataxia and increased thirst (Meena *et al*., 2005). WHO recommended maximum acceptable concentration of zinc in drinking water is 5.0 mg/L. Main sources of zinc discharge into the environment include automobiles, petroleum refining, pulp and paper industry, steel industry, organic chemicals, inorganic chemicals, fertilizers, steel power plants, acid-mine drainage and metal plating (Sharma *et al*., 2004).

2.2 HEAVY METAL REMOVAL FROM AQUEOUS SOLUTIONS

Various water treatment technologies have been developed for the purification of aqueous water contaminated by heavy metals (Farooq *et al.*, 2010). The most commonly used methods include reverse osmosis, chemical precipitation, adsorption and ion exchange. Among these methods, adsorption has emerged the best and especially for those which cannot be removed by other techniques (Mohan and Kunwar, 2001). The most common adsorbents used for heavy metal removal from aquatic systems are outlined below.

2.2.1 Agricultural by-products and Seeds

Basic components of the agricultural waste materials (hemicellulose, lignin, lipids, proteins, simple sugars, hydrocarbons and starch) contain a variety of functional groups. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, abundant availability, renewable nature and low cost provide a promising alternative to solve environmental problems and also to reduce the preparation costs. In the last several decades, various agricultural wastes have been explored as low-cost adsorbent. Some of them include sawdust (Ajmal *et al*., 1996), coir pith (Parab, 2006), straw (Chun *et al.,* 2004), husks (Eromosele *et al*., 1996), leaf mould (Sharma and Forster, 1996), cork powder (Machado *et al*., 2002), fruit gum dust (Samantaroy *et al*., 1997), sugar beet pulp (Altundogan, 2005), rice bran (Oliveira *et al.,* 2005), rice hulls (Marshal and Wartelle, 2004) and wheat bran (Farooq *et al*., 2010). These agricultural waste materials have been used in their natural form or after some physical or chemical modification. Functional groups like carboxyl, hydroxyl, sulphydryl and amido present in these biomaterials, make it possible for them to attach metal ions from waters (Farooq *et al*., 2010).

2.2.2 Zeolites

Zeolites have crystalline, hydrated alumino-silicates of alkali and alkaline earth cations, having infinite three-dimensional structures. There are 40 natural and over a hundred synthetic zeolites. Only seven (mordenite, clinoptilolite, chabazite, erionite, ferrierite, phillipsite and analcime) occur in sufficient quantity and purity to be considered exploitable (Kesraoui *et al.*, 1994). They are also considered as selective adsorbents. Zeolites-based materials are extremely versatile and their main use include detergent manufacture, ion-exchange resins, catalytic applications in the petroleum industry, separation process and as an adsorbent for water, carbon dioxide and hydrogen sulfide. Various zeolites have been employed for the removal of pollutants (Motsi *et al*., 2009). Clinoptilolite was reported to have effectively removed heavy metals from aqueous solutions (Can *et al*., 2010). Among the minerals that possess adsorbent properties, zeolites appear as the most promising for metal purification, they have therefore received increasing attention for pollution control. The zeolites can be regenerated using sodium chloride with a regeneration efficiency of more than 90% (Kurniawan and Babel, 2002).

2.2.3 Nano-technology

Nano-porous materials are those materials having pore diameters less than 100 nm. They possess unique surface, structural and bulk properties that underline their important uses in various fields such as ion exchange, catalysis, sensor, biological molecular isolation and purification. Most of the atoms on the surface of the nanoparticles are unsaturated and can easily bind with other atoms. Besides, the operation is simple, and the adsorption capacity is high and rapid. There is therefore a growing interest in the application of nanoparticles as adsorbents. Modified nano partcles and also composite nano materials have been reported to have good adsorbent properties (Afkhami *et al*., 2010).

2.2.4 Organic Resins

Both commercial (Rengaraj *et al.*, 2003) and synthetic organic resins (Wartelle and Marshall, 2005) were investigated for heavy metal remediation. Soybean hulls, sugarcane bagasse and corn stover were converted to functional anion exchange resins using dimethyloldihydroxy ethylene urea (DMDHEU) and choline chloride. Chromate ion adsorption suggested that modification with both DMDHEU and choline chloride was required for the highest efficiencies.

2.2.5 Fibres

Pejic *et al.* (2009) explored sorption potential of waste short hemp fibers for Pb^{2+}, Cd^{2+} and Zn^{2+} ions from aqueous media. However, due to swelling properties, the fibers need to be cross linked to a rigid substrate. Cr (III) and Cr (VI) were significantly removed using synthesized aminated polyacrylonitrile fibers (APANFs).

2.2.6 Carbon Steel

There are very many reports discussed in this review (Sheng *et al*., 2012) where activated carbons demonstrated high Cr (VI) removal from drinking water. The adsorption capacity of the carbon steel powder was deemed high due to ferro-chromium electrochemical redox processes at carbon steel surface sites.

2.2.7 Lignite, Peat, Chars and Coals

Peat, a complex composed of lignin, cellulose, fulvic and humic acids as its major constituents has been recognized as a natural humic substance which can trap cations.
Lignite and peat have received increasing attention for wastewater treatment (Allen *et al*., 1997). Lignin and peat are plentiful, inexpensive and locally available. Peat is comparable to carbon, silica, alumina in both adsorption capacity and cost. Since peat is highly polar, it adsorbs large quantities of metals which make it competitive with other adsorbents (Parab, 2006).

2.2.8 Hydroxide/Hydrotalcite

Hydrotalcite have the structural formula $[M_{1-x}\,IIM_xIII\,(OH)_2]^{x+}A_{x/n}\,n{-}yH_2O$, where MII and MIII denote divalent (e.g. Mg, Ni, and Zn) and trivalent (e.g. Al, Fe, and Cr) metals, respectively. A*n* - represents interlayer anions, such as NO^{3-}, SO_4^{2-}, and CO_3^{2-}, and x typically ranges from 0.17 to 0.33 (Laziridis and Asouhidou, 2003).

The presence of large interlayer spaces and a significant number of exchangeable anions makes Hydrotalcite to be good ion-exchangers and adsorbents. Various techniques have been tested for chromium remediation using various hydroxide/Hydrotalcite compositions (Goswamee *et al*., 1998).

2.2.9 Clay minerals and oxides

The adsorption of Cd (II), Cr (III), Cu (II), Ni (II) and Zn (II) ions on montmorillonite a type of clay using column operators has been investigated (Abollino *et al.,* 2003). Another material from clay mineral to adsorb metal is bentonite, which consists of clay, silt and sand. Clay minerals and oxides are widespread and abundant in both aquatic and terrestrial environments. Finely divided clay minerals and oxides exhibit large surface areas. They adsorb cationic, anionic and neutral metal species. They also take part in cationic and anionic exchange processes.

2.2.10 Alginate Geothite beads

Alginate goethite beads are used for Cr (VI) and Cr (III) removal from binary aqueous solutions. They are prepared by adding a dispersion of sodium alginate (1%, w/v) and goethite (2%, w/v) into a continuously stirred calcium chloride solution (0.3 mol/ L).

2.2.11 Gels

Cr (VI) and Cr (III) adsorption by persimmon tannin (PT) gel (Nakajima and Baba, 2004) effectively removed Cr (VI) but smaller amounts of Cr (III). Maximum Cr (VI) adsorption occurred at pH 3.0. The gel which adsorbed Cr (VI) from solution (pH 1.0 and 3.0) showed no Cr (III) ESR signal, but this Cr (III) signal was observed in the residual solution at pH 1.0. Hexavalent chromium was adsorbed through chromate ester formation at catechol. Cr (VI) should combine with catechol as a hard acid, CrO_2^{2+} cation. Other gels that have been reported include polyacrylamide aerogel (Ramadhan, 2010) and polyacrylamide hydrogels (Kasgoz *et al*., 2008).

2.2.12 Polymers

Cellulosic graft copolymers were made by reacting bast fibers of the kenaf plant (*Hibiscus cannabinus*) with acrylonitrile and methacrylonitrile monomers in aqueous media (Eromosele and Bayero, 2000). The cellulose–polyacrylonitrile (Cell–PAN) graft copolymer was a more effective Cr (III) sorbent than cellulose–polyacrylonitrile (Cell–PAN). The amount of Cr (III) sorbed decreased with an increase in the graft weight fraction. Increasing the graft percent from 38 to 149% lowered Cr (III) sorption in Cell–PAN by 56%. The methyl groups in Cell–PMAN reduced the sorption affinity of the copolymer for Cr (III). The relative stabilities of the metal ion complexes with the hydroxyl and nitrile ligands appear to dominate the sorption processes.

2.2.13 Industrial waste/by-products

A number of industrial wastes have been investigated with or without treatment as adsorbents for the removal of pollutants from wastewaters (Thakur and Parmar, 2013). These include fly ash, steel industry waste (blast furnace slag and sludge), aluminum industry sludge, fertilizer waste leather sludge and paper industry sludge. Like agricultural waste, industrial by-products are inexpensive and abundantly available and have wide pH ranges (1.5-9.0) (Meena *et al*., 2005). In addition to this, these materials are effective for metal removal in inorganic effluent with metal concentration of less than 20 mg/L, in the range of 20-100 mg/L or higher (Hegazi, 2013).

2.2.14 Lignin

This is an amorphous cross-linked resin which serves as main binder for the agglomeration of fibrous cellulosic components (Allen *et al.,* 1997). Lignin also provides a shield against rapid microbial or fungal destruction of the cellulosic fibers**.** Lignin is a major component of wood, accounting for 23–33% of softwood mass and 16–25% of hardwood mass. Lignin, obtained as a by-product from the paper and pulp industry in the form of powder and beads was used for adsorption of Cr (III), Cr (VI), Pb (II) and Zn (II) from aqueous solutions.

2.2.15 Silica gel

Silica gel is a chemically inert, nontoxic, polar and dimensionally stable (< 400°C) amorphous form of SiO_2 (Wang *et al*., 2009). It is prepared by the reaction between sodium silicate and sulfuric acid, which is followed by a series of after-treatment processes such as aging and pickling. There are three classes of silica gel: regular, intermediate and low density gels. Regular density silica gel is prepared in an acid medium and shows high surface area (e.g. 750m^2/g). Intermediate and low density silica gels have low surface areas (300–350 and 100–200m^2/g respectively). The gel is considered a good adsorbent and is used in many industries (Bhatnagar and Sillanpaa, 2010). Modified forms of silica have also been widely explored for the removal of different pollutants.

2.2.16 Activated carbon

Activated carbon is produced by a process consisting of raw material dehydration and carbonization followed by activation. The product obtained is known as activated carbon and generally has a very porous structure with a large surface area ranging from 600 to 2000m^2/g (Bhatnagar and Sillanpaa, 2010). Activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment throughout the world. Charcoal, the forerunner of modern activated carbon has been recognized as the oldest adsorbent known in wastewater treatment. Activated carbon has been found to be a versatile adsorbent, which can remove diverse types of pollutants such as metal ions, anions dyes, phenols, detergents, pesticides, humic substances, chlorinated hydrocarbons and many other chemicals and organisms. In spite of abundant uses of activated carbon, its applications are sometime restricted due to its higher cost. Activated carbon has been shown to have very effective sorption properties for cadmium, chromium, zinc and copper in sewage waters (Argo and Gulf, 1972).

2.2.17 Activated alumina.

Activated alumina is used for a wide range of adsorbent and catalyst applications including the adsorption of catalysts in polyethylene production, in hydrogen peroxide production, as a selective adsorbent for many chemicals including arsenic, fluoride and selenium and sulphur removal from gas streams (Claus Catalyst process). Alumina has been reported to have good adsorbent properties in the removal of pollutants (Naiyaa *et al.,* 2009).

2.2.18 Chitosan

Chitosan is the deacylated product of chitin, a polysaccharide consisting predominantly of unbranched chains of β-(1→4)-2-acetamido-2-deoxy-D-glucose. Chitosan is found naturally in fungi and arthropods in which it is the main component of the exoskeleton. It can be prepared from fishery wastes and is obtained from shrimp, lobster, crab shell and cuttlebone.

2.3 MANGROVES

Mangrove refers to a group of plants which belong to several families (species that distinctly belong to their own evolutionary group). The term indicates an ecological rather than a taxonomical (scientific classification) grouping - the species are not related. Mangroves are woody and grow in the inter-tidal areas between land and sea in the tropic and subtropical latitudes (Kathiresan and Bingham, 2001).

Mangroves are unique plants because of their ability to grow in unstable tough environments. They are unique because they are able to thrive in areas where the water is poor in oxygen content, in salt water, in fresh water and in brackish water (a mixture of salt and fresh water). This is because mangroves have very specialized adaptations that enable them to live in salty waters (Mandy *et al*., 2014). An example of these specialized features that make them adaptive to the coastal environment includes pneumatophores (breathing roots) which allow them to survive in anaerobic sediments. Buttresses and above ground roots enable them to grow in unstable mudflats. Their foliage removes excess salt from the sap and they conserve water to cope with periods of high salinity. Their seeds are buoyant to allow them to disperse and establish themselves in new areas (http://mbgnet.mobot.org/salt/mudflat/mangrove.htm). However, these adaptations vary among taxonomical orders and with the physico-chemical nature of the habitat (Chakraborty *et al*, 2013). Because of these unique adaptations, mangroves thrive well in the estuarine brackish water environment which is in hospitable to other plants.

Mangroves are slow-growing trees taking several years to reach up to 25 meters when they are fully grown. They act as sinks which concentrate pollutants such as toxic chemicals, metal ions, sewage, pesticides and herbicides. However excess pollutants accumulation destroys them. Besides, they play an important role in providing goods and services to human which include aquaculture, forestry, protection against shoreline erosion, firewood and building material and other subsistence products like honey, wax and essence (Tan *et al*., 2012). In addition mangroves wetlands are a good nursery grounds for a number of commercially important aquatic organisms (Mandy *et al*., 2014).

It is found that in spite of their importance, mangrove ecosystems have been exploited and have been subjected to inappropriate management practices including land reclamation and unsustainable forestry, as well as agricultural and aquaculture practices (Chakraborty *et al*, 2013). Due to close proximity to urban development, they are exposed to significant direct contaminant input, including heavy metals (MacFarlane and Burchett, 2002). Urban and agricultural runoff, industrial effluents, boating and recreational use of water bodies, chemical spills, sewage treatment plants, leaching from domestic garbage dumps and mining operations are the major sources of heavy metal inputs in mangrove ecosystem.

In Kenya, about 54,000ha is under mangrove forests most of which is in Lamu and Tana River counties (Doute *et al.*, 1981). These comprise of 9 species but 70% of the species population consists of *Rhizophora mucronata* and *Ceriops tagal*. Other species include *Sonneratia-Rhizophora*-giant *Aviccenia*, *Rhizophora-Bruguiera-Ceriops*, dwarf *Aviccenia-Lumnitzera-Xylocarpus*, *Pemhis acidula* and *Barringtonia racemosa* (Kathiresan and Bingham, 2001). Of the seven types of mangroves, the three most dominant are the red, black and white types.

2.3.1 Black Mangroves

Black mangroves are easily identified by their roots which are specialized to take in oxygen. Roots look like tubular bristles which grow vertically and trap oxygen for its oxygen-starved root systems. These bristles are known as pneumatophores. The black mangrove is tolerant to high saline conditions and the trees grow in isolated groups or woodland formations. Individual trees are fairly large and may grow up to 20-25 meters in height and 40 centimeters in diameter at breast height.

Black mangroves produce seeds in abundance which occurs throughout the year. The seeds are viviparous in nature, meaning they germinate while still being attached to the parent tree. This species regenerates and coppices well and can therefore be managed under a coppice system, which is an even-aged silvicultural system for which the main regeneration method is vegetative sprouting of either suckers or shoots (Kathiresan and Bingham, 2001).

2.3.2 Red Mangroves

This is an evergreen tree, which grows to about 25 meters in height and 40 centimeters in diameter at breast height. Trees are immediately recognized by their elaborate prop and aerial root system which stabilizes the trees. The roots contain a waxy substance that helps keep salt out. Where salt gets through, salt is deposited in older leaves and the tree then sheds them (Mandy *et al.*, 2014).

The seed like parts, the propgules, are large pre-germinated 'seedlings' known locally as 'monkey whistles'. A single seed germinates inside the conical fruit forming a long narrow first root (radical), which is green except for the brown enlarged and pointed end up to 1.25 centimeters in diameter. It can grow up to 30 centimeters in length before it detaches from the mother tree and falls. They need a longer period from 16 to 30 months to mature from flower bud to mature seedlings. Red mangroves do not respond well to cutting and are very sensitive. If 50% or half the leaves are removed from the tree then it will die. The wood can be converted into good quality charcoal and the bark produces high quality tannin which is suitable for leatherwork (Kathiresan and Bingham, 2001).

2.3.3 White Mangroves

These are the shortest of the three species (reaches 5.6 meters and a diameter of 30 centimeters) and have un-buttressed roots. This species normally grows in clay or silty clay soils in the back portion of Mangrove swamps, and remains unaffected by tidal inundation, except during spring tides (Mandy *et al*., 2014). The bark is light brown to reddish dark brown and the leaves are ovate. The leaves have adapted to their salty environment by developing special openings (glands) that allow salt to pass from inside the tree to the outside. The leaves are coated with speckled white salt crystals which give this species its name, i.e. white mangroves.

2.4 ADSORPTION

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms; the adsorbate (Thakur and Parmar, 2013). It is different from absorption, whereby a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption, ion exchange, and chromatography are sorption processes in which certain adsorbate are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. Adsorbents used are usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm.

Adsorption is governed by four consecutive steps.

1. Transport in the bulk of the solution (bulk diffusion).
2. Diffusion across the liquid film boundary surrounding adsorbent particles (film diffusion).
3. Intraparticle diffusion in the liquid contained in the pores and adsorbate along the pore walls (pore diffusion).
4. Sorption and desorption within the particle and on the external surface (adsorption).

The adsorption step takes place in three phases. The first phase is the rapid uptake phase in which there is instantaneous utilization of the most readily available adsorbing sites on the adsorbent. The second phase called transition phase, which involves additional removal of the adsorbate attributed to the diffusion of the adsorbate from the surface film into the micro pores of the adsorbent. The last phase is a state of equilibrium attained after some time.

2.4.1 Types of Adsorption Processes

Adsorption is divided into two major categories: Physisorption and chemisorption.
In physisorption, the molecules of adsorbate are held by van der Waal's forces. Van der Waal's interactions are long range but are weak, and the energy released when a particle is physisorbed is of the same order of magnitude as the enthalpy of condensation (Atkins, 1999). Since van der Waal forces are not sufficiently strong they do not influence appreciably the reactivity of the molecules adsorbed. In this type of adsorption, the equilibrium is reversible and is established rapidly.

Chemisorption involves the formation of a chemical linkage between the adsorbed molecule and the surface of adsorbate and thus, it is highly selective unlike physical adsorption. According to Langmuir's original concept of chemisorption, the adsorbed molecules are held to the surface by valence forces of the same type as those occurring between bound atoms in molecules. The enthalpy of chemisorption is very much greater than that of physisorption (Atkins, 1999).

2.4.2 Adsorption isotherms models

An adsorption isotherm is an invaluable curve describing the phenomenon governing the retention (or release) or mobility of a substance from the aqueous porous media or aquatic environments to a solid-phase at a constant temperature and pH (Limousin *et al*., 2007).
Adsorption equilibrium (the ratio between the adsorbed amount with that remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution in a dynamic balance with the interface concentration (Reddy *et al.,* 2011). Typically, the mathematical correlation which constitutes an important role towards the modeling analysis, operational design and applicable practice of the adsorption systems, is usually depicted by graphically expressing the solid-phase against its residual concentration. Its physicochemical parameters together with the underlying thermodynamic assumptions provide an insight into the adsorption mechanism, surface properties as well as the degree of affinity of the adsorbents (Aravind *et al*., 2013).

Over the years, a wide variety of equilibrium isotherm models (Langmuir, Freundlich, Brunauer–Emmett–Teller, Redlich–Peterson, Dubinin–Radushkevich, Temkin, Toth, Koble–

Corrigan,Sips, Khan, Hill, Flory–Huggins and Radke–Prausnitz isotherm), have been formulated in terms of three fundamental approaches. Kinetic consideration is the first approach to be referred. Hereby, adsorption equilibrium is defined as a state of dynamic equilibrium, with both adsorption and desorption rates being equal. Whereas, thermodynamics, being a base of the second approach is based on thermodynamics which provide a framework of deriving numerous forms of adsorption isotherm models. Potential theory, the third approach, usually conveys the main idea in the generation of characteristic curve. However, an interesting trend in the isotherm modeling is the derivation in more than one approach thus leading to the difference in the physical interpretation of the model parameters (Reddy *et al*., 2011)

2.4.2.1 Langmuir isotherm model

The Langmuir isotherm was developed by Irving Langmuir in 1916. The isotherm describes quantitatively the buildup of a layer of molecules on an adsorbent surface as a function of concentration of adsorbed materials in the liquid phase in which it is in contact. Langmuir assumes that a surface consists of a given number of equivalent sites where species can physically or chemically bind.

Langmuir isotherm is based on the following assumptions (Aravind *et al*., 2013):

- Adsorption cannot proceed beyond monolayer coverage onto a surface containing finite number of adsorption sites.
- Adsorbent surface sites are equivalent (with uniform energies of adsorption) and can accommodate at most one molecular or atomic species of the adsorbate.
- Adsorbate species on different sites do not interact with each other and there is no transmigration of the adsorbate on the plane of the surface.

When the whole surface of the adsorbent is completely covered by a unimolecular layer of the adsorbate, further adsorption is not possible and it indicates a saturation of adsorbent.
Graphically, it is characterized by a plateau, an equilibrium saturation point where once a molecule occupies a site, no further adsorption can take place. Moreover, Langmuir theory has related rapid decrease of the intermolecular attractive forces to the rise of distance. The mathematical expression of Langmuir isotherm models are:

$$q_e = \frac{Q_e b c_e}{1 + b c_e} (nonlinear \ \ form) \tag{1}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_{\max} b} + \frac{1}{Q_{\max}} C_e \quad (linear \ \ form) \tag{2}$$

Where: q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mgL^{-1}), Q_{max} the monolayer adsorption capacity (mgg^{-1}) and b is the Langmuir constant which reflects the binding strength between metal ions and adsorbent surface (Lmg^{-1}). b is the reciprocal of the concentration at which half saturation of the adsorbent is reached.

2.4.2.2 Freundlich isotherm model

Freundlich isotherm is known to describe the non-ideal and reversible adsorption and is not restricted to the formation of monolayer. This empirical model can be applied to multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over the heterogeneous surface.

$$q_e = K_F C^{1/n} \quad (non\,linear \ \ form) \tag{3}$$

$$\log q_e = K_F + \frac{1}{n} \log C_e \ (linear \ \ form) \tag{4}$$

Where: q_e is the amount of solute adsorbed per unit weight of adsorbent (mgg^{-1}), C_e the equilibrium concentration of solute in the bulk solution (mgL^{-1}), K_F a constant indicative of the relative adsorption capacity of the adsorbent (mgg^{-1}) and the constant $1/n$ indicates the intensity of the adsorption. n is considered as the heterogeneity of the adsorbate and its affinity for the adsorbent. A higher value of n (or a smaller value of 1/n) indicates a stronger bond between the adsorbate and the adsorbent.

2.4.3 Adsorption kinetic studies

The kinetics of heavy metal adsorption onto the mangrove biomass can be predicted using pseudo-first-order and pseudo-second-order models. Pseudo-first-order model is used to describe the reversibility of the equilibrium between solid and liquid phases (Vijaya and Yun, 2008). The model assumes that the metal cation binds only on one sorption site on the sorbent surface. The pseudo-first-order model is expressed by the equation shown below.

$$\log(q_e - q_t) = \log c_e - \frac{K_1}{2.303}t \tag{5}$$

Where: q_e and q_t are the amounts of heavy metal adsorbed (mg g^{-1}) at equilibrium and at the time (t min) and k_1 is the rate constant of the pseudo-first-order adsorption process (min^{-1}). Linear plots of log (q_e - q_t) versus t are used to predict the rate constant (k_1) and adsorption at equilibrium (mg g^{-1}), which are obtained from the slope and intercept respectively. The pseudo-second-order equation assumes that the rate limiting step might be due to chemical adsorption. According to this model, metal cations can bind to two binding sites on the adsorbent surface. The equation can be expressed as shown below.

$$\frac{t}{q_t} = \frac{1}{k_2 q^2{}_e} + \frac{1}{q_e}t \tag{6}$$

Where: k_2 is the rate constant of the pseudo-second-order adsorption ($gmg^{-1}min^{-1}$). If the adsorption kinetics obeys the pseudo-second-order model, a linear plot of t/q_t versus t can be observed. The slope of the plot will give the value of calculated adsorption at equilibrium ($q_e$calc), while the intercept gives the value of the rate constant (k_2).

CHAPTER THREE

3.0 MATERIALS AND METHODS

Mangrove samples (leaves bark and roots) were collected from Dongo Kundu (Port area) in Mombasa County on 20th of February, 2013.

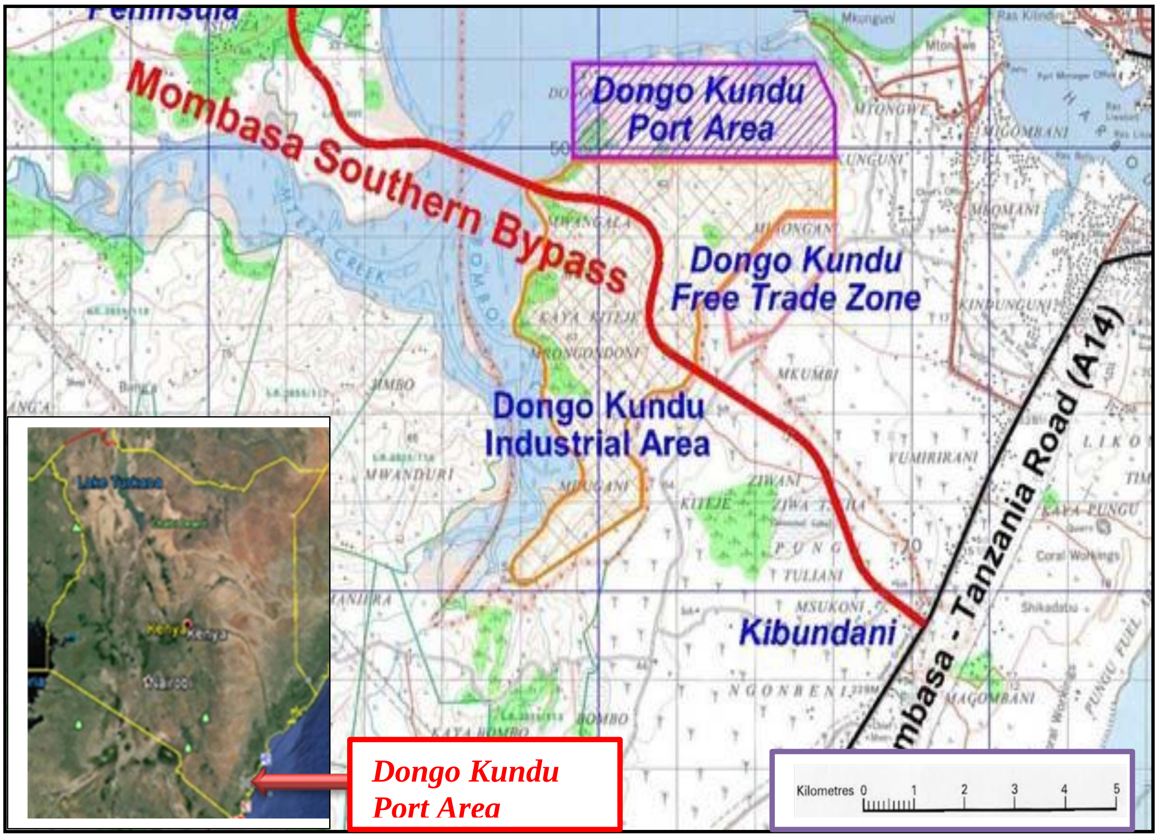

Figure 1: Map of sampling site in Dongo - Kundu port area; Mombasa County. (Source: www.wikimapia.org; July, 2014).

The samples were washed with water to remove soil, adhering dirt and soluble particles. Cleaned samples were then oven dried at 80°C for 24 hours in order to obtain biomass in completely dried form. The dried mangrove samples were then ground into fine powder using mechanical grinder after which the powder was soaked and washed severally with both cold and hot tap water until clean. Clean mangrove powder was then soaked for 24 hours in cold distilled water, washed thoroughly and then dried in an oven at 80°C for 24 hours. Dried sample were finally sieved into different particle sizes namely, < 300µm, > 300 < 425µm and > 425µm and stored in plastic containers for further analysis.

Figure 2: Mangroves Trees along Dongo Kundu Coastline, Mombasa Kenya. (Source: Author).

3.1 BATCH ADSORPTION EXPERIMENTS

Batch experiments were conducted using 60ml propylene bottles to which metal ions solution and biomass were added. These bottles were agitated in an orbital shaker at a constant speed of 200rpm to study the effect of parameters such as pH, adsorbent dosage, initial metal ion concentration, contact time and temperature. Samples were withdrawn at appropriate time intervals and filtered. The filtrates were used for analysis of the residual metal ion concentration using an atomic absorption spectrophotometer (AAS). The percentage metal ions removed by various parts of mangroves were calculated from the differences between the initial (C_0) and equilibrium (C_e) adsorbate metal ion concentration which is given by the equation:

$$\% \text{ Removal} = \; = \frac{C_0 - C_e}{C_0} \times 100 \qquad (7)$$

The effect of pH on metal ion removal was studied over a pH range of 2-8. The pH was adjusted by addition of dilute aqueous solutions of 0.1M HCl or 0.1M NaOH. In order to determine optimum adsorption (i.e. amount of metal ion adsorbed per unit mass of adsorbent), 30mL portions of metal solutions were dosed with different amounts of mangrove biomass and placed on an orbital shaker set at a predetermined speed and for a predetermined equilibration time.

The kinetics of adsorption was determined by analyzing adsorptive uptake of the metal ions from the aqueous solutions at different time intervals. Adsorption isotherms were computed using adsorption data obtained when different metal ion concentrations were used on fixed amounts of mangrove biomass at equilibrium. In addition, the effect of temperature on sorption characteristics was investigated by varying the temperature from 25 to 70°C using a thermo stated oven with temperature controls. To study the effects of this parameter, a known concentration of metal ion solution was used on a known weight of mangrove biomass. The solutions were kept at their natural pH.

All pH measurements were made using Exstik II EC 250 pH/conductivity/TDS meter. A test sieve (Retsch 5657) was used to separate the ground sample into different sizes. A thermometer and an incubator (model Gallenkamp orbital incubator) were also used to monitor the effect of temperature on the adsorption. Solutions were constantly agitated using an orbital shaker (Maximix Type 65800, Thermolyne) for all the experiments except the experiment involving temperature where the Gallenkamp orbital incubator was equipped with a shaker. Gravity filtration was done through micro filter with 0.47um pore size and a stop watch was also used to monitor time. A mechanical grinder was used for grinding while an analytical balance (Fisher scientific A 160) was used for all weight measurements. Residual and initial concentrations were determined using Flame atomic absorption spectrophotometer (CTA 2000 AAS). Volumetric flasks (1000, 2000, 500, 250, 100, 50, 25 and10 mL) were used in preparations and dilutions of the solutions. Propylene bottles were used for conducting the experiments.

All reagents used were of analytical grade. Working solutions were prepared by appropriate dilutions of the stock solutions of cadmium sulphate ($3CdSO_4.8H_2O$), copper (II) sulphate

($CuSO_4.5H_2O$), lead (II) nitrate (Pb (NO_3)$_2$ and Zinc (II) sulphate ($ZnSO_4.7H_2O$). Stock solutions of 1000 mg/L were prepared by dissolving appropriate masses in double distilled water as shown in Table 1. Adjustments of pH were made using 0.1M hydrochloric acid and 0.1M sodium hydroxide. Sodium hydroxide (0.1 M) solution was prepared by dissolving 4.0g in double distilled water. Hydrochloric acid (0.1 M) solution made by dissolving an appropriate amount of 12M concentrated acid (Aldrich Company) in double distilled de-ionized water.

3.2 ADSORBENT CHARACTERIZATION

The Fourier transform infrared (FTIR) spectra of the sample were obtained using Fourier transform infrared spectrophotometer (Shimadzu, FTIR System 8400 Model, Japan) in the range of 500 to 4,000 cm^{-1}. The spectra of mangroves were recorded before copper, cadmium, lead and zinc adsorption. FTIR spectrum of the sample was obtained by KBr pellet method. A homogenous mixture of the sample and KBr in the ratio 1:5 was made. The pellet was made by taking a mixture in a KBr die and a press of 5 ton was applied using hydraulic pressure for 2 minutes. Then the pellet was removed and placed in a pellet holder. The instrument was switched on and a background scan obtained without placing the pellet. The pellet was placed and the scan obtained. The data was plotted using standard software provided with the instrument.

For elemental analysis, PAN analytical Axiosmax X-ray Fluorescent spectroscopy was used An amount of 1.0g of mangrove roots powder of particle size < 300um was placed in a sample holder before and after copper, lead, zinc and cadmium adsorption. The samples were subjected to the XRF spectrometer system where each of them was measured for 30 seconds. The spectra obtained as a result of X-ray excitation using rhodium x-ray source were then analyzed and concentration of the element present in the samples plotted using standard computer software provided with the instrument.

3.3 PREPARATION OF STOCK AND WORKING SOLUTIONS

Stock solutions (1000ppm) of copper, lead, cadmium and zinc metal were prepared by dissolving appropriate amounts of their salts (Table 1) in distilled water and topping up the volume to the mark. The formula below was used to calculate the amount of the salt weighed:

$$W = \frac{mw}{aw} \times \frac{100}{p} \times \frac{v}{100} \tag{8}$$

where : W is the weight of the salt used (g), mw is the molecular weight of the salt (gmol^{-1}), aw is the atomic weight (g), P is the percentage purity of the salt (%) and v is the volume of the stock solution to be prepared (mL).

Table 1: Amount of Salt Weighed to make Stock Solutions (1000ppm)

Metal	**Metal salt**	**MW**	**Amount weighed (g)**	Volume of volumetric flask (mL)
Cadmium	$3CdSO_4.8H_2O$	769.56	13.7096	2000
Copper	$CuSO_4.5H_20$	249.68	7.8984	2000
Lead	$Pb(NO_3)_2$	331.20	3.2132	2000
Zinc	$ZnSO_4.7H_20$	287.54	8.8400	2000

Working solutions were prepared from stock solutions (prepared in table 1) using the formula given below:

$$C_0V_0 = C_1V_1 \tag{9}$$

Where: C_0 = Concentration of the stock solution, ppm (mg L^{-1}).

C_1 =Concentration of the working standard solution, ppm (mg L^{-1}).

V_0 = Volume of the stock solution to be withdrawn for dilution, ml.

V_1 = Volume of the working solution to be prepared, ml.

3.4 OPERATING CONDITIONS FOR AAS ANALYSIS

Table 2: Operating Conditions for AAS Analysis

Conditions	**Cu**	**Zn**	**Cd**	**Pb**
Wavelength (nm)	324.2	213.9	228.8	283.3
Lamp current (mA)	3.5	4	5	3.5
Fuel	acetylene	acetylene	acetylene	acetylene
C_2H_2 Flow (L/min)	3.5	1.5	1.5	1.5
Support	air	air	air	air
Spectral band pass (nm)	0.5	1.0	0.5	0.5
Flame stoichiometry	Oxidizing	Oxidizing	Oxidizing	Oxidizing
Standard interval (ppm)	2-8	0.5-5	0.5-2	2-10

Source: AAS instruction manual CTA 2000 and Spectra-AA.

3.5 INVESTIGATING FACTORS THAT AFFECT ADSORPTION

3.5.1 Effect of Sample Weight and Particle Size.

(a) (b) (c)

Figure 3: Mangrove; (a) Leaves, (b) Bark and (c) Roots.
(Source: Author)

Dried samples were crushed using a mechanical grinder and sieves of different mesh sizes (425, 300, 75 µm) were employed to produce different micrometer size particle populations (> 425, > 300 < 425, and < 300). An amount of 0.25 g < 300 µm particle size of mangroves roots were weighed into a 60 mL polypropylene container. To the material, 30 mL of 50ppm aqueous Cu^{2+} were added and the mixture equilibrated for 30 minutes under agitation of 200 rpm. The mixture was then filtered and the filtrate tightly closed in a container awaiting determination of the residual concentration by AAS. The procedure was repeated using the same volume and concentration but different masses of 0.50g, and 1.0 g of the mangroves. The procedure was repeated using mangroves of particle sizes; > 300 µm and > 425 µm. The whole procedure was repeated using the same volume and concentration of Zn^{2+}, Cd^{2+} and Pb^{2+} in place of Cu^{2+} solution.

3.5.2 Effect of Shaking Speed on Adsorption of Metal Ions

An amount of 0.20g of mangroves portions were weighed into several polypropylene containers containing 50mL of 30ppm of copper (II) solution and the mixtures allowed to equilibrate on an orbital shaker operated at speed ranging from 100 to 600rpm for 20 minutes. The mixtures were then filtered and the concentrations of the filtrates determined using AAS.

3.5.3 Comparative Adsorption of Different Parts of Mangrove Plant

An amount of 0.125g of < 300 µm root samples were weighed in polypropylene containers and mixed with 30ml of 50 ppm Cu^{2+}ions. The mixtures were allowed to equilibrate on an orbital shaker operated at 200 rpm for 20 minutes after which the mixture was filtered and the residual concentration of the filtrate taken using atomic absorption spectrophotometer. The procedures were repeated using different weights of the same particle size of the root samples. The above procedures were also repeated using the bark and leaves of the same particle size of < 300 µm.

3.5.4 Effect of Equilibration Time and Initial Concentration on Adsorption of Metal Ions

The effect of contact time was studied at room temperature. Copper (II) solution of initial concentration 50ppm was prepared by serial dilution of stock solution (1000ppm). A volume of 20mL of the above mentioned solution was added into 60mL propylene containers containing 0.5g of the adsorbent for different contact times (0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 minutes). No pH adjustments were made and all the studies were carried out at their natural pH. After a predetermined time interval the contents of the container were filtered into propylene containers and the residual concentrations of copper determined by

AAS. These procedures were repeated with 200ppm and 1000ppm of the copper solutions. The procedures were repeated using Cd^{2+} (50, 200 and 1000 ppm), Zn^{2+} (50, 200 and 1000 ppm) and Pb^{2+} (50, 200 and 1000ppm).

3.5.5 Effect of Temperature on Adsorption of Metal Ions

To study the effect of temperature, Cu (II) solution of initial concentration 200ppm was prepared by serial dilution of 1000ppm. An amount of 0.5 g of mangroves and 20 mL of 200 ppm of Cu^{2+} were put in the orbital shaker set at 200rpm and the two allowed to attain thermal equilibrium for about 30 minutes at the required temperature ($25^{\circ}C$, $30^{\circ}C$, $40^{\circ}C$, $50^{\circ}C$, $60^{\circ}C$ and $70^{\circ}C$). The mixture was then filtered and residual concentration of metal determined by atomic absorption spectrometry. The procedure was repeated using aqueous solutions of Cd^{2+} (200ppm), Pb^{2+} (200ppm) and Zn^{2+} (200ppm) ions.

3.5.6 Effect of pH on Adsorption of Metal ions

The effect of pH was studied by varying solution pH from 2 to 8 using 0.1M HCl and 0.1M NaOH. A volume of 20mL of copper (II) sulphate solution with initial concentration of 50ppm prepared from serial dilution of stock solution (1000ppm) were added to the 0.25g mangrove roots in a polypropylene containers for each of the pH values after which the mixture was equilibrated on an orbital shaker for 20 minutes, filtered and concentration of Cu^{2+} measured using AAS. The procedure was repeated for 200 ppm copper ions Zn^{2+} (50, 200ppm), Cd^{2+} (50, 200, ppm) and Pb^{2+} (50, 200ppm).

3.5.7 Effect of Mangrove Roots Adsorbent Dosage

Aqueous solutions of Cu^{2+} ions (50, 100, 200, 300, 400, 500 and 600ppm) were prepared from the stock solution using appropriate dilution factors. Different weights (0.125, 0.25, 0.5, 1.0, 2.0g) of mangroves were then weighed into 60 mL polypropylene containers. 20 ml portions of the copper ion solution of known concentrations were added to each of the containers and equilibrated on an orbital shaker for 20 minutes. The mixtures were filtered into 50ml polypropylene containers and the concentration of copper determined using atomic absorption spectrophotometer. The above procedure was repeated with Zn^{2+}, Cd^{2+}, and Pb^{2+} ions.

3.5.8 Effect of Initial Concentration of Metal ions on Adsorption

Copper (II) ion solutions of different concentrations, ranging from 50-600ppm were prepared. A volume of 30ml of each of Cu^{2+} solutions were added to 0.25g of sample particle size < 300µm. The mixtures were then equilibrated for 30 minutes on an orbital shaker operated at 200 rpm after which the mixtures were filtered and residual concentration determined. The procedure was repeated using different masses (0.25, 0.5 and 1.0g) but same volume of adsorbate and residual concentrations for each run determined using atomic absorption spectrophotometer (CTA 2000-AAS). The procedure used for AAS analysis was repeated using Cd^{2+}, Zn^{2+} and Pb^{2+}.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSIONS

4.1 ADSORBENT CHARACTERIZATION

4.1.1 Fourier Transform Infrared Spectrum

Fourier Transform Infrared (FTIR) analysis was carried out in order to identify the functional groups in the adsorbent that might be involved in the adsorption process. The FTIR spectrum of untreated Mangrove roots is shown in Figure 4.

The FTIR spectra of untreated mangrove roots displayed a number of absorption peaks, which indicates the complex nature of the adsorbent. The characteristic broad band peak between 3372cm^{-1} and 3358.80cm^{-1} indicates the presence of hydrogen-bonded -OH groups in mangrove roots sample. The 1378.04cm^{-1} absorption band is attributable to the O-H in plane deformation in polyphenols (Nakano *et al*., 2001).

The absorption band observed at 2930.03cm^{-1} is assigned to the C-H aliphatic stretch of methyl and methylene groups. The 1739cm^{-1} absorption band may also be attributed to carbonyl group, C = O, while the region 1150-1400cm^{-1} represents deformation of carbon-carbon bond in the phenolic groups as reported by Ozer and Ozer (2003). The signal at 1330.79cm^{-1} and 1056.92cm^{-1} in the spectrum are due to O-H bending belonging to a phenol group while the absorption band at 1640cm^{-1} and 1618cm^{-1}suggests presence of C = C alkenes. In addition the band position at 1321.15cm^{-1}and 1370.4cm^{-1} represents C-H cellulose while the peak at 1254.61cm^{-1} and 1158.17cm^{-1} represents an O-H phenolic. The weak bands of the FTIR spectrum at 1108.03cm^{-1}and 1158.17cm^{-1} represents the existence of C-O functionalities on mangrove roots surface while the characteristic peak between 647.07cm^{-1} and 536.87cm^{-1} is associated with C-S stretching.

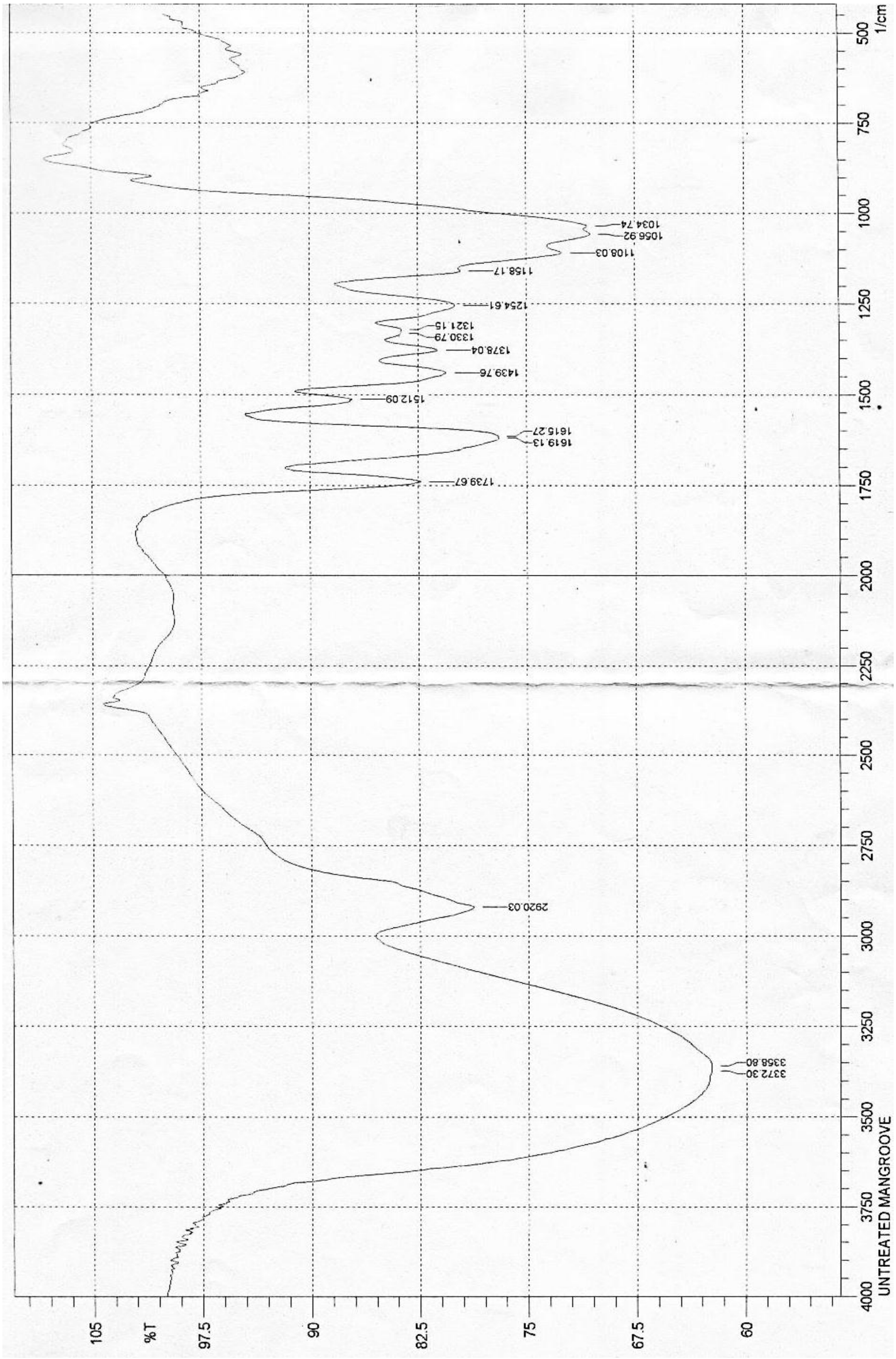

Figure 4: FT-IR Spectrum of Untreated Mangrove Roots.

The presence of these polar groups on the mangrove roots surface is likely to provide the considerable cation exchange capacity to the adsorbent (Abdel, 2009). Seey and Jain (2012) studied characterization of mangrove bark based on the FTIR spectra. Results indicated the presence of –OH, -COOH, -NH_2, -COO- and C = C which could act as important binding sites for cationic dyes and heavy metal ions as well.

Numerous hydroxyl groups in the molecules of these compounds represent main active sites for binding of ionic compounds, usually by an ion-exchange mechanism. However, some other binding mechanisms may occur on the root sorbents, such as hydrogen bonding or hydrophobic interactions on the non-polar moieties of the root matrix (Tan *et al.,* 2012).

4.1.2 X-Ray Fluorescence

Different elements have characteristic X-ray peaks at different wavelengths. Fluorescence intensity of each spectral line is related to the element concentration (Zhang *et al.,* 2012). The XRF spectrometer was used to analyze the elemental composition of adsorbents. Elemental characterization of mangrove roots before and after treatment with copper (II), lead (II), zinc (II) and cadmium (II) ions with initial concentration of 50ppm is shown in Figures 5 to 9.

XRF analysis is made to predict the type and concentration of elements embedded with crystallographic structure (Hegazi, 2013). The XRF spectrum of untreated mangrove roots (Figure 5) indicates the presence of calcium at 3.6keV and iron at 6.0keV. Rhodium at 2.4keV emerged from rhodium beam which was used as a source of energy.

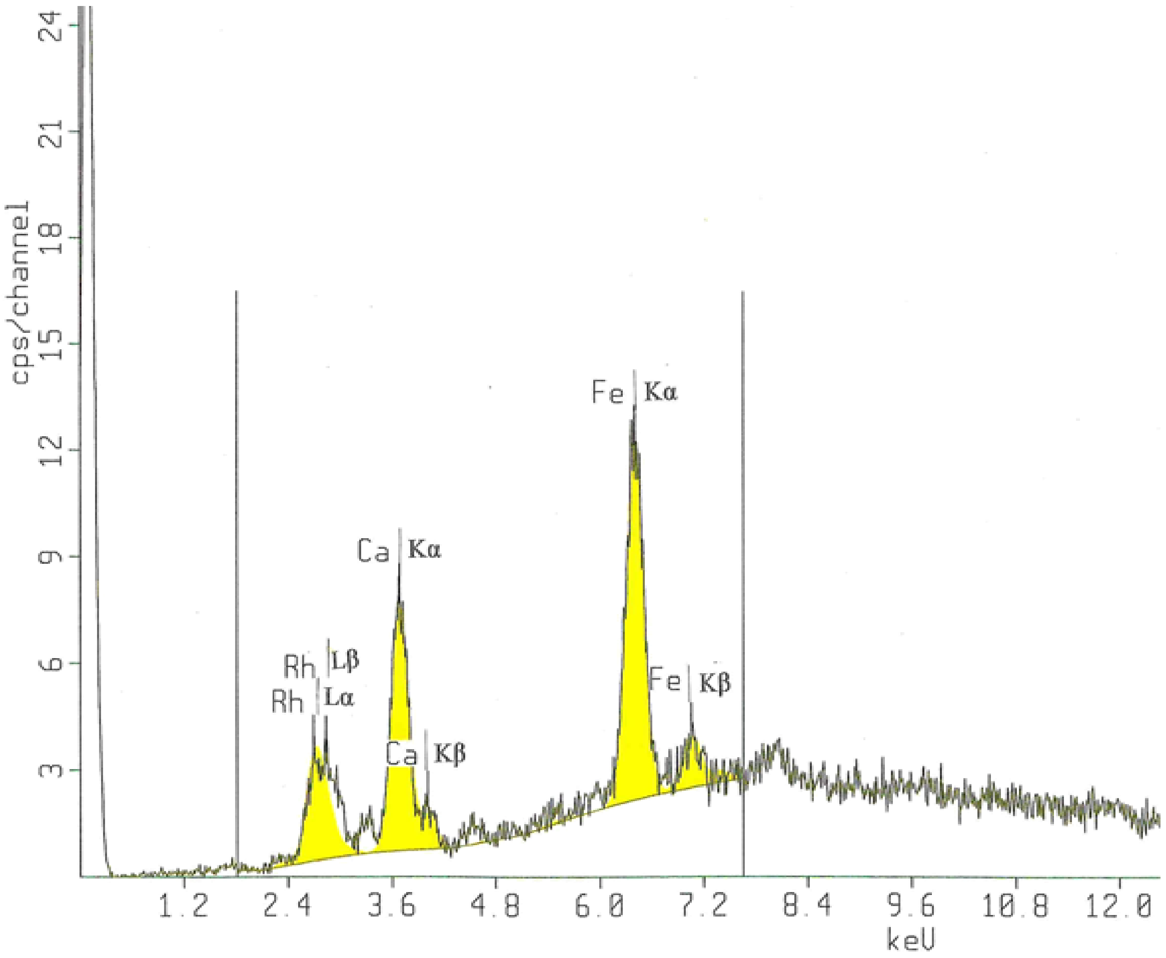

Figure 5: XRF Spectrum of Untreated Mangrove Roots.

The presence of these elements in mangrove roots can be explained due to the favorable availability of the metals in plants mainly those growing in flooded soils (Tarley and Arruda, 2004). Low concentrations of these elements and the absence of Cu, Pb, Zn and Cd indicate the potentiality of mangrove roots for trace metals effluent treatment. The elemental composition of mangrove roots treated with Pb (II) ions is shown in Figure 6.

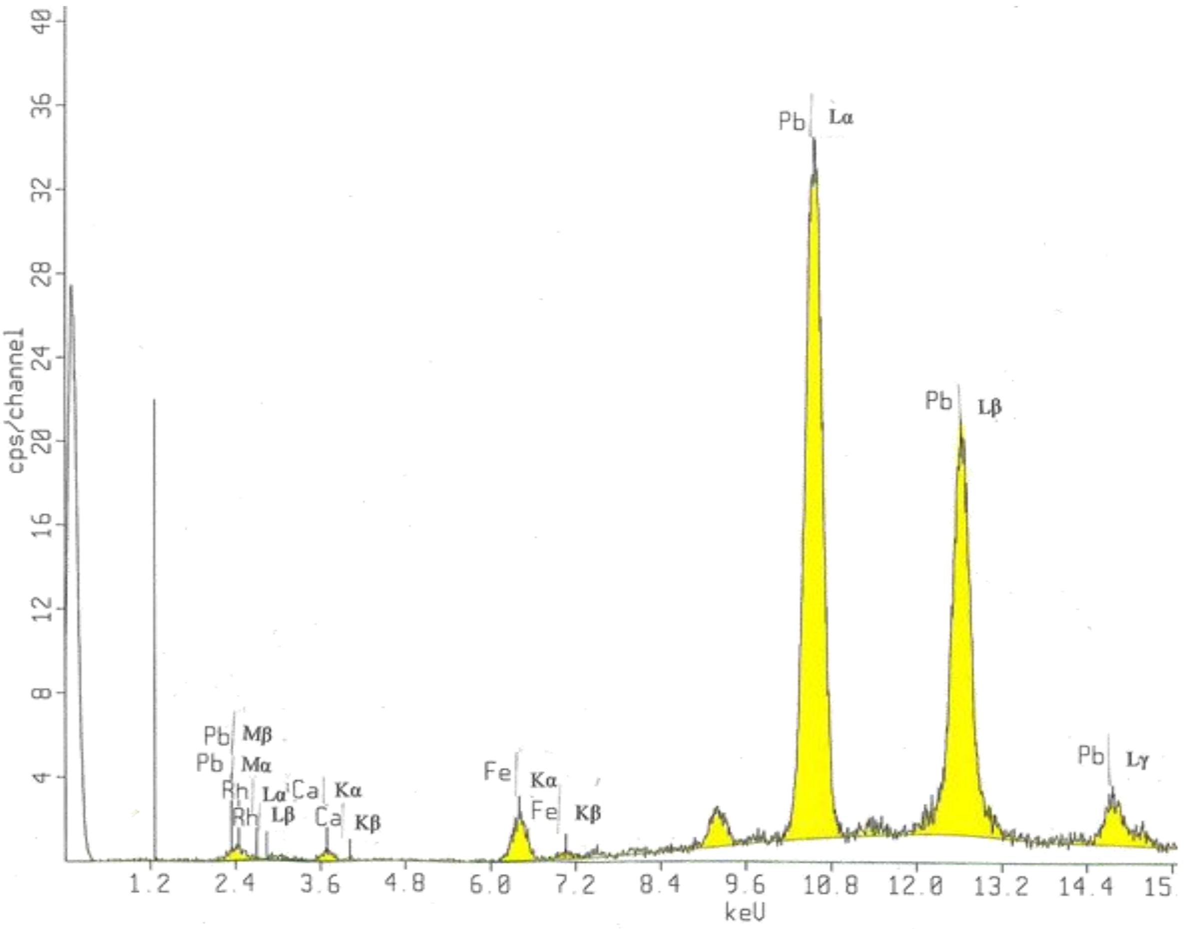

Figure 6: XRF Spectrum of Mangroves treated with 50ppm Pb^{2+} ions solution.

The results shows that mangrove roots treated with Pb (II) ions has an increase in the relative quantities of lead and a decrease in iron and calcium compared to untreated mangrove roots. These variations of element content may somewhat influence the metal ions adsorption onto the adsorbents by ion exchange (Zhang *et al.*, 2012). Increase in Pb (II) uptake by lead treated mangrove roots were probably due to the lower concentrations of more easily exchangeable iron as well as adsorption sites available (Figure 5).

The spectrum (Figure 6) is dominated by the Pb Lα lines at 10.80keV, Pb Lβ at 12.60keV and Pb Lγ lines at 15.0keV. The calcium and iron lines, although small, are readily identifiable in the spectrum (Figure 6). The rhodium peak in the spectrum comes from the X-ray energy used (rhodium source). Elemental composition of mangrove roots treated with Zn (II) ions is shown in Figure 7.

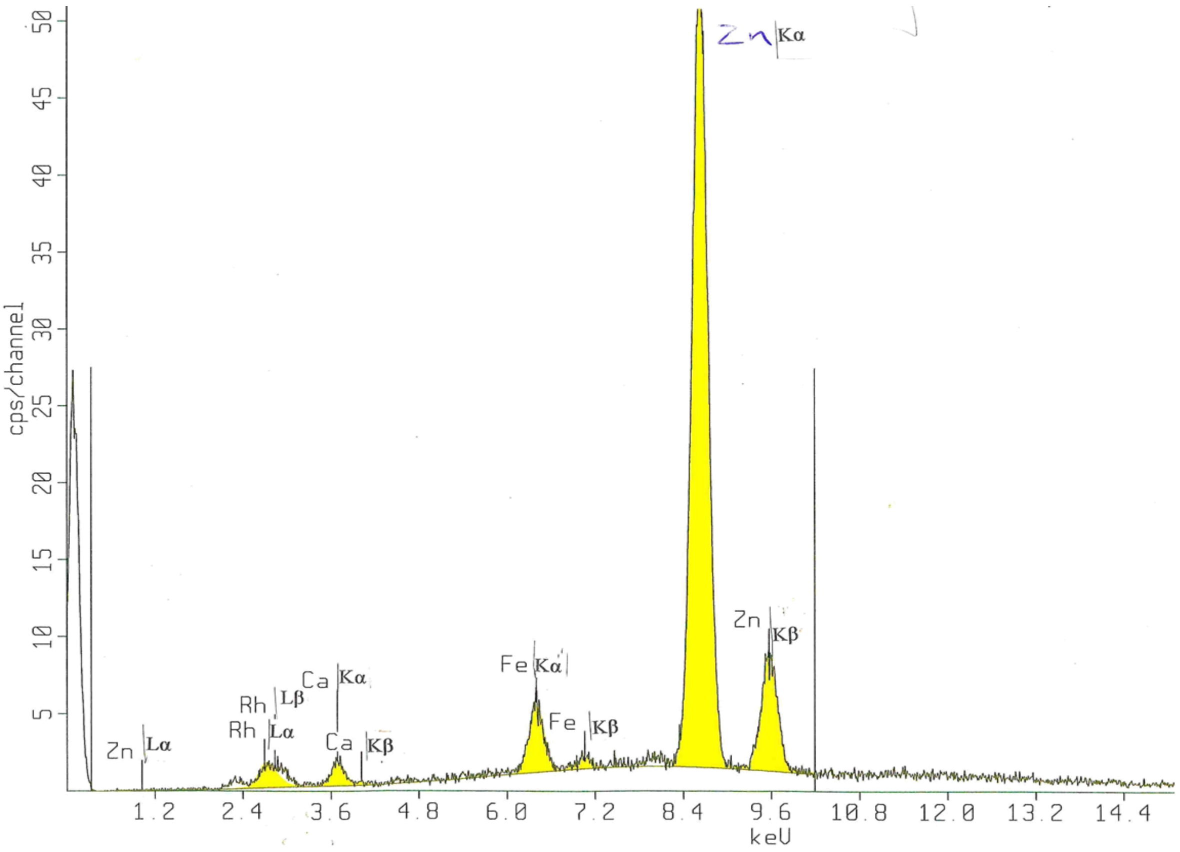

Figure 7: XRF Spectrum of Mangrove Roots treated with 50ppm Zn^{2+} ions solution

There was a significant difference between XRF spectrum of zinc treated and untreated mangrove roots. It is very clear from Figure 5 that there was no trace of zinc ions on untreated mangrove roots. Upon treatment with Zn (II) the amount of Zn (II) which was initially undetected, increased tremendously as shown in Figure 7. This provided strong evidence for adsorption of Zn (II) on the adsorbent.

The spectrum is dominated by the Zn kα line at 8.4keV and Zn kβ line at 9.6keV. In addition there are other elements that were detected at lower energy of the spectrum as shown in Figure 7. These were Ca kα and Ca kβ at 3.6keV and Fe kα and Fe kβ lines occurring at energy 6.8 -7.2keV.

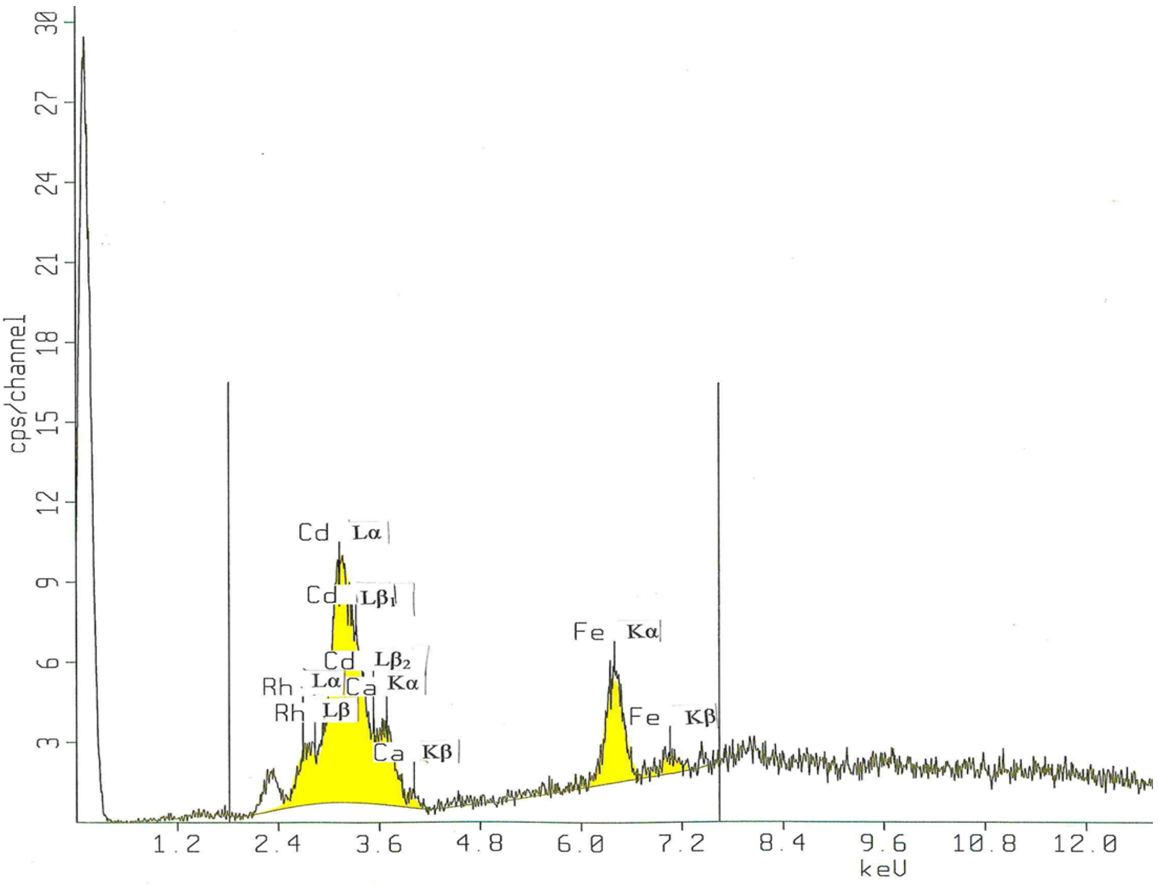

Figure 8: XRF of Mangrove Roots treated with 50ppm Cd^{2+} ions solution

Qualitative analysis on Cd (II) treated mangrove roots by X-ray Fluorescence spectroscopy shows the predominance of Cadmium emissions which are overlapping with Calcium emission lines. This overlapping could be explained by the resolution of the spectrometer being insufficient to resolve the peaks with identical or nearly identical emission energies (Hegazi, 2013).

It is also clear from Figure 8 above that the predominant peak (Cd lines) were shifted to the lower energy of the spectrum (below 3.6 keV) while spectral lines of Fe Kα and Fe Kβ occurred between 6.0 and 7.2keV.

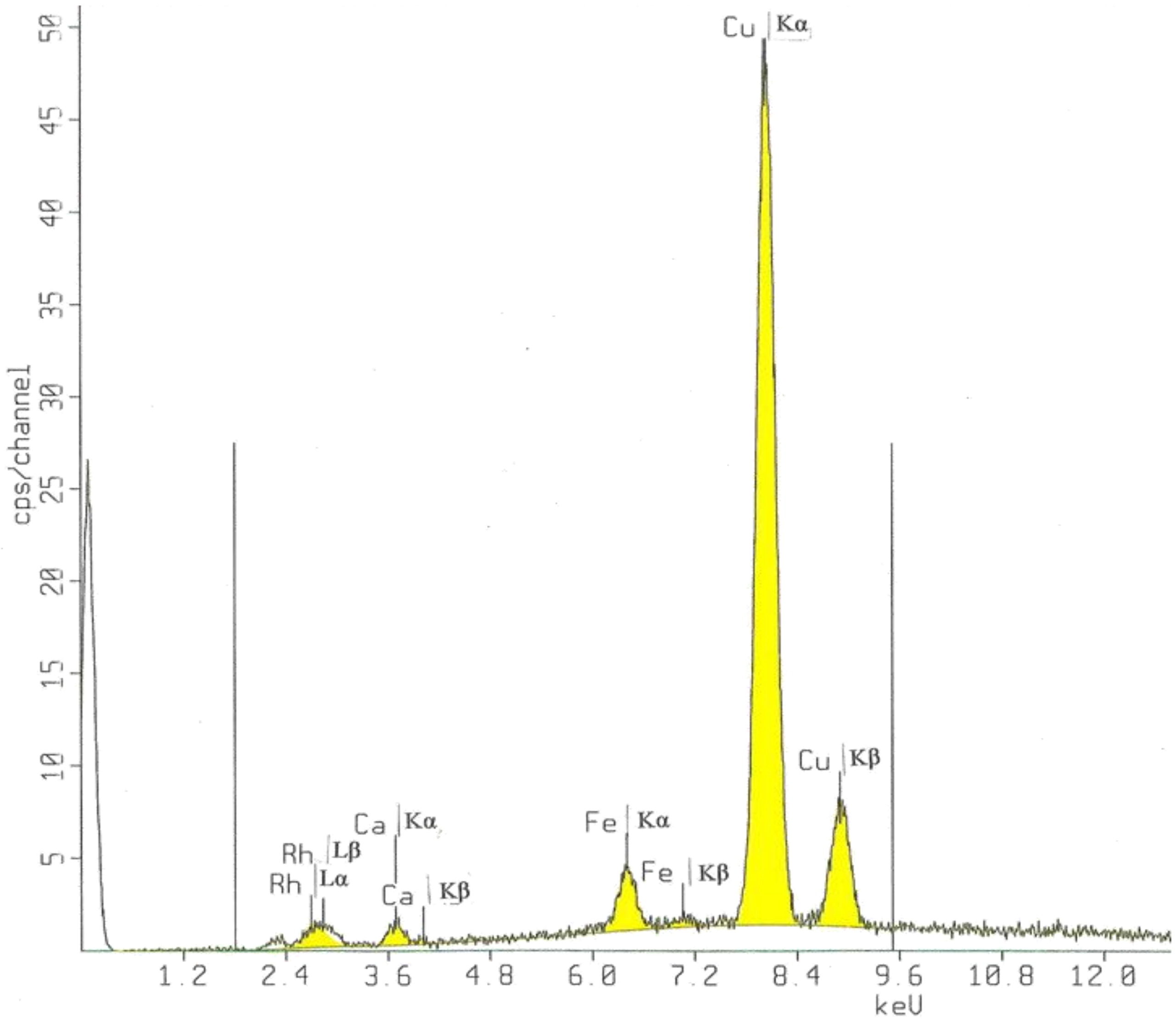

Figure 9: XRF Spectrum of Mangrove Roots treated with 50ppm Cu^{2+} ions solution.

The X-Ray fluorescent spectrum of untreated mangrove roots (Figure 5), showed that the adsorbent (mangrove roots biomass) has mainly calcium and iron. However, after spiking with Cu (II) ions, the percentage adsorption of copper ions increased significantly. The increase in the % adsorption could be attributed to the presence functional groups on the mangrove roots and the presence of iron and calcium which are known to improve the adsorption process (Hegazi, 2013). The transition elements and their oxides are used as catalysts because of their ability to change oxidation or in case of metals, to adsorb other substances on their surface as a catalyst. These results provide strong evidence for adsorption of Cu (II), Cd (II), Zn (II) and Pb (II) ions on mangroves roots.

4.2 ADSORPTION STUDIES OF COPPER (II) IONS USING AAS

All the studies were conducted by batch experiment in stoppered propylene 60mL containers with a stopper. No pH adjustments were made except for the study carried out to investigate the pH. Studies were conducted at room temperature except the studies carried out to establish the effect of temperature.

4.2.1: Comparative Adsorption by Different Parts of Mangrove Plant: Leaves, Bark and Roots

Earlier studies have indicated that adsorbent dosage was an important parameter affecting adsorption capacity and removal efficiency (Acharya *et al*., 2009). Therefore the effects of metal ions uptake by adsorbents derived from different sections of the mangrove plant and their weight were investigated. The results obtained are presented in Figure 10.

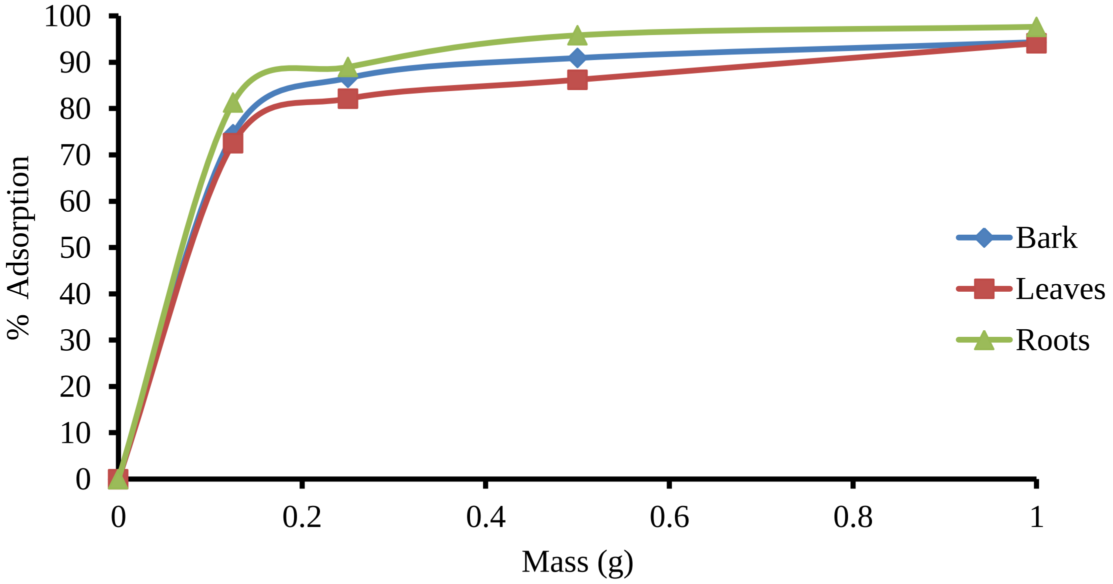

Figure 10: Effect of Parts of Mangrove Plant and Mass on the % Adsorption of 50ppm Cu^{2+} ions Solutions.

From the results it was observed that roots had the highest % adsorption of 98.22% when 2.0 g of root sample was mixed with 50ppm of Cu (II) solution. The roots were closely followed by the bark (97.76 %) and then the leaves at 97.2 %. While observing the effect of dry weight of mangroves biomass on adsorption potential, it is evident from Figure 10 that the removal of copper increased with increase in the adsorbent dosage for all tree parts. It was evident that the removal of copper increased from 81.3% to 98.22% for root sample, 74.45% to 97.76% for bark and 72.55% to 97.2% for leaves sample when the adsorbent dose was increased from 0.1g to1.0g. This was to be expected because for a fixed initial solute concentration, increase in total adsorbent doses provides a greater surface area or adsorption sites and increases the adsorption potential. However, it was also noted that after dosage of 1.0g, there was no significant change in % removal of copper. This could be overlapping of active sites at higher dosage, i.e., there was no appreciable increase in effective surface area resulting due to conglomeration of exchanger particles.

It was also clear that all parts of plant biomass had a high potential for the uptake of the metal ions from solutions which implies that the whole plant can be utilized in the removal of heavy metal ions on a scaled up basis. It can be concluded that mangroves roots have a relatively higher ability to adsorb copper (II) ions in single component aqueous systems compared to bark and leaves of the same particle size. Roots were therefore used for the rest of the subsequent sorption experiments. Several researchers have reported similar results (Cho *et al*., 2005; Deydier *et al*., 2003; Noeline *et al*., 2005; Moufliha *et al*., 2005; Taty *et al.,* 2003).

4.2.2 Effect of Initial Concentration of Cu (II) Ion on Adsorption

The initial concentration remarkably affected the uptake of Cu (II) ions in solution. The initial concentration of Cu (II) solution was varied from 50ppm to 600ppm. The results obtained clearly depict the effect of initial concentration of Cu (II) solution on copper removal using mangroves roots. The results were presented in a graphical form as percentage removal versus initial copper concentration.

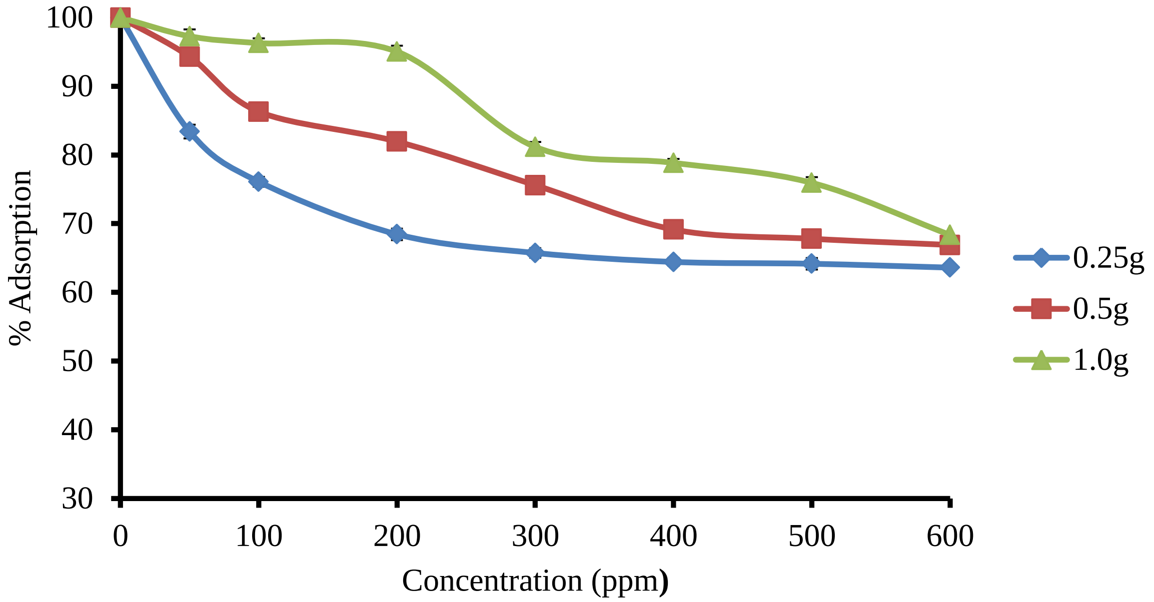

Figure 11: Effect of Initial Cu (II) ions Concentration on Adsorption by Mangrove Roots.

It is evident from Figure 11 that increase in initial concentration of Cu^{2+} ions resulted in decrease in % adsorption. This was because at high initial concentrations, the number of moles of Cu^{2+} ions available to the surface area were high, so functional adsorption became dependent on the initial concentration.

This adsorption characteristic indicates that surface saturation is dependent on the initial metal ion concentrations (Hanafi *et al*., 2007). The initial concentration provided an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phase. Srinath *et al.* (2002) found out that the maximum removal was at the lowest concentration of 30ppm. This could be due to higher cell density attained in lower concentrations than at higher concentrations.

The decrease in the % adsorption could also be attributed to lack of sufficient surface area to accommodate much more metal available in solution. At lower concentrations, all the Cu^{2+} could interact with the binding sites and thus a higher % adsorption than at higher Cu^{2+} concentrations. At higher concentrations, lower percentage adsorption was due to saturation of the adsorption sites.

The water purification efficiency can be improved by diluting the waste waters containing high metal concentrations. In addition the removal of lower concentration metal ions in short equilibrium time has great industrial applications as in most of the effluents the metal ions are in lower concentrations.

Similar results have been reported by other scientists for other adsorbate–adsorbent system (Cho *et al*., 2005; Deydier *et al*., 2003; Noeline *et al*., 2005; Axtell *et al*., 2003; Taty *et al*., 2003; Moufliha *et al*., 2005; Chandra *et al*., 2004; Tokimoto *et al*., 2005).

4.2.3 Effect of Particle Size and Adsorbent Dosage (Weight) of Mangroves Roots on Adsorption of Cu (II) ions

The contact surface between any sorbent and the liquid phase plays an important role in sorption phenomena. For this reason the effect of particle size of mangroves roots on removal of Cu^{2+} ions was studied using three different sizes (< 300µm, > 300 < 450µm and > 425µm). Figure 12 shows the percentage removal of Cu^{2+} ions from aqueous solution as a function of weight of mangrove roots of three different sizes.

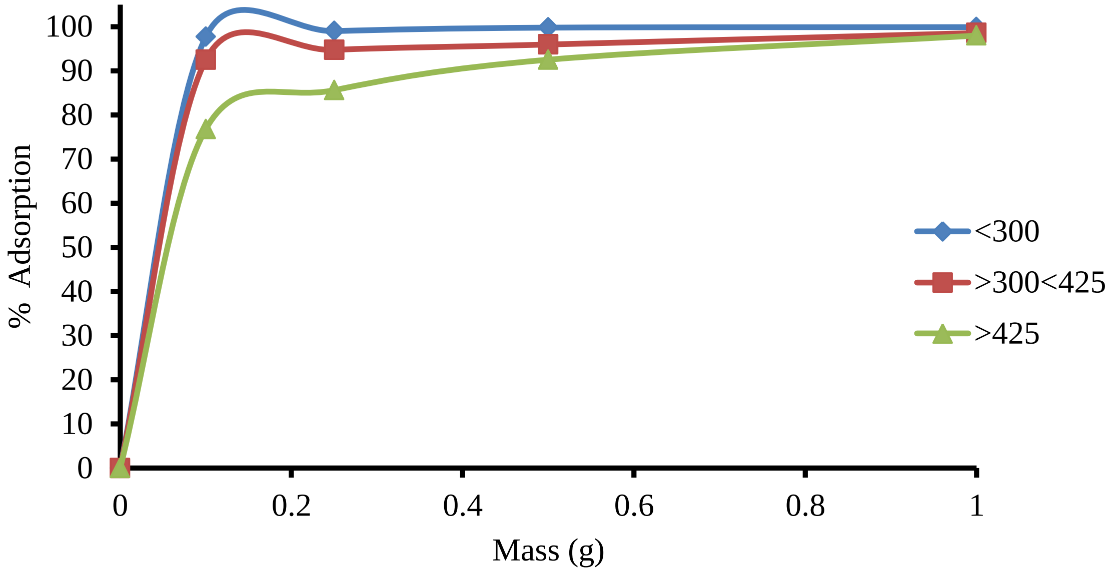

Figure 12: Effect of Particle Size and Weight of Mangrove Roots on % Adsorption of 50 mg/L of Cu^{2+} ions.

It is evident from Figure 12 that the % adsorption of Cu^{2+} ions increased with the weight of the adsorbent employed. It also decreased with increase in the particle size of the adsorbent.

Results shown above revealed that maximum adsorption was attained at 1.0g for 30ml Cu^{2+} solution. This suggests that after a certain weight of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of adsorbent (Nomanbhay and Palanisamy, 2005). For smaller amounts of adsorbent, the metal ions were competing for adsorption at limiting adsorption sites. However, as the quantity of the adsorbent increased, the availability of adsorption sites increased, resulting in greater % adsorption of the metal ion.

The maximum adsorption was at smallest particle size. This was most probably due to increase in the total surface area, which provided more adsorption sites for metal ions. The obtained results indicated that more finely grounded biomass took up the metal ions more rapidly and the equilibrium was attained faster than those achieved with large sized biomass. Bai and Abraham (2001) also observed that the adsorption capacity of *R. nigricans* decreased as the particle size increased from 90 to 500µm.

To ascertain the effect of the adsorbent/adsorbate ratio on the % adsorption, further studies were conducted to establish the effect of Cu^{2+} ion concentration on the adsorption observed. Rozaini *et al*. (2010) also observed that the critical value of dosage of modified mangrove bark was 1.0 g for both Ni (II) and Cu (II) ions. Increase in the amount of adsorbent added into a fixed concentration ions solution will increase the availability of active sites of the adsorbent. Therefore, adsorption percentage and efficiency will also increase.

The particle size of mangrove roots can influence their adsorption capacities due to the change in total surface area which is necessary for metal adsorption. Banerjee *et al*. (2012) reported that the smaller particles of watermelon shell showed higher removal efficiency of Cu (II). These results are consistent with findings reported by other authors, Kannan and Veemaraj (2010) observed that the removal of Cd (II) increased from 10.07% to 53.16% with decreasing particle size of Jackfruit seed carbon, from 250 to 90µm. They attributed this to the increase in the available surface area. Boota *et al*. (2009) also reported similar findings for sequestering Cu (II) and Zn (II) using *C. reticulate*. In contrast, Taha *et al*. (2011) reported that a decrease in particle size of potato peels did not profoundly change the adsorption capacities of Pb (II), Cd (II) and Zn (II).

4.2.4 Effect of Equilibration Time and Initial Concentration on Adsorption of Copper (II) ions

Removal of Cu (II) depends on its contact time with the mangrove roots adsorbent. Adsorption of copper at different contact time was studied for initial copper concentration of 50ppm and 1000ppm at their natural pH. The experiment was conducted by varying the contact time from 0 to 60 minutes at 5 minutes interval.

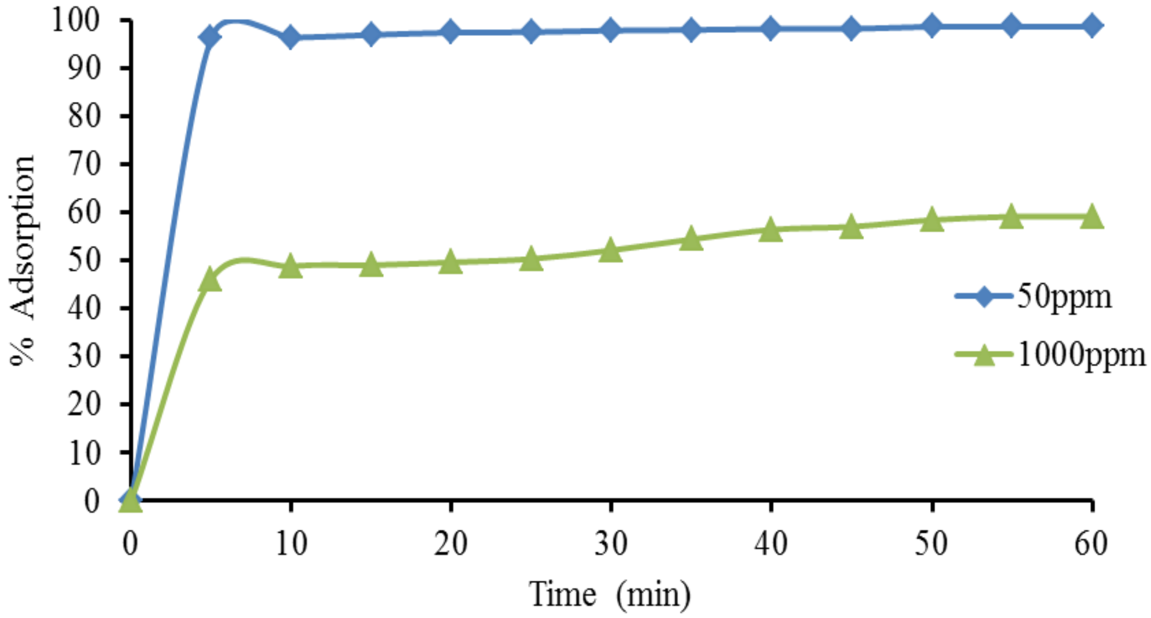

Figure 13: Effect of Contact Time on Adsorption of Cu^{2+} ions onto 0.5g of Mangrove Roots.

From Figure13, it is clear that there was more than 96% removal for 50ppm copper solution and 46% removal for 1000ppm within the first 5 minutes. Equilibrium was established after 10minutes. The change in the rate of removal might be due to the fact that initially all adsorbents sites were vacant and the solute concentration gradient was high so the rate of adsorption was also high. Later the copper uptake by the adsorbent became stagnant due to the decrease in the number of adsorption sites as well as copper concentration (Kumar *et al.,* 2012).

At equilibrium, the rate of adsorption is equal to the rate of desorption. Therefore after equilibrium is reached no significant increase in % removal with increase in contact time was observed. Namasivayan and Yamuna (1999) reported the same trend during the adsorption of Cr (III) onto biogas residual slurry. The results observed in this study are also similar to the results reported in the removal of lead from aqueous solution by activated phosphate (Moufliha *et al*., 2005), use of agricultural products for the reduction of aqueous lead (II) (Gardea *et al*., 2002), and the removal of copper (II) ions from aqueous solution by micaceous mineral of Kenyan origin (Attahiru *et al*., 2003).

4.2.5 Effect of Shaking Speed on Adsorption of Copper (II) ions

The shaking speed determines the frequency of collisions between the adsorbent surface and the adsorbate (Cu^{2+}ions). The effect of shaking speed was done by varying the shaking speed from 100-600rpm.

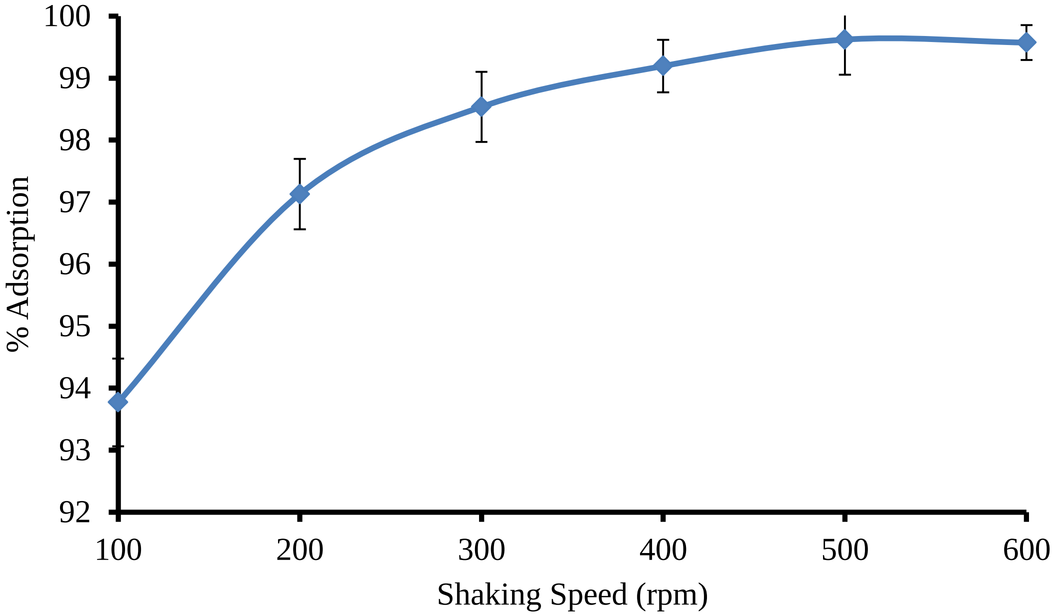

Figure 14: Effect of Shaking Speed on Sorption of 30 ppm Cu^{2+} ions on 0.2g of Mangrove Roots.

From Figure 14, an increase in shaking speed increased % adsorption from 93.77 to 99.6%. Increase in % adsorption was due to reduction in the boundary layer thickness around the adsorbent which ensured better mass transfer of copper ions from the bulk of the solution to the adsorbent surface thereby shortening the equilibrium time. However, shaking speed beyond 500 rpm led to a slight reduction in the % adsorption as the increased kinetic energy means that the adsorbate and adsorbent did not have sufficient time to form any chemical or physical bond and also the newly formed bonds between the metal ions and the adsorbent surface broke.

4.2.6 Effect of Temperature on Cu (II) ions Adsorption

Temperature affects the adsorption rate by altering the molecular interaction and the solubility of the adsorbate (Singh *et al.*, 2001). Adsorption studies were carried out at varying temperatures (25 to 70°C) and the results presented as % removal of copper versus temperature as illustrated in Figure 15.

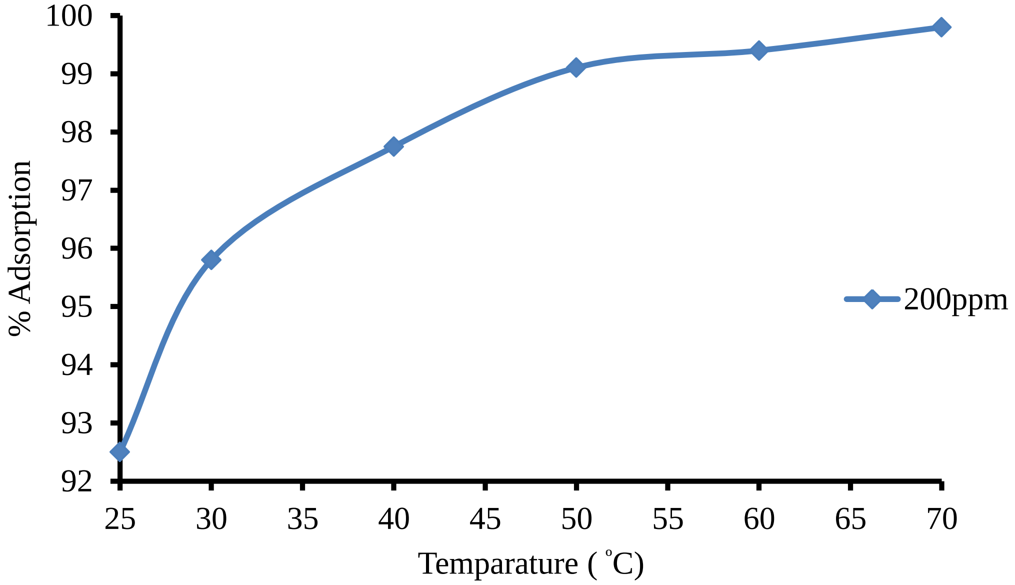

Figure 15: The Effect of Temperature on Adsorption of 200ppm Cu^{2+} ions by 0.5g Mangrove Roots.

The percentage removal of copper with initial concentration of 200ppm increased from 92.5% to 99.4% for a temperature rise from 20°C to 70°C. The enhanced adsorption of copper (II) ions may be due to change in pore size and enhanced rate of intra-particle diffusion. The increase in metal adsorption with increase in temperature could also be due to dissociation of some compounds available in the adsorbent which may provide more sites for adsorption. The increase in percentage removal of the metal ions with temperature increase suggests that the adsorption process is an endothermic reaction.

Park *et al*. (2010) and Banerjee *et al*. (2012) reported similar observation and argued that adsorption of heavy metals was endothermic in nature. It was suggested that higher temperature improved the elimination of heavy metals owing to an increase in its surface activity and kinetic energy. In the same way, Garcia and Colin (2010) also observed that the adsorption of Pb (II) and Cd (II) by the stalk sponge of Zea Mays increased 1.1–1.8 times with increasing temperature from 20 to 40°C.

In contrast, some researchers have reported that adsorption processes are exothermic which means that adsorption capacity is inversely proportional to the temperature (Sahmoune *et al.*, 2011). Kumar *et al.* (2012) found that the adsorption of Cd (II) by cashew nut shell decreased from 80.13% to 74.32% with the rise in temperature from 30° C to 60° C. This was attributed to the decrease in surface activity of adsorbent.

4.2.7 Effect of pH on Adsorption of Cu (II) ions

Hydrogen ions concentration is one of the important factors that influence the adsorption behavior of metal ions in aqueous solutions. It affects the solubility of metal ions in solution, replaces some of the positive ions found in active sites and affects the degree of ionization of the adsorbate during the process of adsorption (Amboga *et al.*, 2014). This is because it affects solution chemistry and also the speciation of the metal ions. The pH value of a solution strongly influences not only the site dissociation of the biomass' surface, but also the solution chemistry of the heavy metals: hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, precipitation, the speciation and the adsorption availability of the heavy metals (Wang *et al.*, 2009). This is because adsorption involves interaction between the adsorbate and the functional groups like carboxyl, hydroxyl, thiol, amido, carbonyl, sulphonate, amine, imine, imidazole, phosphonate, thio-ester and phospho diester present in these bio materials (Volesky, 2007). This makes it possible for them to attach the metal ions from waters (Farooq *et al.*, 2010). Therefore the pH is an important parameter controlling the process of adsorption. The results obtained are shown in Figure 16.

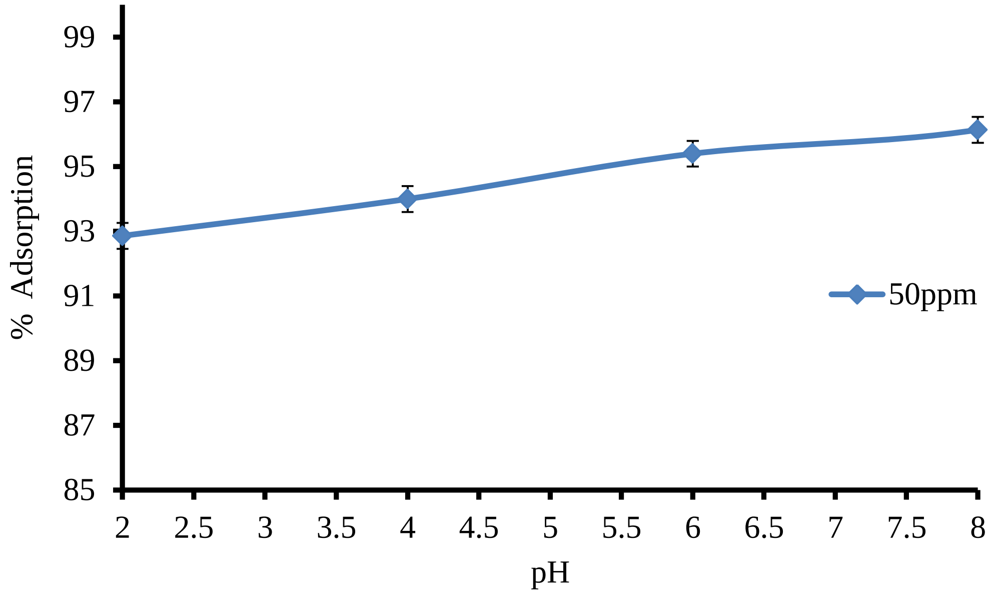

Figure 16: Effect of pH on the % Adsorption of 50ppm Cu^{2+} ions by 0.5g of Mangrove Roots.

It was observed that a gradual increase in the copper removal from 92% to 95.4% occurred when the pH values of the solutions was varied from 2.0 to 6. Figure 16 demonstrates that the mangroves possessed optimum sorption capacity for Cu (II) ions at pH 6.

The low removal efficiency at low pH is apparently due to the presence of higher concentration of H^+ ions in the solution which compete with the Cu (II) ions for the adsorption sites of the mangrove roots. With the pH increasing, the H^+ ions concentration decreases leading to increased Cu (II) uptake. In addition the increase in the metal removal as the pH increases (i.e. as the solution becomes more basic) can be explained on the basis of a decrease in competition between proton and metal species for the surface sites, and by the decrease in positive surface charge, which results in a lower columbic repulsion of the adsorbing metal ions (Kumar *et al.*, 2012).

At higher pH values (> 6), precipitation is dominant or both ion exchange and aqueous metal hydroxide formation may become significant mechanisms in the metal removal process (Kongsuwan *et al.*, 2006). This condition is often not desirable as the metal precipitation could lead to a misunderstanding for the adsorption capacity. In practice, metal precipitation is generally not a stabilized form of heavy metal as the precipitation can sometime be very small in size, and upon the neutralization of the effluent from the waste water treatment plant, the solubility of the metals increases resulting in a re-contamination of the waste outlet stream (Kongsuwan *et al.*, 2006).

Rozaini *et al.* (2010) observed that for mangroves modified with formaldehyde the adsorption increased with the increasing of pH and achieved optimum adsorption for Ni (II) ions and Cu (II) ions at pH 5. This phenomenon could be explained by increasing total net negative charges of surface adsorbent which intensified electrostatic forces in the adsorption process. Moreover with increasing pH, total number of negative groups available for the binding of metal ions increased and therefore competition between proton and metal ions became less pronounced.

4.2.8 Adsorption Isotherm Studies for Cu (II) ions

It is important to have a satisfactory description of the equilibrium state between the two phases in order to successfully represent the dynamic behavior of any adsorbate from solution to the solid (adsorbent) phase. Equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms, usually the ratio between the quantity adsorbed and that remaining in the solution at a fixed temperature at equilibrium. Equilibrium studies are described by adsorption isotherm characterized by certain constants whose values express the surface properties and affinity of the sorbent. In this study, the distribution of adsorbate Cu (II) between the adsorbent and the bulk of the solution when the system is in equilibrium was important to establish the capacity of the adsorbent for adsorbing the adsorbate. Two important sorption isotherm models were selected to fit experimental data, namely; Langmuir and Freundlich. The results are displayed in Figures 17 and 18 respectively.

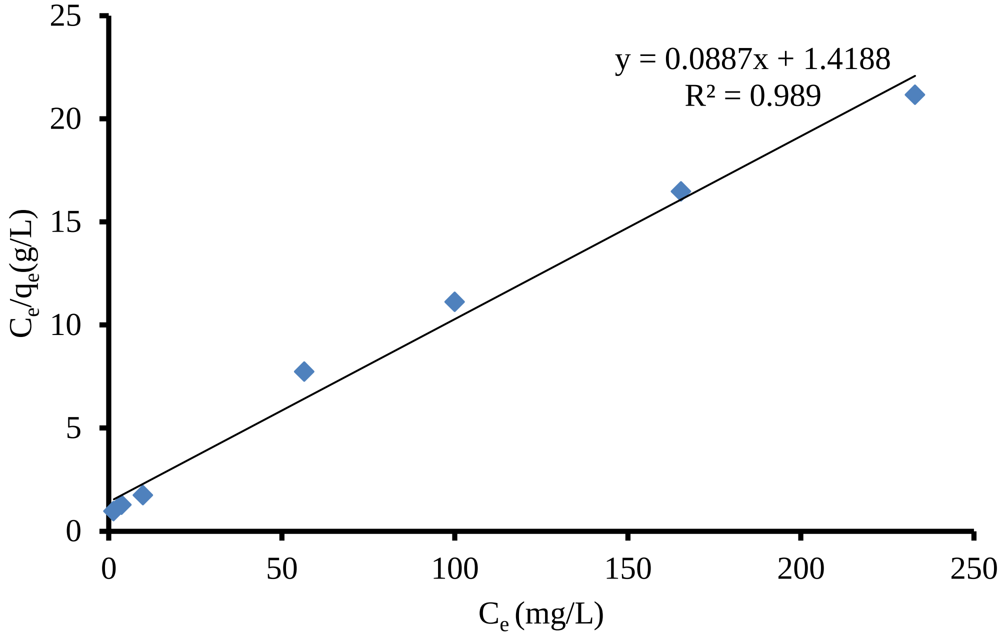

Figure 17: Langmuir Linearized Isotherm for Cu (II) Adsorption onto 1.0g Mangrove Roots.

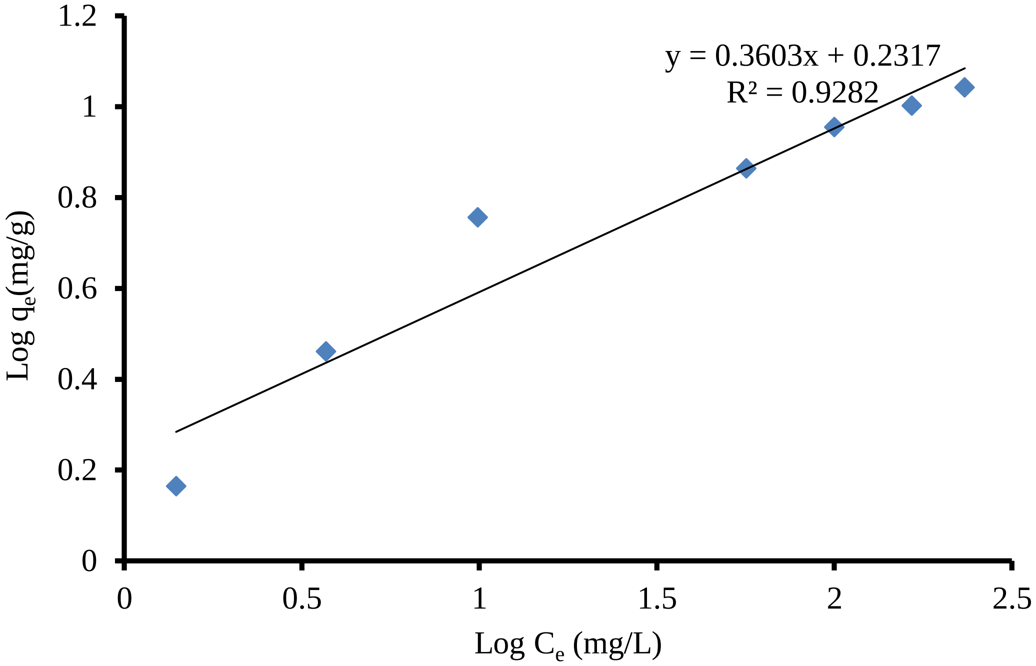

Figure 18: Freundlich Plot for Adsorption of Cu (II) onto 1.0g Mangroves Roots.

Comparing the correlation coefficients values of Freundlich adsorption isotherm with those of Langmuir adsorption isotherm it is clear that the adsorption of copper onto the mangrove roots biomass was correlated well with Langmuir equation (R^2 = 0.989) as compared to

Freundlich equation ($R^2 = 0.928$) under the concentration range studied. Table 3 shows the Langmuir and Freundlich isotherm constants and the correlation coefficients.

Table 3: Langmuir and Freundlich Parameters for Cu (II) ions Adsorbed using 1.0g Mangroves Roots

Langmuir			**Freundlich**		
Q_{max}**(mg/g)**	***b*****(L/mg)**	R^2	K_F	***n***	R^2
11.3636	0.0621	0.989	1.702	2.778	0.928

The Langmuir isotherm model was chosen for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the mangrove roots surface. The adsorption capacity, Q_{max}, which is a measure of the maximum adsorption capacity corresponding to complete monolayer coverage, showed that the mangroves roots had a mass capacity of (11.36mg/g) for Cu^{2+}. Rozaini *et al.* (2010) reported the removal efficiencies were clearly affected by the operation parameters. Equilibrium data was best found to fit Freundlich isotherm model indicating heterogeneous adsorption of Ni (II) and Cu (II) ions on the surface of bark adsorbents. Monolayer and heterogeneous adsorption capacity of MBB for Ni (II) and Cu (II) ions was found as 7.25 and 6.95 mg g^{-1} respectively. The adsorption data was also found to follow pseudo-second-order kinetic and reached equilibrium rapidly, within 60 min at pH 5.

4.2.9 Adsorption Kinetics of Cu (II) ions

A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process (Jain *et al*., 2003). Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Adsorption rate gives important information for designing batch adsorption systems. Figure 19 below shows a plot of Copper (II) adsorption versus contact time.

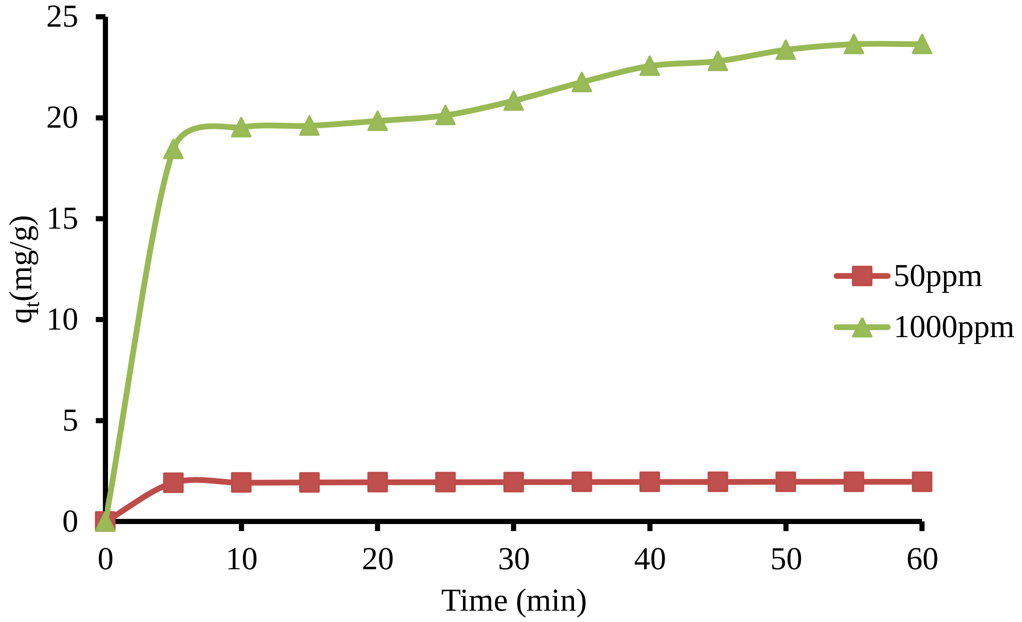

Figure 19: Effect of Contact Time on Uptake of Cu (II) ions by 0.5g Mangrove Roots.

The adsorption for 1000ppm solution was found to be rapid at the first period of the process and then the rate of adsorption slowed and finally stagnated with the increase in contact time. For a concentration of 50ppm, the adsorption process was almost stagnant throughout and the equilibrium time was attained after 5 minutes. This clearly demonstrates that mangrove roots have plenty of adsorption sites that can accommodate heavy metals.

The kinetic data was analyzed using two kinetic models, pseudo-first-order model and pseudo-second-order model. The results of the kinetic modeling are displayed in Figures 20 to 23. The plots of t/q_t versus t at different time intervals were almost linear, especially at low concentration which indicated the validity of rate equation of second order kinetics. The values of R^2 showed a good correlation.

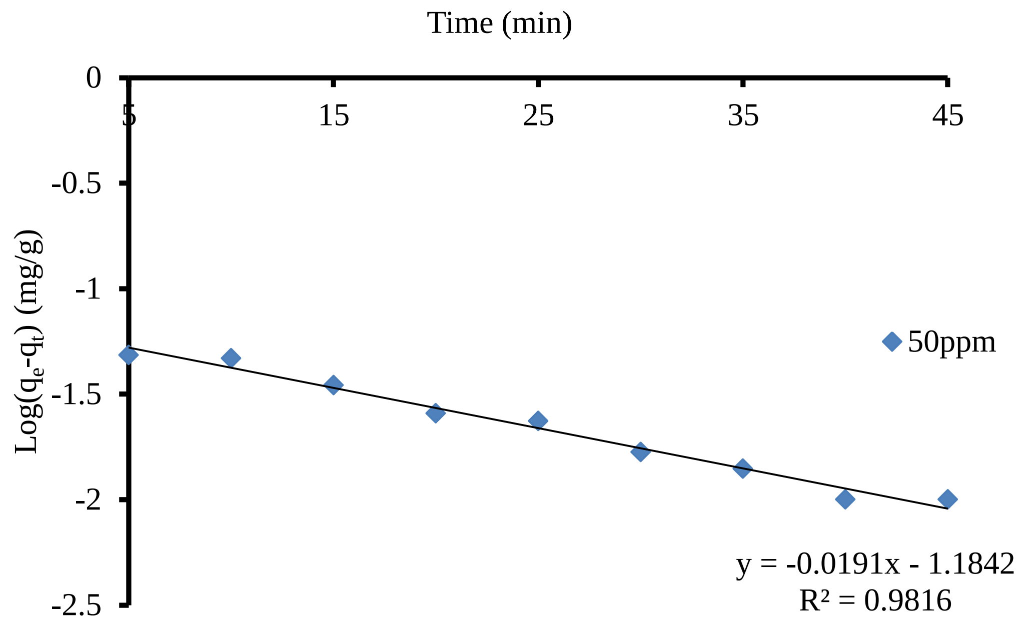

Figure 20: Pseudo-First-Order Plot of Cu (II) Adsorption onto 0.5g Mangrove Roots for 50ppm of Cu (II) ions.

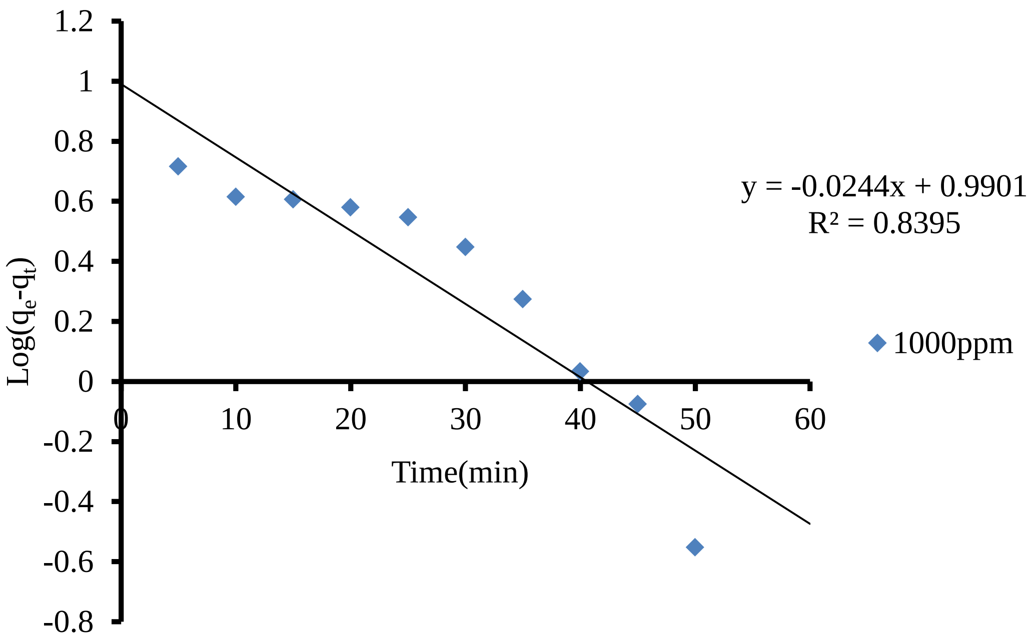

Figure 21: Pseudo-First -Order Plot for Adsorption of 1000ppm Cu (II) onto 0.5g Mangroves Roots.

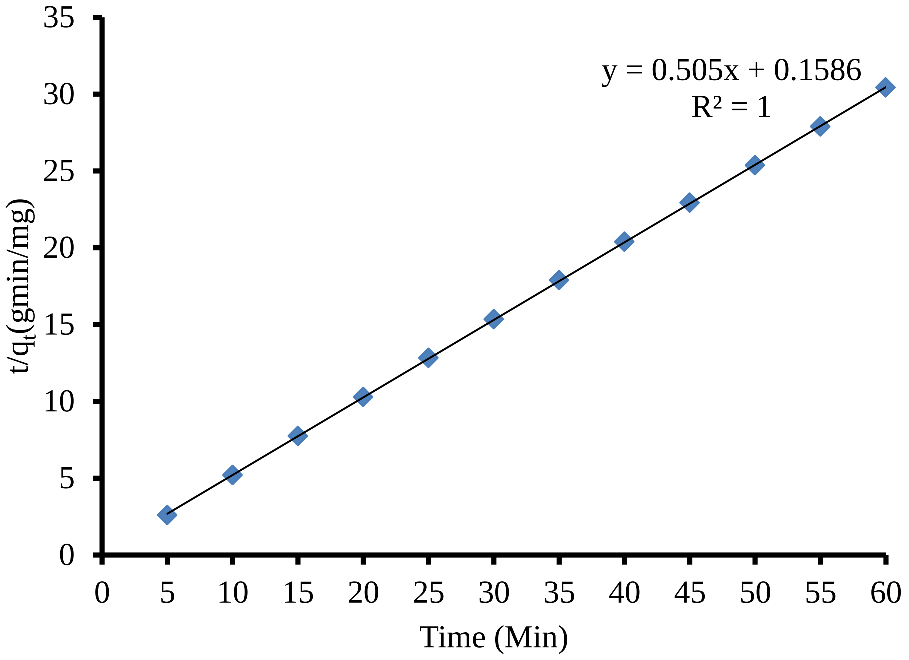

Figure 22: Pseudo-Second-Order Plots for Adsorption of 50ppm Cu (II) ions onto 0.5g Mangroves Roots.

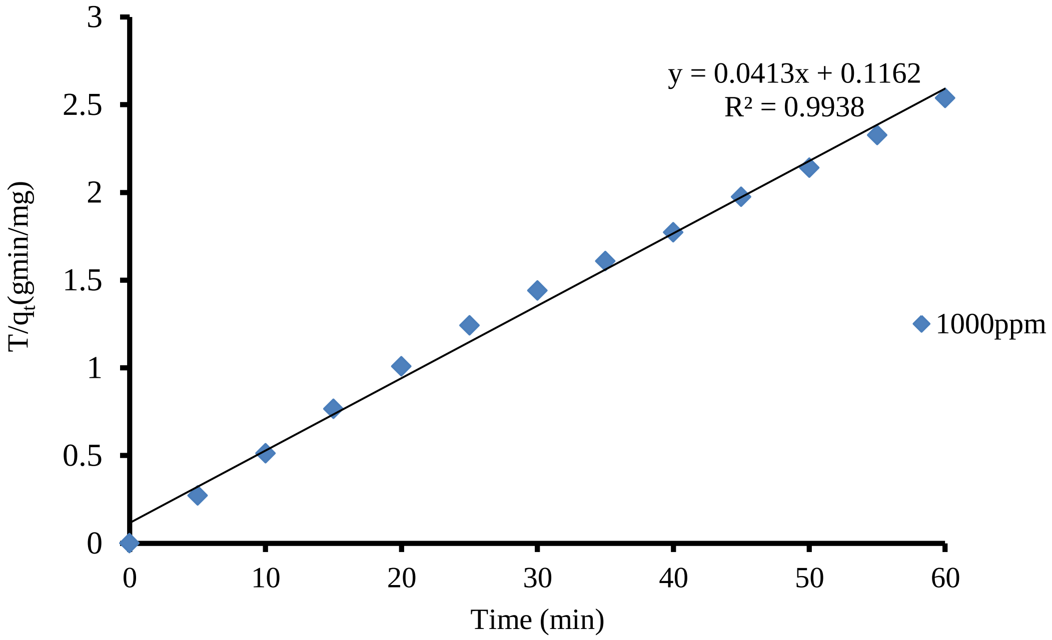

Figure 23: Pseudo-Second-Order Plots for Adsorption of 1000ppm Cu (II) ions onto 0.5g Mangrove Roots.

Table 4: Pseudo-First-Order and Pseudo–Second-Order Rate Constants for Adsorption of Cu (II) ions on 0.5g Mangrove Roots.

Pseudo-first-order				**Pseudo-second -order**		
[Cu] mg/L	**$Q_{e(mg/g)}$**	**Constant (min^{-1})**	**R^2**	**Q_e(mg/g)**	**Constant (g/mg/min)**	**R^2**
50	0.0654	0.0438	0.981	1.98	1.614	1.00
1000	9.772	0.0553	0.839	24.39	0.0145	0.993

The results obtained suggests that the adsorption of copper onto mangrove roots fits the pseudo-second -order model which is based on the assumption that the rate limiting step may be chemisorption. This is due to a higher correlation coefficient (R^2) value of 1.00 compared to a value of 0.981 based on a concentration of 50 mg/L and 1000mg/L respectively. This gives an idea that adsorption process followed second order kinetics.

The results of this study agrees well with the results obtained in the adsorption of Cu(II) using activated phosphates (Moufliha *et al*., 2005) and lignite surface (Balasubramanian and Ahamed, 2000).

4.3 ADSORPTION STUDIES OF ZINC (II) IONS USING AAS

4.3.1 Effect of Equilibration Time and Initial Concentration on adsorption of Zn (II) ions

Adsorption of zinc was studied for initial zinc concentration of 50ppm, 200ppm and 1000ppm. The contact time was varied from 0 to 60 minutes. The percentages of zinc adsorbed at varying contact time keeping other parameters constant are presented in Figure 24.

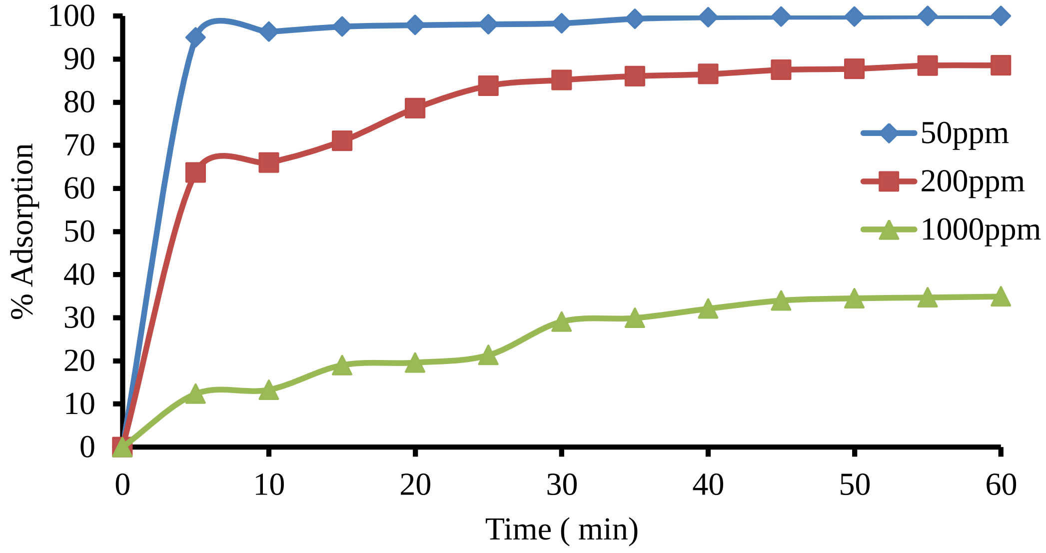

Figure 24: Effect of Concentration and Contact Time on Adsorption of Zn (II) ions by 0.5g of Mangroves Roots.

It is evident from Figure 24 that above 95% removal took place within the first 5 minutes and equilibrium was established after 5 minutes for initial concentration of 50ppm. The % removal was found to increase from 95% to 98%, 63.7 to 85.15% and 12.35 to 29.11% from 5 minute to 30 minutes of contact time and initial concentration of 50ppm, 200ppm and 1000ppm respectively.

The change in the rate of removal might be due to the fact that initially all adsorbents sites were vacant and the solute concentration gradient was high, so the rate of adsorption was also high. Later, the zinc uptake by the adsorbent stagnated due to the decrease in the number of adsorption sites as well as zinc concentration. At equilibrium, the rate of adsorption was equal to the rate of desorption. After equilibrium, it was found that there was no significant increase in % removal with increase in contact time. Similar results were observed by Ahmad *et al*. (2009), Zhang *et al*. (2012) and Amboga *et al*. (2014).

4.3.2 Effect of Weight of Adsorbent and Particle Size on Adsorption of Zn (II) ions

The number of available binding sites and exchanging ions for the adsorption depends upon the amount of adsorbent in the adsorption system. Figure 25 below shows the removal of Zn^{2+} ions as a function of particle size and weight of mangrove roots at room temperature.

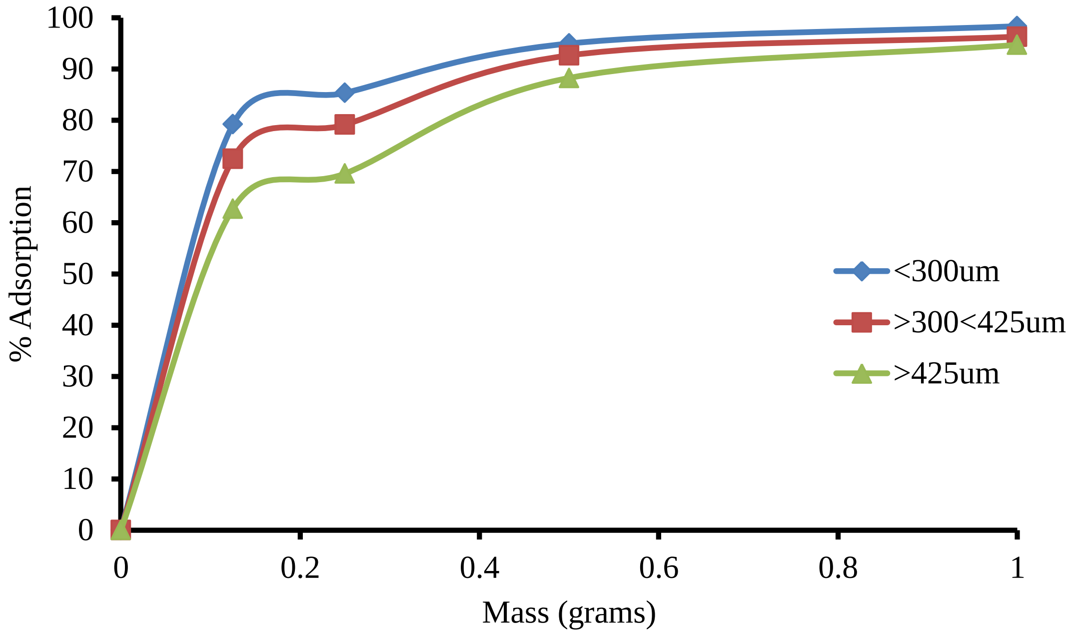

Figure 25: Effect of Weight and Particle Size on 50ppm Zn (II) ions Adsorption by Mangroves Roots.

From Figure 25 it can be seen that there was 79.2 %, 72.48% and 62.74% adsorption when 0.1g of mangroves roots was used to adsorb 50ppm using particle sizes < 300um, >300 <425um and > 425um respectively. Decreasing the average particle size of the adsorbent increased the surface area, which in turn increased the adsorption capacity.

It can also be noted that the adsorption potential increased with increase in biomass dosage (0.1 to 1.0g). However, there was no significant increment in percentage adsorption on further raising the mass beyond 0.5g. This was because all available binding sites for the metal ions in solution had been used up and therefore no significant increase in % metal removal with dosage increase. Similar results were observed by Attahiru *et al*. (2003) who worked on adsorption of copper from aqueous solutions using Micaceous mineral.

4.3.3 Effect of Initial Concentration of Zinc (II) ions on Adsorption

The results presented in Figure 26 depict the effect of initial concentration of zinc solution on zinc removal using mangroves roots.

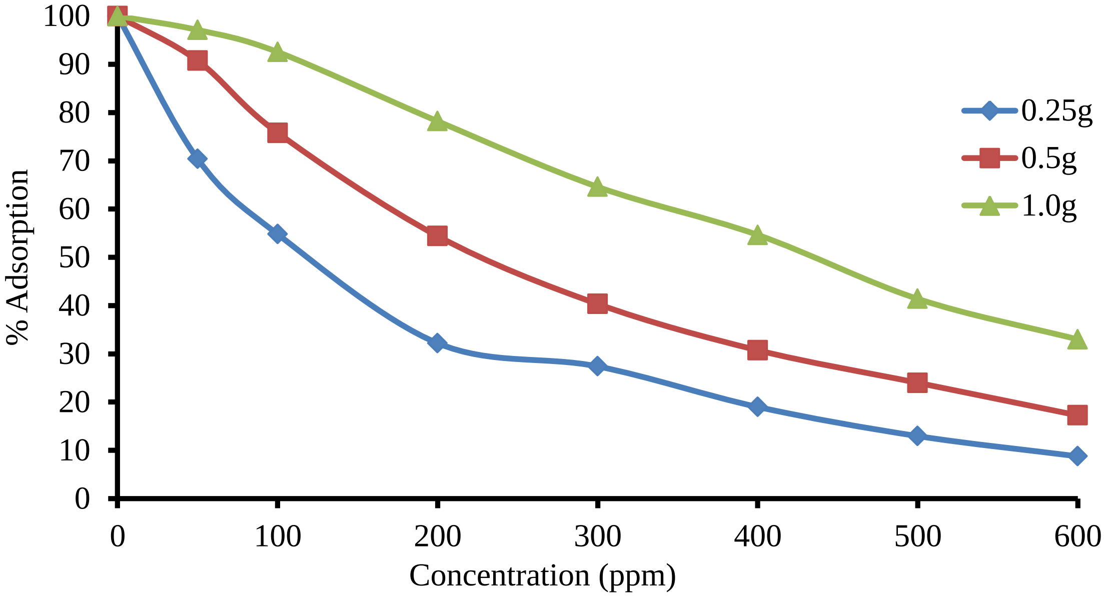

Figure 26: Effect of Initial Concentration of Zn (II) ions on Adsorption of Mangrove Roots.

It is evident from the graph that increase in initial concentration of Zn^{2+} ions on mangrove roots resulted in decrease in % adsorption. This was because at high initial concentrations, the number of moles of Zn^{2+} ions available to the surface area were high, so functional adsorption became dependent on the initial concentrations. This could also be attributed to lack of sufficient surface area to accommodate much more metal ions available in solution. This was confirmed by increasing the mass of the adsorbent which had an effect of increasing the percentage adsorption at a fixed initial concentration. At a lower concentration, all the zinc ions presents in solution could interact with the binding sites and thus the % adsorption was higher than those at higher zinc ion concentrations.

Researchers have carried out several studies to clarify the effect of initial concentration on metal uptake by different adsorbents. Kumar *et al*. (2012) reported that an increase in Cd (II) concentration, from 10 to 50 mg/L, resulted in a decrease in Cd (II) removal percentage from 80.13% to 66.57%. Ashraf *et al*. (2011) also reported a similar trend for the case of removing Pb (II), Cu (II), Zn (II) and Ni (II) by the banana peel. At the highest metal concentration (150 mg/L), the removal efficiencies of Cu (II), Pb (II), Zn (II) and Ni (II) were 92.52%, 79.55%, 63.23% and 68.10% while at the lowest metal concentration (25 mg/L), the removal percentages of these metals were 94.80%, 86.81%, 84.63% and 82.36%, respectively. Kannan and Veemaraj (2010) reported that the percentage removal of Cd (II) by jack fruit seed decreased from 66.28% to 22.43% with an increase in initial Cd (II) concentration from 10 to 100 ppm. Kannan and Veemaraj (2010) and Kumar *et al*. (2012) attributed this behavior to the saturation of adsorption sites on adsorbent surface, whilst Kumar *et al*. (2011) explained this by the lower rate of transporting metal ions from solution to rice husks surface.

Conversely, Giri *et al*. (2012) reported that as the initial Cr (VI) concentration increased from 10 to 100 mg/L, the removal of Cr (VI) by *E. crassipes* root activated carbon increased from 77.22% to 92.24%. They suggested that the initial metals concentration provided a driving force to overcome mass transfer resistance of Cr (VI) ions between the aqueous and solid phase. Hence, further work is required to elucidate this disagreement in the literature.

4.3.4 Effects of pH on Adsorption of Zn (II) ions

The impact of solution pH on 50ppm Zn (II) ions adsorption was investigated using mangroves adsorbent and conducted at different pH values (ranging from 2.0 to 8.0). The pH adjustment was done with the addition of either 0.1 M NaOH or 0.1 M HCl. The results are displayed in Figure 27.

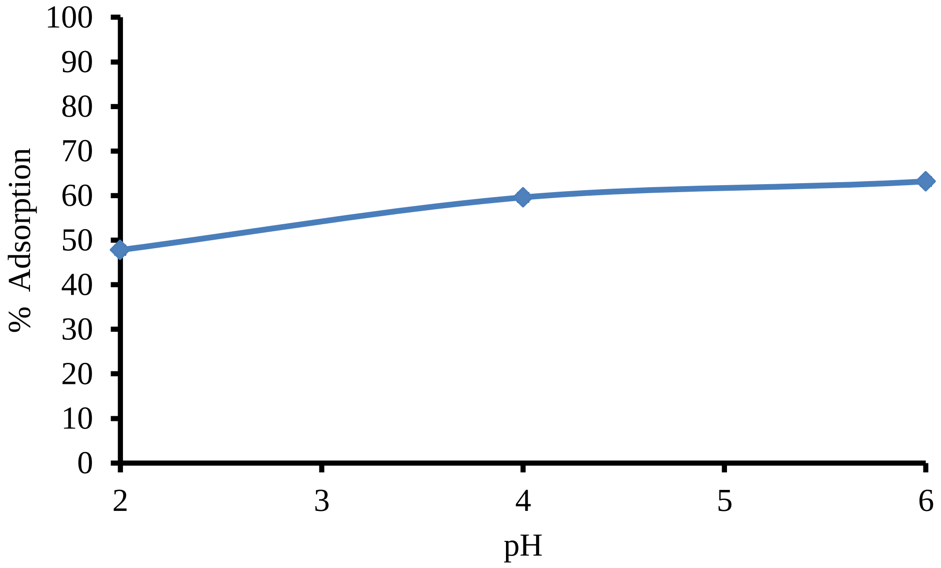

Figure 27: Effect of pH on % Adsorption of 50ppm Zn (II) ions by 0.5g of Mangroves Roots.

From Figure 27, the % adsorption of Zn (II) ions increased gradually from 47.8% at a pH range of 2 to 63.2% at a pH of 6. Optimum pH value for adsorption capacity and removal efficiency of heavy metal ions was 6.

At a low pH, the adsorption of zinc was low (below 50%). This could be attributed to competition between hydrogen and zinc ions with an apparent preference for hydrogen ions on the sorption sites. This phenomenon restricts the approach of the metal cations as a consequence of repulsive force between the metal cations and the protons both of which are positively charged. As pH was increased, the intensity of negative charges on the biomass surface increased, increasing the attraction of metallic ions with positive charge and allowing the adsorption on to the cell surface.

Rozaini *et al.* (2010) reported that at low pH (<3), there was excessive protonation of the active sites at carbon surface and that restricted the formation of links between metal ion and the active site. At moderate pH values (3-6), linked H^+ ions were released from the active sites and adsorbed amount of metal ions were generally found to increase. At higher pH values (>6), the precipitation was dominant or both ion exchange and aqueous metal hydroxide formation (not necessarily precipitation) could become significant mechanisms in the metal removal process. Sheng *et al.* (2012) showed that Moso and Ma bamboo activated carbons possessed optimum pH values for heavy metal ions as 5.81–7.86 and 7.10–9.82 respectively.

pH seems to play a significant role in controlling the adsorption of heavy metals. pH values can affect the surface charge of adsorbent, the degree of ionization and speciation of heavy metals, the competition of the metal ions with coexisting ions in solution (Park *et al.*, 2010). This pH dependency could be explained by the involvement of functional groups in metal uptake and metal chemistry (Kumar *et al.*, 2012).

As a rule, as solution pH increases, the adsorptive removal of cationic metals increases, whereas that of anionic metals decreases. At lower pH, the overall surface charge of mangrove roots will be positive. The H^+ ions compete effectively with the metal cations causing a decrease in adsorption capacity. When pH values increase, the mangrove roots surface becomes increasingly negatively charged which favors the metal ions uptake due to electrostatic interaction. At very high pH, the adsorption stops and the hydroxide precipitation starts (Njoku *et al.*, 2011; Taha *et al*., 2011).

Similar tendencies were found in adsorption processes using diverse agricultural wastes adsorbents. Giri *et al*. (2012) studied the effect of pH on the removal of Cr (VI) using *Eichhornia crassipes* root activated carbon where they reported that the Cr (VI) adsorption efficiency increased from 41.22% to 85.52% for 10 mg/L, 45.34% to 89.23% for 50 mg/L and 50.23% to 92.24% for 100 mg/L with the increase of pH from 1.5 to 4.5. Taha *et al.* (2011) investigated the role of pH in the adsorption of Pb (II), Cd (II) and Zn (II) ions using potato peels and observed that the removal efficiency increased with increasing pH values from 2 to 6; after pH 6, there was a decrease in metal ion removal.

Similarly, Reddy *et al.* (2011) in the case of removal of Ni (II) with *Moringa oleifera* bark found that under highly acidic conditions the removal percentage of Ni (II) was very small. The adsorption increased with the increase in pH from 3.0 to 6.0 and then decreased in the range of pH between 7.0 and 8.0. These results agree with those reported by Feng *et al.* (2011). It was revealed that the percent adsorption for Pb (II), Cd (II) and Ni (II) by grafted copolymerization-modified orange peel was minimal at pH 2.0 and increased with increasing pH from 2.0 to 5.5.

4.3.5 Effect of Temperature on Zn (II) ions Adsorption

Studies on effect of temperature on adsorption of Zn (II) ions were carried out at varying temperatures (25 to 70°C) and the results were presented as % removal of zinc versus temperature. Figure 28 below shows the effect of temperature on adsorption of Zn^{2+} ions by mangrove roots.

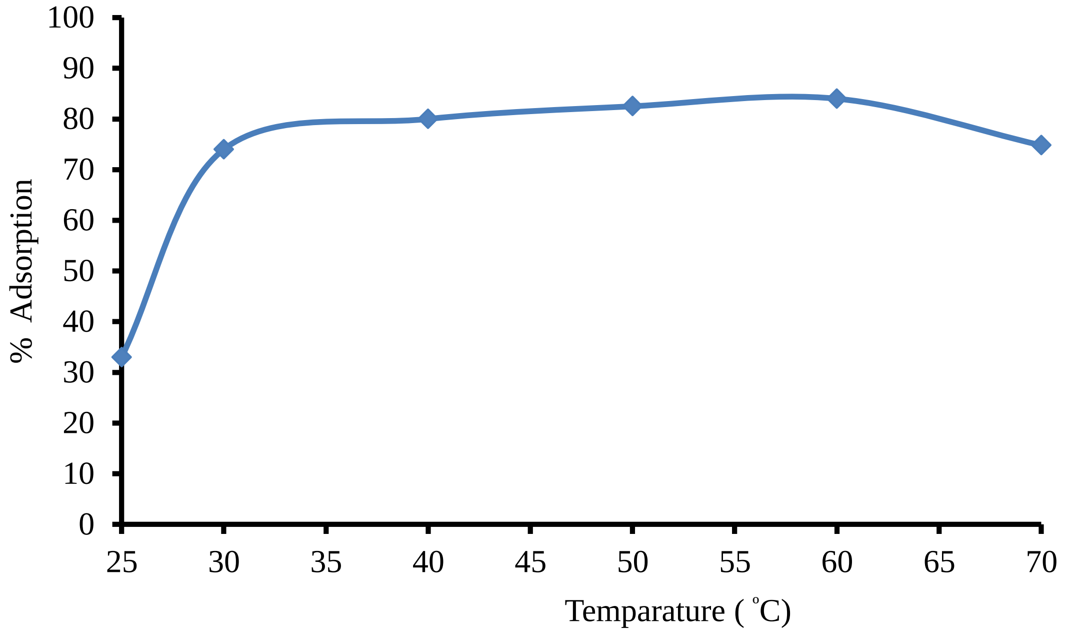

Figure 28: Effect of Temperature on % Adsorption of 200ppm Zn (II) ions by 0.5g Mangrove Roots.

The % adsorption at 25°C was 33 % while at a higher temperature (60°C) was 84 % as shown in Figure 28. However, at 70°C the % adsorption dropped slightly to 74 %. This indicates that adsorption process is endothermic and therefore favored by high temperatures. This confirms earlier reported results that indicated that adsorption reactions are endothermic, and therefore adsorption capacity increased with increase in temperature Banerjee *et al*. (2012).

The decrease in the adsorption capacity at a higher temperature may be due to damage of the active binding sites in the biomass (Ozer and Ozer, 2003). The decrease in % adsorption could also be due to a distortion of some sites of the adsorbent surface available for metal adsorption (Kapoor and Viraraghavan, 1997).

4.3.6 Adsorption Isotherm Studies for Zn (II) ions

Adsorption isotherm studies were carried out by varying the Zn (II) concentration from 50 to 1000 mg/L. The studies were done at room temperature and the experimental results were as displayed in Figures 29 and 30 below.

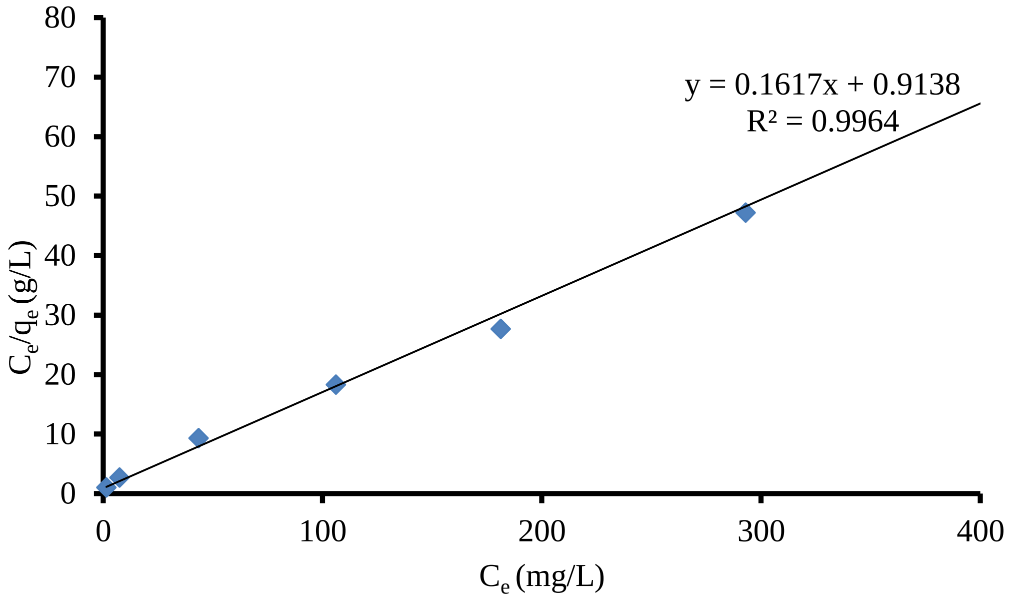

Figure 29: Linearized Langmuir Isotherm for Adsorption of Zn (II) ions by 1.0g Mangrove Roots.

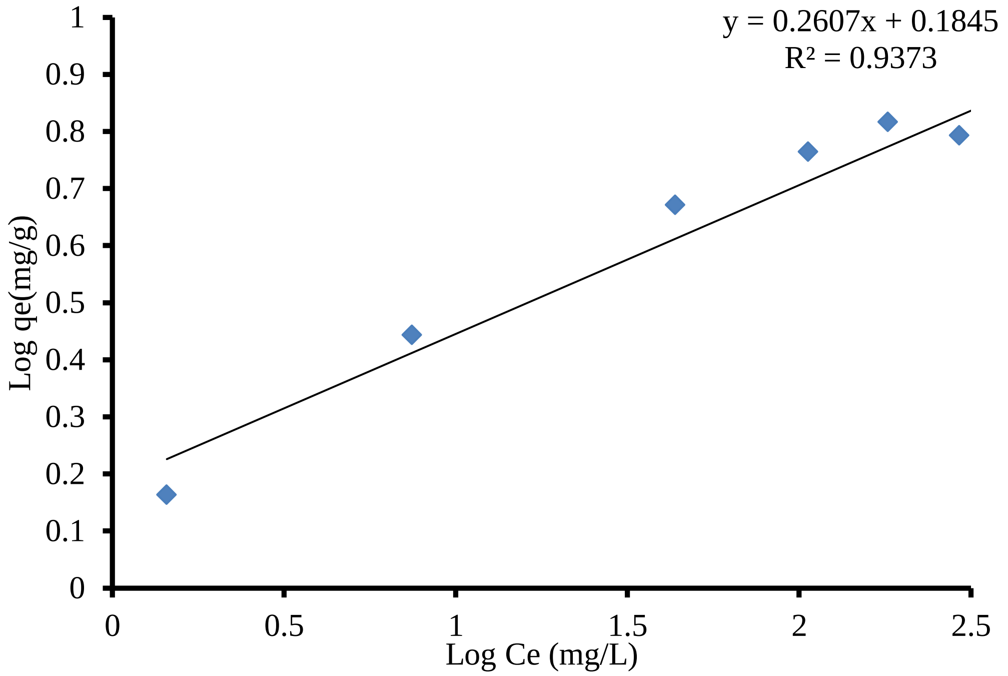

Figure 30: Freundlich Isotherm for Adsorption of Zn(II) onto 1.0g Mangroves Roots.

Summary of Langmuir and Freundlich Constants and correlation coefficients are given in Table 5 below.

Table 5: Langmuir and Freundlich Constants for Zn (II) ions Adsorption onto 1.0g Mangrove Roots.

Langmuir			**Freundlich**		
Q_{max}(mg/g)	***b*(L/mg)**	**R^2**	**K_F**	***n***	**R^2**
6.211	0.176	0.996	1.528	3.846	0.937

The correlation coefficient values obtained from the Freundlich and Langmuir isotherms are shown in Table 5. The results indicated that the adsorption pattern for Zn (II) on mangrove roots follows both the Freundlich isotherm ($R^2 = 0.937$) and the Langmuir isotherm ($R^2 = 0.996$). However, the Langmuir isotherm was best fitted for the adsorption of zinc ions on mangroves roots.

According to Sathish *et al*. (2014), any adsorption system which obeys both the Freundlich and Langmuir isotherms indicates that the solute forms a homogenous monolayer on the adsorbate. In the current study, adsorption of Zn (II) onto mangrove roots obeys both Freundlich and Langmuir isotherms suggesting that Zn (II) formed a monolayer on the surface of mangroves roots.

4.3.7 Adsorption Kinetics of Zn (II) ions

The experimental data was evaluated using pseudo-first-order and pseudo-second –order models. Results were as displayed in Figure 31.

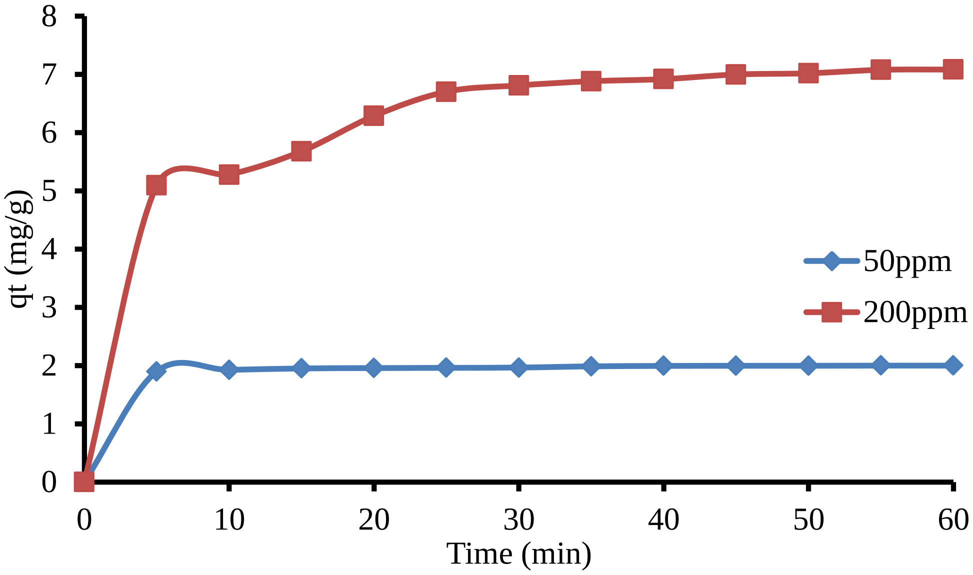

Figure 31: Effect of Contact Time on Zn (II) ions uptake by 0.5g of Mangroves Roots.

The amount of metal uptake increased with increase in the concentration and time. From Figure 31, the amount of uptake (q_t) after 60 min of contact time increased from 5.096 to 7.0844 mg/g for a concentration of 200ppm. For a concentration of 50ppm, the adsorption process was almost stagnant throughout and the equilibrium time was attained after 5 minutes. This still emphasizes earlier observation that mangrove roots have plenty of binding sites for binding of the Zn (II) ions.

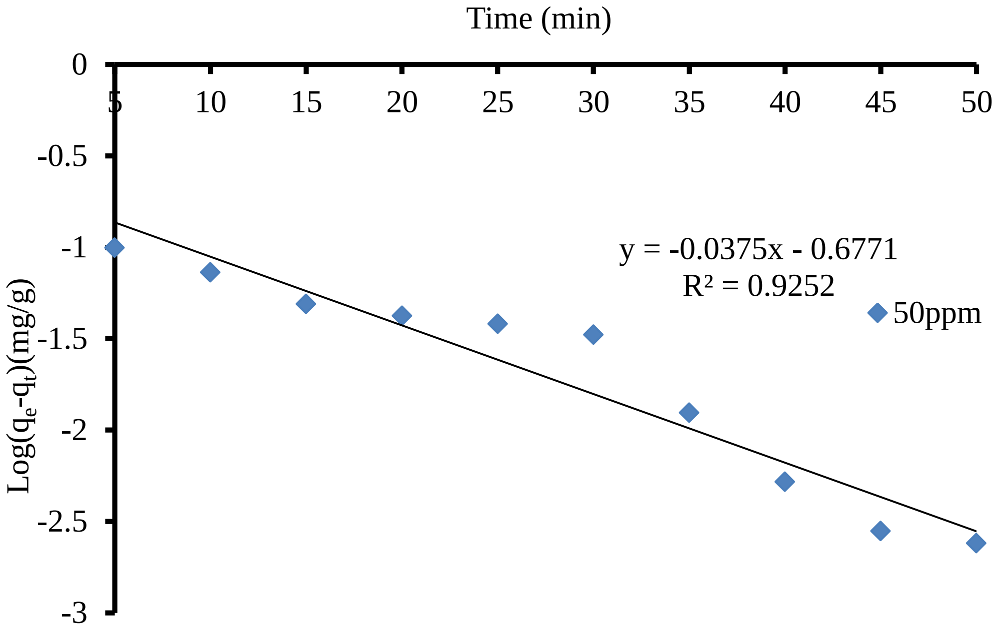

Figure 32: Pseudo-First-order Plot for Adsorption of 50ppm of Zn (II) ions onto 0.5g Mangroves Roots

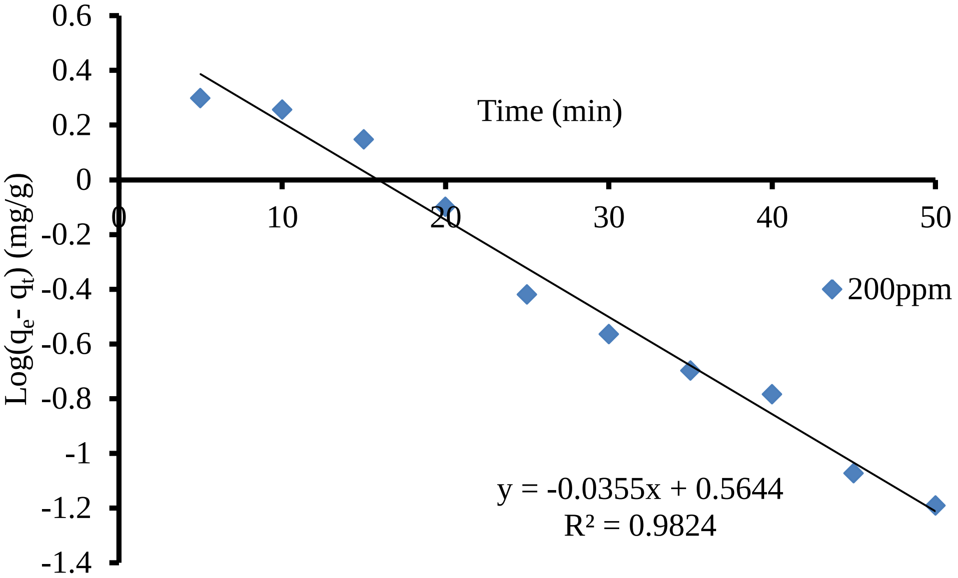

Figure 33: Pseudo-First-order Plot for Adsorption of 200ppm of Zn (II) ions onto 0.5g Mangroves Roots

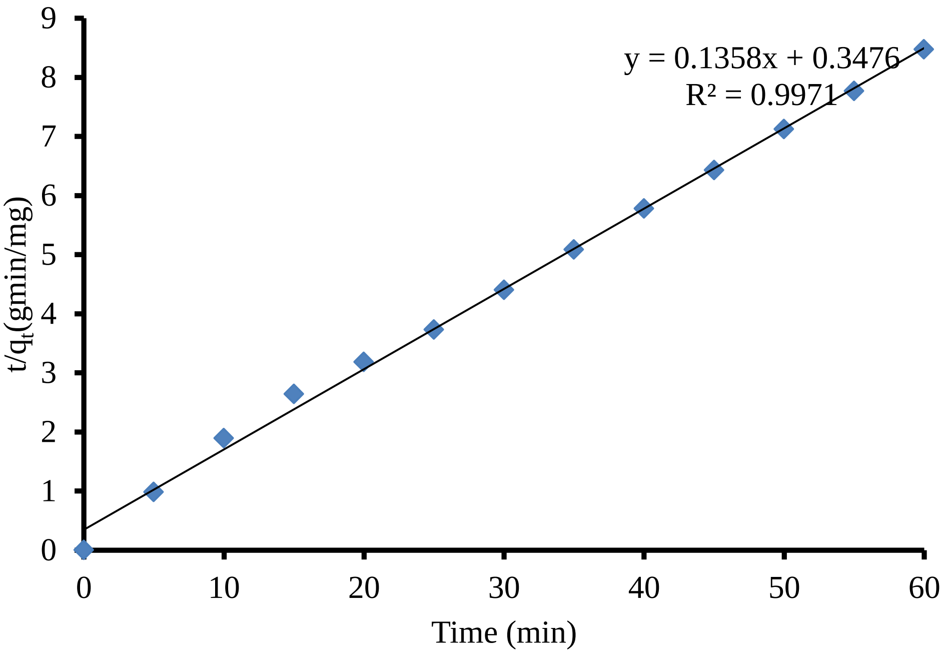

Figure 34: Pseudo-second- Order Plots for Adsorption of 200ppm Zn (II) ions by 0.5g Mangroves Roots.

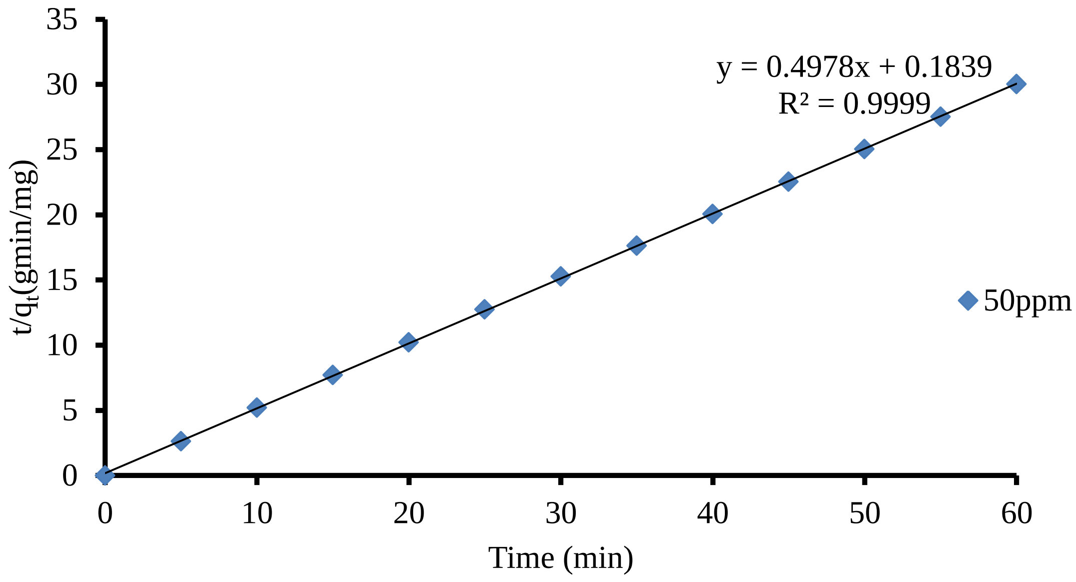

Figure 35: Pseudo-second-Order Plots for Adsorption of 50ppm Zn (II) ions by 0.5g Mangrove Roots.

Table 6: Pseudo-First-Order and Pseudo –Second-Order Rate Constants for Adsorption of Zn (II) ions onto 0.5g Mangrove Roots

Pseudo-first-order				**Pseudo-second -order**		
[Zn] mg/L	**$q_{e(mg/g)}$**	**Constant (min^{-1})**	**R^2**	**q_e(mg/g)**	**Constant (g/mg/min)**	**R^2**
50	0.2104	0.0851	0.925	2.012	1.349	0.999
200	3.664	0.0806	0.982	7.407	0.053	0.997

Results in Table 6 shows the adsorption kinetic rate constant, correlation co-efficient and value of experimental q_e. From the results it can be concluded that pseudo-second-order equation provided the best correlation coefficient (R^2) at both low and high concentrations. The results suggest that chemisorption was the rate-determining step in the adsorption of Zn (II) ions on mangrove roots.

4.4 ADSORPTION STUDIES OF CADMIUM (II) IONS USING AAS

4.4.1 Effect of equilibration Time and Initial Concentration on Adsorption of Cd (II) ions

Contact time plays a great role in the effective removal of heavy metals using adsorbents. The influence of contact time on adsorption capacity for Cd (II) ions is shown in Figure 36.

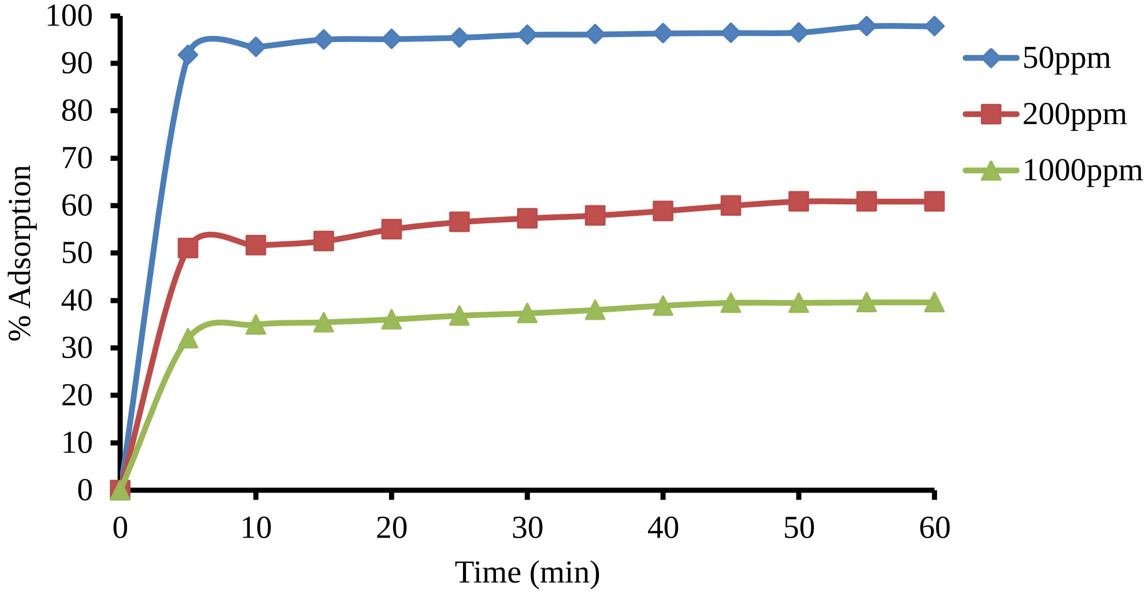

Figure 36: Effect of Contact Time on Adsorption of Cd (II) ions by 0.5g Mangroves Roots.

From the results, it can be seen that at a lower initial concentration of 50ppm, a higher adsorption rate of 91.6 % was attained after 5 minutes of contact. However, at a higher initial concentration of 1000ppm, a reduced adsorption percentage of 32% was achieved for the same contact time.

The lower % adsorption for higher initial concentration(1000ppm) of cadmium ions could be attributed to the exhaustion of the binding sites as previously mentioned earlier in the dissertation (Sari and Tuzen, 2008). The adsorption efficiency increased with rise in contact time up to about 20 minutes after which it was almost constant. This could be due to the metal ions available for binding having been spent up especially at low concentrations (50ppm). Similar results were reported by Etorki (2014).

4.4.2 Effect of Weight of Sorbent and Particle Size on Adsorption of Cd (II) ions

The effect of varying the adsorbent mass on the adsorption of 50ppm Cd (II) ions was studied using adsorbent dosages in the range of 0.125 – 2.0 g as shown in Figure 37.

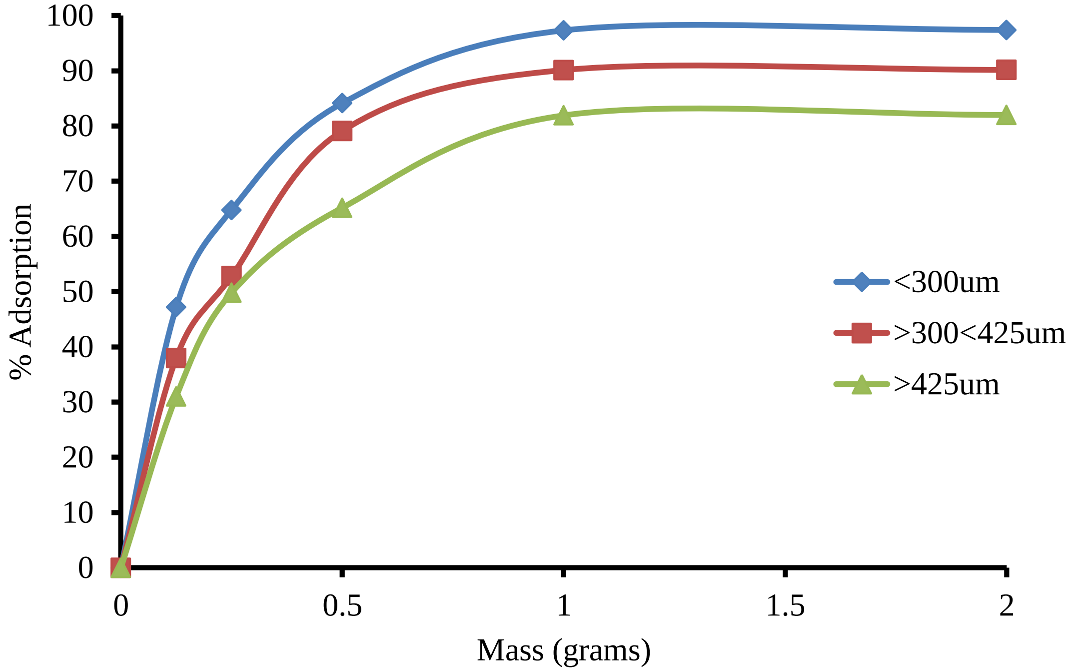

Figure 37: Effect of Weight and Particle Size on 50ppm Cd (II) ions Adsorption by Mangrove Roots.

It is clearly seen that the removal efficiency increased as the mass of mangrove roots increased. It is also seen that the % adsorption increased with decrease in particle size. Decrease in particle size led to an increase in the surface area, thus availability of more binding sites on the adsorbent surface to take up the metal ions in solution.

Sathish *et al*. (2014) reported that adsorption of Cr (VI) on modified leaf powder increased with decreased particle size 1.4–0.5 mm, then decreased proportionately with further reduction in particle size. The increased adsorption with decreased particle size could be attributed to the fact that smaller particle size has more surface area than the larger particles. However, fine particles (< 0.5 mm) form agglomerate in the solution and decrease the overall surface area which results in lesser uptake of metals.

4.4.3 Effect of Initial Concentration of Cd (II) ions on Adsorption

The feasibility and efficiency of an adsorption process depends not only on the properties of the adsorbent but also on the concentration of the metal ion solution. The initial metal ion concentration provides an important driving force to overcome all mass transfer resistances of the metal between aqueous and solid phase. Several experiments were conducted to investigate the effect of varying the initial concentration of the Cd^{2+} ions on adsorption onto a fixed mass of Mangrove roots biomass. The results are shown in Figure 38.

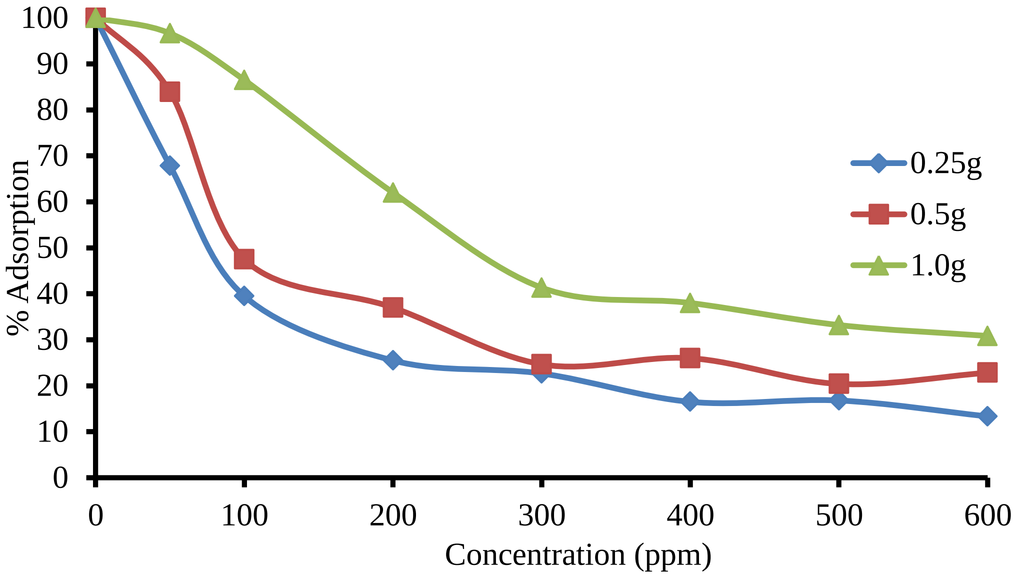

Figure 38: Effect of Initial Concentration of Cd (II) ions on Adsorption by Mangrove Roots.

It can be seen from the results (Figure 38) that at lower concentrations, there was high percentage (96.64%) adsorption of metal ions onto the biomass. This was because at lower initial solute concentrations, the ratio of initial moles of solute to the surface area was low; consequently functional adsorption became independent of concentration. This could also be attributed to the availability of many adsorption sites on mangrove roots thus less competition among the metal ions for the binding sites. However, at higher initial concentration, the adsorption decreased to about 30.8 % for 1.0 g of biomass. It can also be seen that when the concentration increases the numbers of binding sites become saturated, accommodating only a portion of the available metal ions looking for binding sites. This emphasizes the fact that adsorption follows Langmuir isotherm with monolayer coverage.

Similar results were observed by Shankar *et al*. (2014), Jayakumar *et al*. (2013) and Ahmad *et al*. (2009).

4.4.4 Effect of pH on Adsorption of Cd (II) ions

pH is an important parameter controlling the process of adsorption of metal ions. The effect of pH on the adsorption of 50ppm Cd (II) ions onto mangrove roots was studied by varying pH values in the range of 2.0 to 8.0.

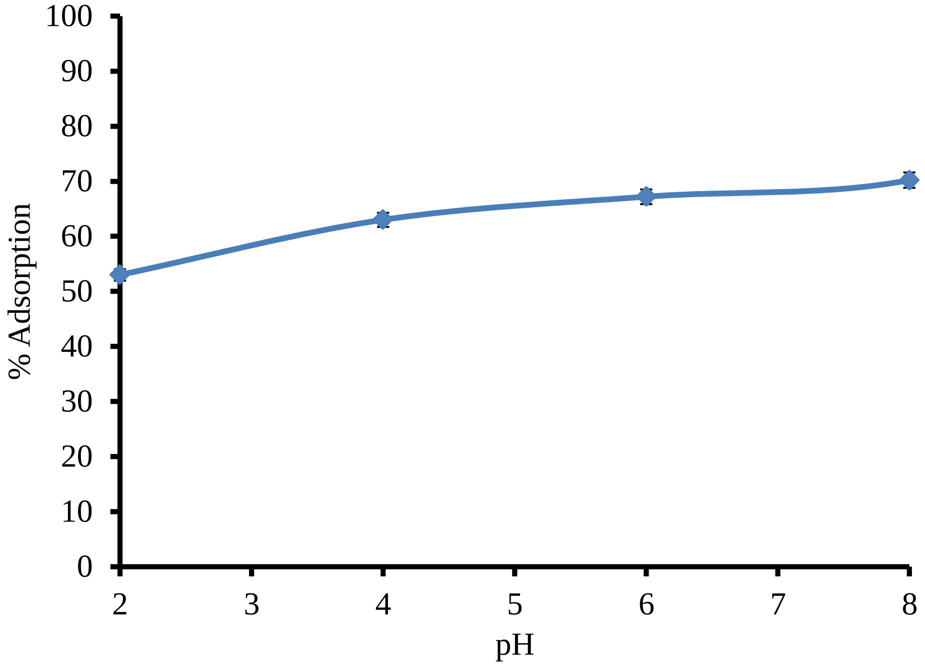

Figure 39: Effect of pH on % Adsorption of 50ppm Cd (II) ions by 0.5g of Mangroves Roots.

Maximum adsorption was 70.2 % recorded at a pH of 8.0 for a concentration of 50ppm. At a lower pH, the adsorption yield of cadmium was very low (below 50%). This was possibly because of the increased positive (proton) density on the biomass surface restricting the approach of the metal cations by repelling them. At a lower pH, the H_3O^+ ions competed with the metal ions for the adsorption sites on the adsorbent, therefore, adsorption of the metal ions increased with increase in pH from 2 to 8 (Aravind *et al*., 2013).

In contrast, when the pH was increased, the biomass surface was more negatively charged and the adsorption of the cations which were positively charged was facilitated reaching a maximum of 70.2%. At pH > 8, the Cd (II) ions got precipitated due to hydroxide anions forming cadmium hydroxide precipitate. The hydroxide form of metal could also compete with the metals ions at the actives sites of the adsorbent thereby decreasing the adsorption (Kongsuwan *et al.*, 2006).

4.4.5 Effect of Temperature on Cd (II) ions Adsorption

Adsorption studies were carried out at varying temperatures (25 to 70°C) and the results were presented as % adsorption of cadmium versus temperature. Figure 40 illustrates the effect of temperature on the adsorption of 50ppm Cd (II) ions.

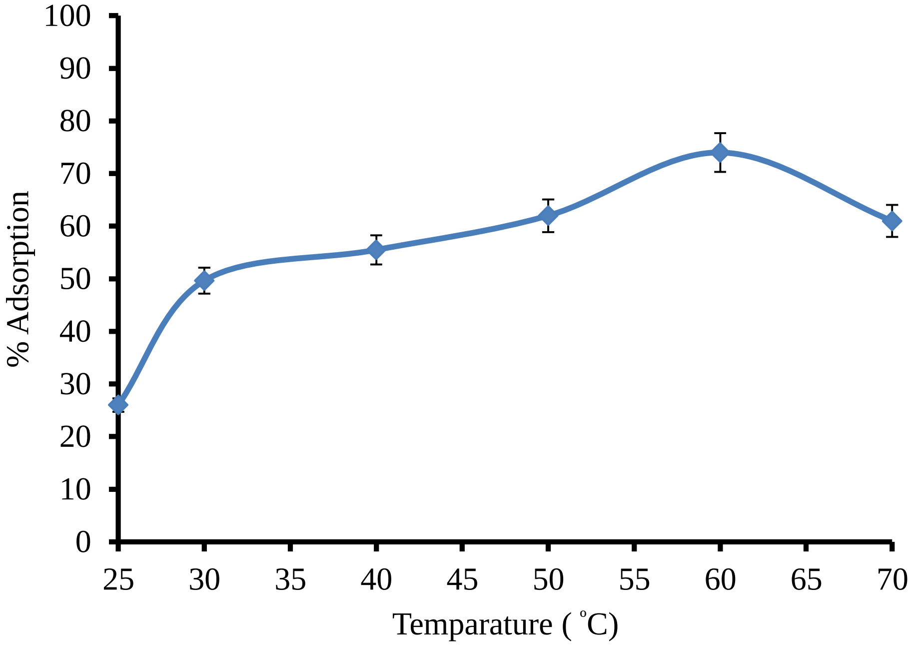

Figure 40: Effect of Temperature on % Adsorption of 200ppm Cd (II) ions by 0.5g Mangroves Roots.

Percentage removal of copper with initial concentration of 200ppm increased from 26% to 74% for a temperature change from 25°C to 70°C. It can also be seen from Figure 40 that % adsorption increased with increase in temperature up to 60°C after which it dropped with further increase in temperature.

The observed decrease in the adsorption of Cd (II) ions with temperature increase could be due to either damage of the binding sites (Ozer and Ozer, 2003) or increasing tendency to desorb metal ions from the interface to the solution (Sari and Tuzen, 2008).

The decreased adsorption efficiency may also be attributed to many parameters. This includes the relative increase in the escaping tendency of Cd (II) ions from the solid phase to the bulk of the solution; deactivation of the adsorbent surface or destruction of some active sites on the adsorbent surface due to bond ruptures or due to weakness of the adsorptive forces between the active sites of the adsorbent and the adsorbate species and also between adjacent molecules of the adsorbed phase (Meena *et al.*, 2005). The results indicated an endothermic nature of Cd (II) ions adsorption onto the mangrove roots biomass.

4.4.6 Adsorption Isotherm Studies for Cd (II) ions

Adsorption capacity of an adsorbent can be described by equilibrium adsorption isotherms, which are characterized by definite constants whose values express the surface properties and affinity of the adsorbent for different pollutants (Darsun *et al.*, 2005). In this study, two important adsorption isotherm models were selected to fit experimental data, namely; Langmuir and Freundlich isotherm models. The results are shown in Figures 41 and 42 respectively.

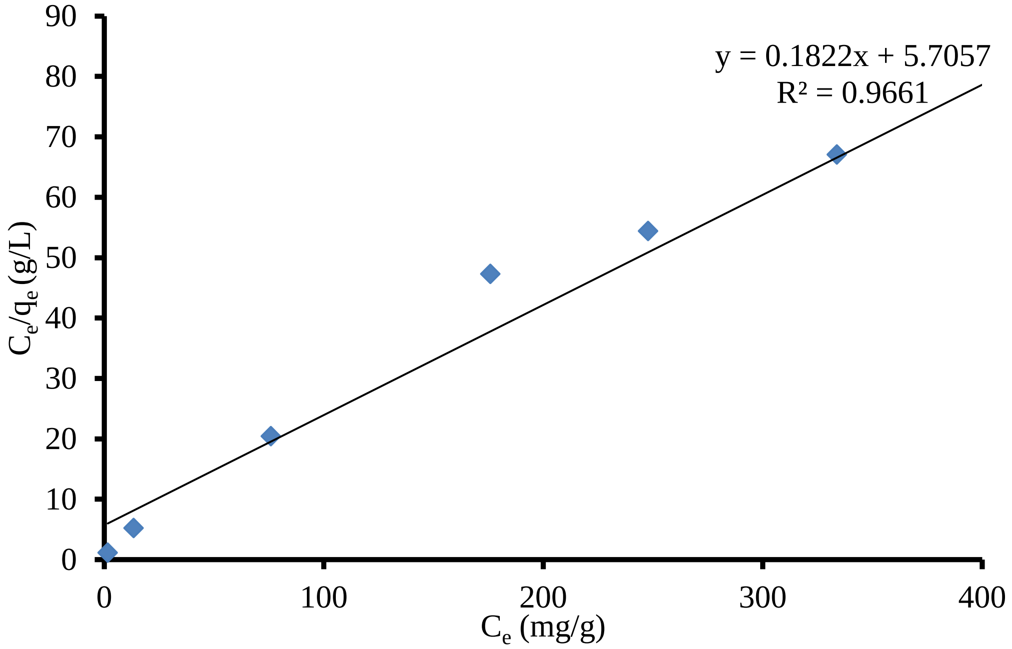

Figure 41: Langmuir Isotherm Plot for Adsorption of Cd (II) by 1.0g Mangrove Roots.

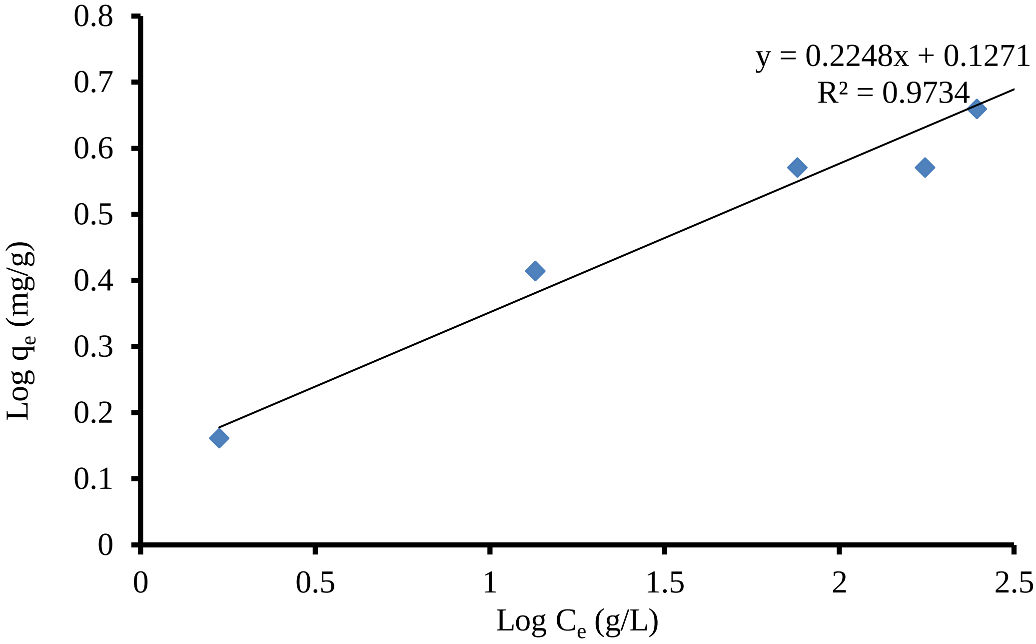

Figure 42: Freundlich Isotherm Plot for Adsorption of Cd (II) by 1.0g Mangroves Roots.

Table 7: Langmuir and Freundlich Isotherm Constants and Correlation Coefficients for Adsorption of Cd (II) ions by 1.0g Mangroves Roots.

Langmuir			**Freundlich**		
Q_{max}(mg/g)	***b*(L/mg)**	**R^2**	**K_F**	***n***	**R^2**
5.4945	0.032	0.966	1.34	4.464	0.973

Langmuir and Freundlich parameters were obtained by plotting C_e/q_e versus C_e and Log q_e versus Log C_e respectively. The validity of the isotherm models was tested by comparing the theoretical correlation coefficient and experimental correlation coefficient. Based on the correlation coefficients (R^2), it was clear that the adsorption of cadmium ions on mangrove roots was best fitted to Freundlich adsorption isotherm for the entire range of concentrations. The fitting of the experimental data on Freundlich isotherm could be due to heterogeneous distribution of active sites on the mangrove roots surface, since the Freundlich equation assumes that the surface is heterogeneous. The values of *n* for Freundlich isotherm were found to be greater than 1, indicating that metal ions were favorably adsorbed by mangrove roots.

4.4.7 Adsorption Kinetics for Cd (II) ions.

In order to examine the controlling mechanisms of adsorption process, kinetic models were used to test the experimental data. The data was analyzed using pseudo-first-order and pseudo-second- order models. The results are displayed in the Figures 43 to 46.

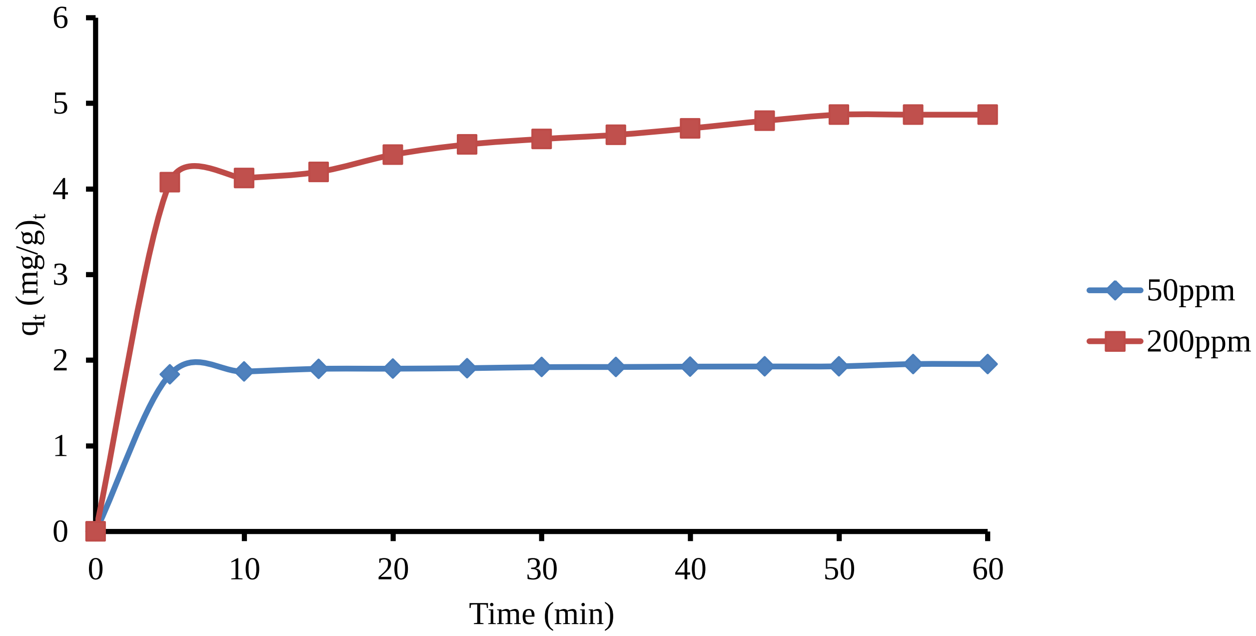

Figure 43: Effect of Contact Time on 50ppm and 200ppm Cd (II) ions uptake by 0.5g Mangrove Roots.

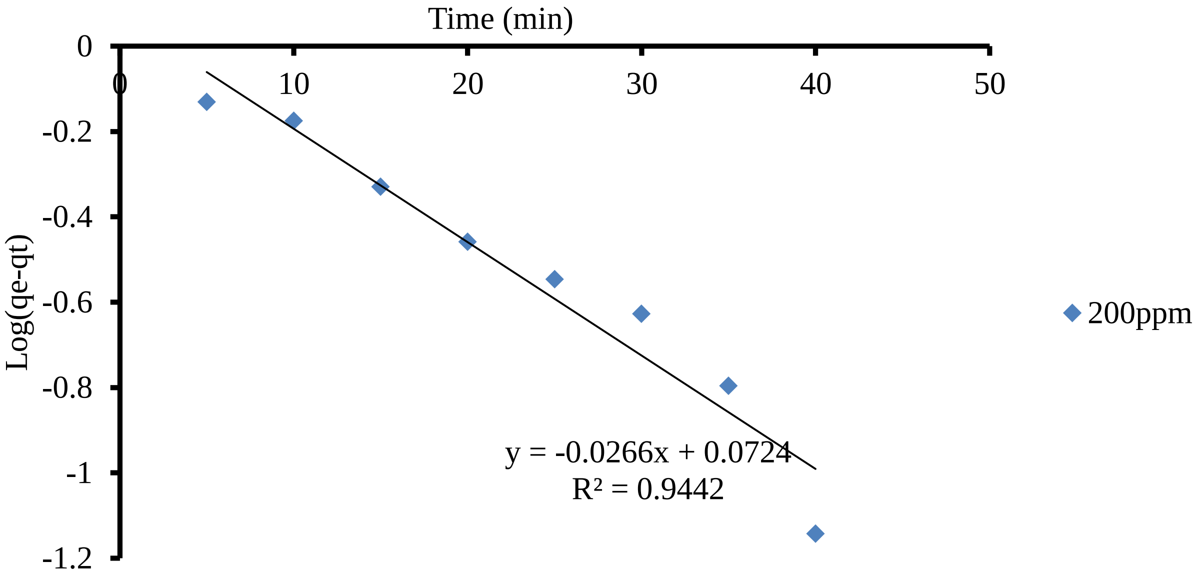

Figure 44: Pseudo-First-Order Plot for Adsorption of 200ppm Cd (II) onto 0.5g Mangrove Roots.

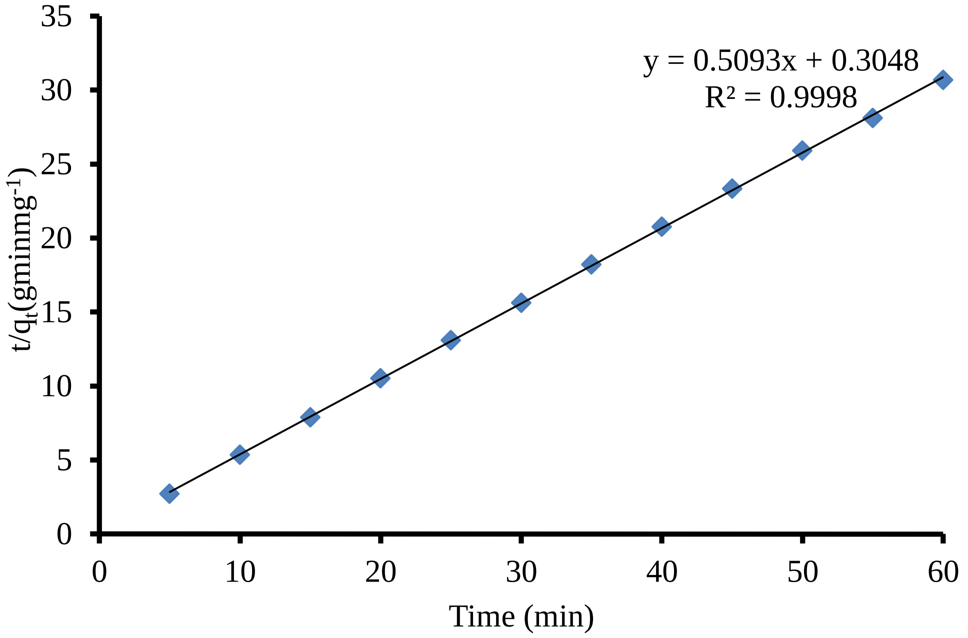

Figure 45: Pseudo-Second-Order-Plots on Adsorption of 50ppm of Cd (II) onto 0.5g Mangrove Roots.

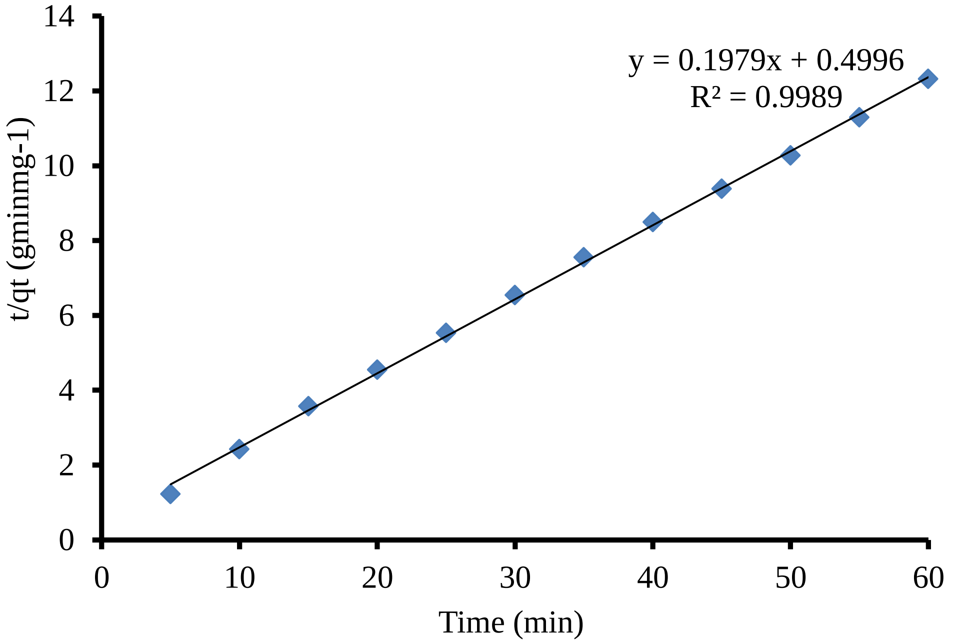

Figure 46: Pseudo-Second -Order- Plots on Adsorption of 200ppm of Cd (II) onto 0.5g Mangrove Roots.

Table 8: Comparison of Pseudo-First-Order and Pseudo Second Order Rate Constants at Different Cd (II) ions Concentrations

Pseudo-first-order				**Pseudo-second -order**		
[Cd] mg/L	**Q_e (mg/g)**	**Constant (min^{-1})**	**R^2**	**Q_e (mg/g)**	**Constant (min^{-1})**	**R^2**
50	0.1114	0.0299	0.919	1.9646	0.8523	0.999
200	1.180	0.05987	0.944	5.076	0.0778	0.998

From the above results the pseudo-second order plots have a higher correlation coefficient R^2=0.999 compared to R^2=0.919 for the pseudo-first-order model for an initial concentration of 50ppm. Therefore, adsorption of Cd (II) fits pseudo-second order mechanism with a rate constant of 0.8523 g/mg/min. This suggests that Cd (II) ions are attached to the adsorbent surface by complexation. That is, cadmium ions can bind to two binding sites on the mangroves roots surface.

4.5 ADSORPTION STUDIES OF LEAD (II) IONS USING AAS

4.5.1 Effect of Equilibration Time and Initial Concentration on Adsorption of Pb (II) ions

The percentage of lead adsorbed at varying contact time keeping other parameters constant is presented in Figure 47 below. According to the Figure, at lower initial Pb (II) ion concentration (50ppm) the % adsorption was very high even attaining the 96% mark within 5 minutes of contact time. At high concentration of 1000 ppm, a reduced adsorption (62%) was observed within the same contact time of 5 minutes, and even after the set 60 minutes (81.8 %). This implied that upon contact of the biomass with the metal ions, the metal ions were rapidly taken up by the mangrove roots biomass.

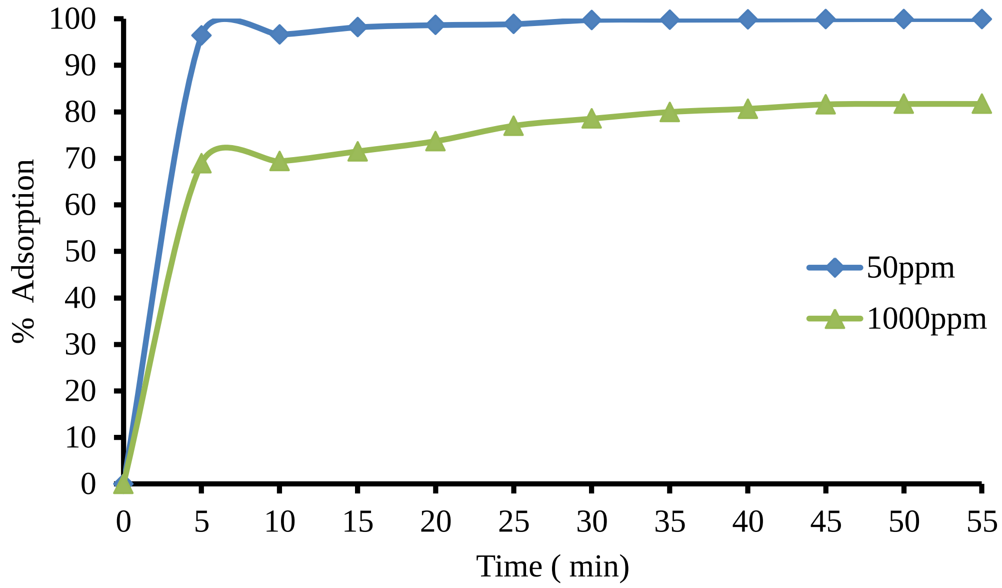

Figure 47: Effect of Contact Time and Concentration on % Adsorption of Pb (II) ions by 0.5g Mangrove Roots.

As shown in Figure 47, adsorption increased rapidly with time and then reached a point where there was no change in adsorption with increase in contact time. The initial fast adsorption could be explained also through physical adsorption since adsorption phenomenon characteristically tends to attain instantaneous equilibrium. The number of active sites in the system was fixed and each active site could adsorb only one ion in a monolayer therefore metal uptake by the sorbent surface was rapid initially and then decreased as the availability of active sites decreased thus slowing down the transfer of metal ion from solution to the adsorbent surface. Guinesi and Cavalheiro (2006) stated that adsorption sites at equilibrium are saturated; therefore cannot adsorb any more of the metal ions. Jane *et al*. (2014) reported that removal of Cr (VI) ions from aqueous solution using activated carbon increased with contact time and obtained a saturation point at 90 minutes.

4.5.2 Effect of Weight of Adsorbent and Particle Size on Adsorption of Pb (II) ions.

The effect of particle size of mangrove roots on removal of Pb (II) ions was studied using three different sizes (<300 µm, >300 µm and > 425 µm). Figure 48 shows the percentage removal of Pb^{2+} ions from aqueous solution as a function of weight of mangrove roots of three different sizes.

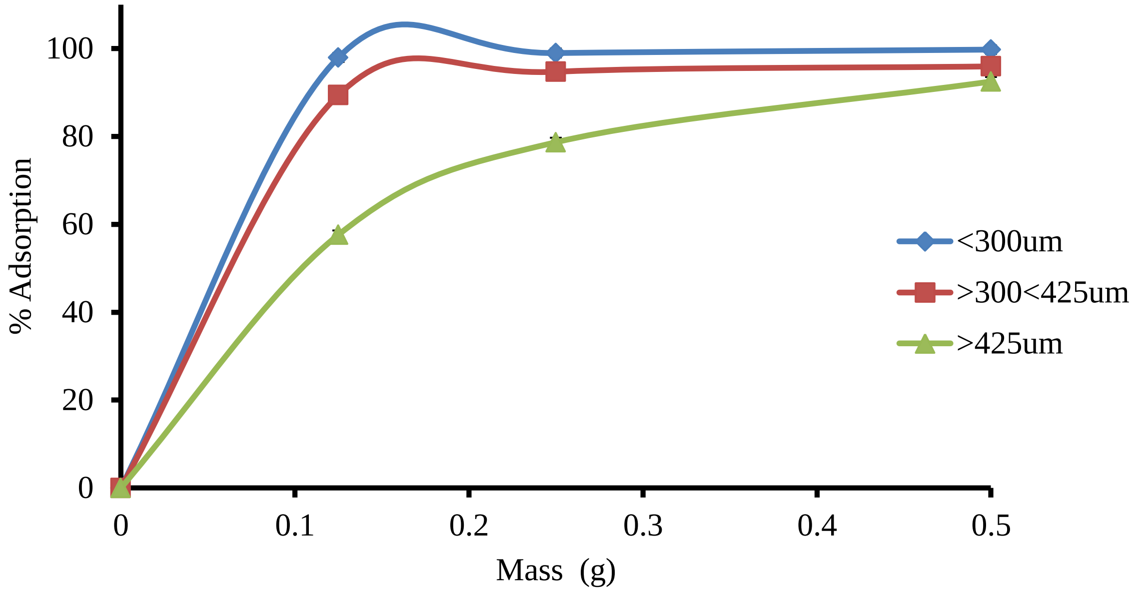

Figure 48: Effect of Weight and Particle Size of Mangrove Roots on Adsorption of 50ppm Pb (II) ions.

From Figure 48, it is evident that there was an increase in the % adsorption with increase in mass for all the particle sizes. The increase in the adsorption was due to the availability of more binding sites for metal ions. The decrease in particle size also had an influence of increasing the % adsorption as the particle size decreased. The smallest particle size i.e., < 300µm gave the highest % adsorption. The smaller the particle size, the larger the surface area exposed to interact with the metal ions in solution. This reaffirms the fact that adsorption takes place via surface mechanism. Increase in surface area meant more binding sites were in contact with the adsorbate. The increase in particle size had a reverse effect of decreasing surface area, reducing number of binding sites hence decreasing the % adsorption.

Similar results were observed by Nhapi *et al.* (2011) who worked on rice husks and Ahmad *et al.* (2009) who worked on treated sawdust of sissoo wood. Suhada *et al*. (2013) demonstrated that the adsorption of Pb (II) ions increased linearly as the amount of adsorbent (mixture of activated charcoal and peanut shell) increased from 1.0 g to 3.0 g and became constant from 3.0 g to 5.0 g.

4.5.3 Effect of initial concentration of Pb (II) ions on adsorption

The rate of adsorption is a function of initial concentration of metal ions which makes concentration an important factor to be considered for effective adsorption (Ahalya *et al.*, 2005). The experimental data illustrating the effect of initial metal ion concentration on the rate of adsorption of Pb (II) ions onto the Mangrove roots biomass is presented in Figure 49.

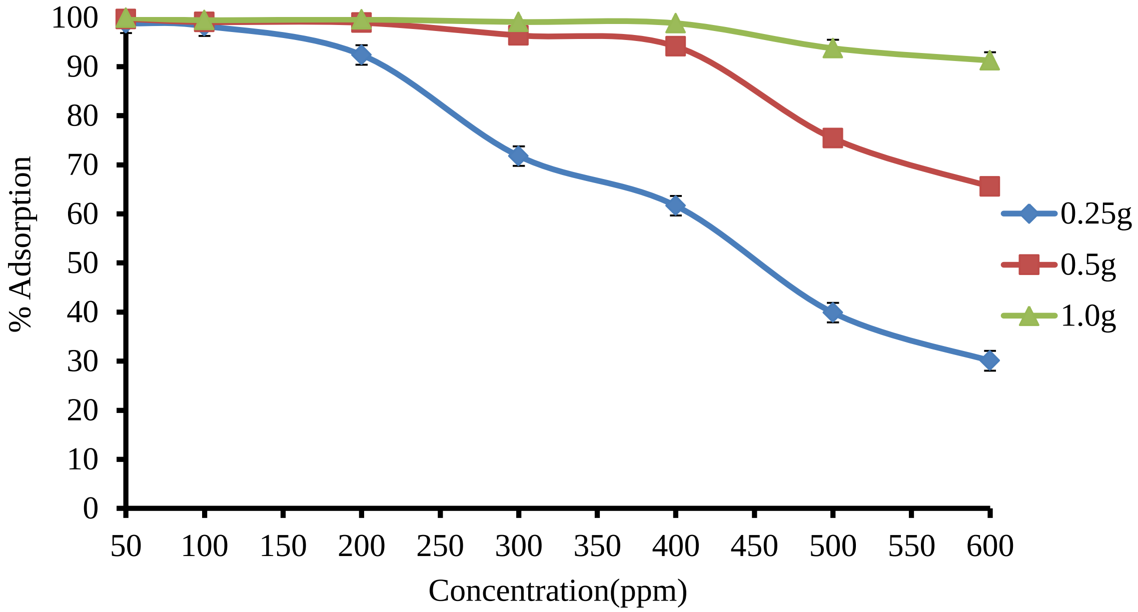

Figure 49: Effect of Initial Concentration of Pb (II) ions on Adsorption Mangrove Roots

When the initial metal ion concentration was increased from 50 to 100 ppm the % adsorption was almost the same (100 %) for all the masses. However, as the concentration changed from 100 to 600 ppm the % adsorption decreased from 99 % to 91.2%, 65.6% and 30% for 1.0g, 0.5g and 0.25g respectively. When the initial concentrations was increased the % adsorption of the Pb (II) ions decreased.

This could be due to saturation of the active adsorption sites on the mangrove roots at higher concentrations. Metal ions need to migrate to the biomass surface by intra-particle diffusion and greatly hydrolyzed ions diffused at a slower rate (Lawal *et al.*, 2010), these accounts for the reduction in the percentage adsorption. It can also be seen that an increase in the amount of the mangroves biomass led to an increase in the % adsorption. This could probably be due to the ratio of mass of adsorbent to concentration of the adsorbate. Similar results have been observed by Ayub *et al*. (2002), Kobya *et al*., (2005) and Najim and Yassim, (2009).

4.5.4 Effect of Temperature on Pb (II) ions Adsorption

To determine the effect of temperature, experiments were carried out by varying temperatures from 25 to 70°C. The results are shown in Figure 50.

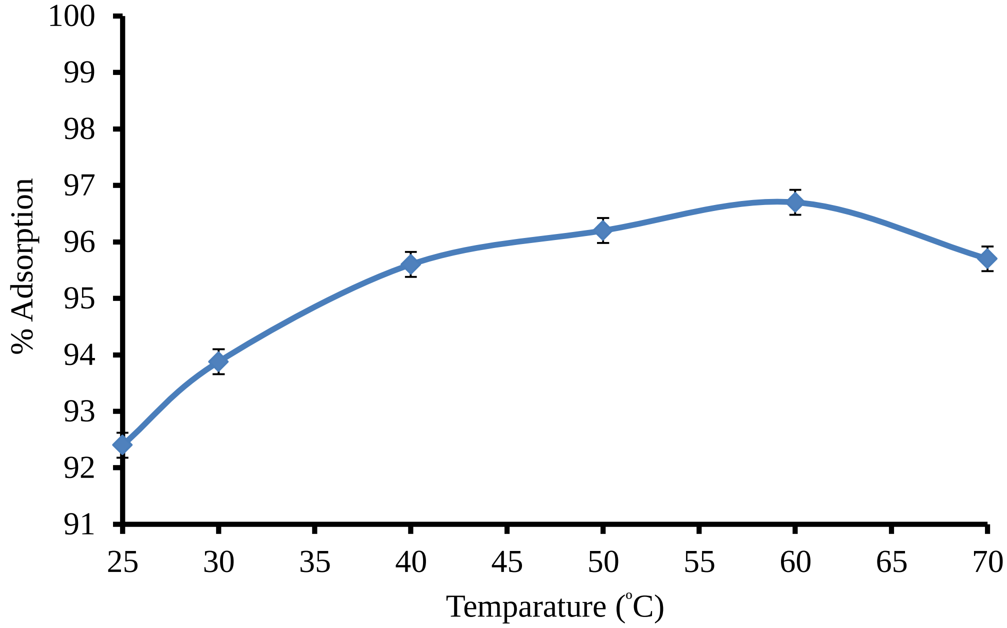

Figure 50: Effect of Temperature on % Adsorption of 200ppm Pb (II) ions by 0.5g of Mangroves Roots.

It can be seen from Figure 50 that the % adsorption at 25°C was 92.4% while at a higher temperature of 60°C it was 96.7%. However, at 70ºC the % adsorption dropped slightly to 95.7%. This indicates that adsorption process is an endothermic reaction, therefore favored by temperatures above room temperatures.

The increase in metal adsorption with increase in temperature could also be due to dissociation of some compounds available in the adsorbent which may provide more sites for adsorption. Increase in adsorption could also be attributed to increase in number of available active sites or decrease in the boundary layer thickness surrounding the adsorbent.

Adsorption researchers have performed a large number of studies on the effects of temperature on metal uptake. The change in solution temperature affects not only diffusion rate of metal ions but also the solubility of metal ions (Park *et al.*, 2010). Depending on surface functional groups of a given adsorbent, temperature has a given impact on the adsorption capacity. However, it is a common conclusion of many studies that the influence of temperature is to a limited extent and only in a certain temperature range (Sahmoune *et al*., 2011). The adsorption process can be affected by temperature in different ways depending on the exothermic or endothermic nature of the process.

Many researchers have reported that adsorption processes are endothermic in nature. Park *et al*. (2010) argued that higher temperatures improve the elimination of heavy metals owing to an increase in its surface activity and kinetic energy. In the same way, Garcia and Colin (2010) also observed that the adsorption of Pb (II) and Cd (II) by the stalk sponge of maize increased 1.1–1.8 times with increasing temperature from 20 to 40°C. Banerjee *et al*. (2012) reported similar observation in case of adsorption of Cu (II) by watermelon shell

In contrast, Kumar *et al*. (2012) found that the adsorption of Cd (II) by cashew nut shell decreased from 80.13% to 74.32% with the rise in temperature from 30° C to 60° C. They attributed this to the decrease in surface activity of adsorbent. Similar trend was noticed by Elsayed *et al*. (2010) in case of Zn (II), Cd (II) and Mn (II) adsorption onto maize stalks. The adsorption percentage decreased from 52% to 28% for Zn (II) ions, from 34% to 16% for Cd (II) ions and from 39% to 13% for Mn (II) ions as the temperature increased from 25 to 55°C. The authors explained this trend by the damage of active adsorption sites of adsorbents or increasing number of metal ions escaped from the adsorbents surface to the solution. The same behavior can be detected in a research performed by Boota *et al*. (2009) sequestering Cu (II) and Zn (II) ions by *Citrus reticulate*.

4.5.5 Effect of pH on Adsorption of Pb (II) ions

The pH of aqueous solutions is an important controlling parameter in the adsorption process. In order to study the effect of pH on Pb (II) adsorption onto Mangrove roots, the pH of solution was varied from 2.0 – 6.0.

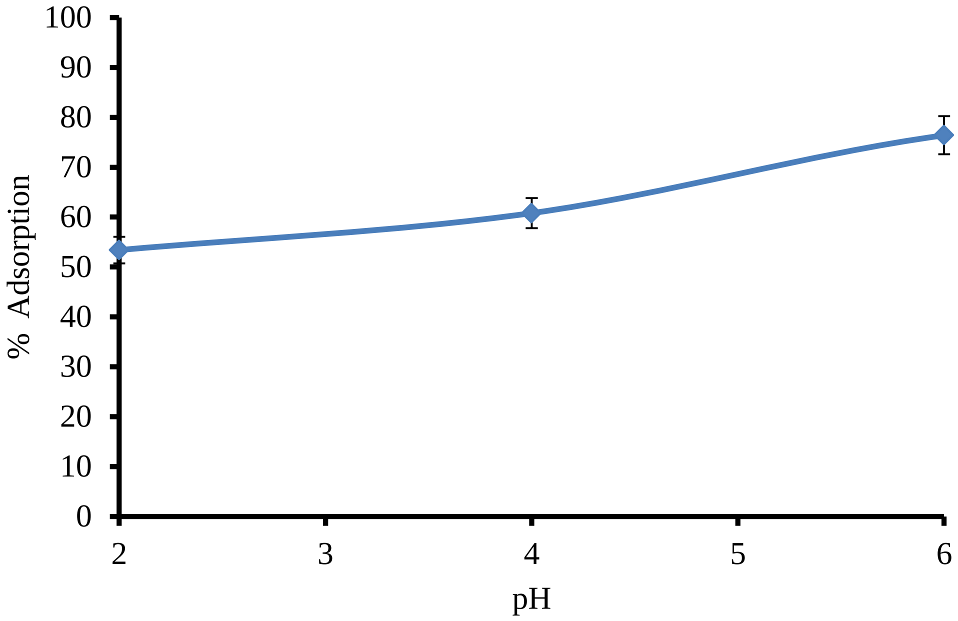

Figure 51: Effect of pH on % Adsorption of 50ppm Pb (II) ions on 0.5g Mangrove Roots.

From Figure 51, it is observed that the adsorption of Pb (II) varies with pH. There was a gradual increase in Pb (II) uptake as the pH value increased from 2.0 to 8.0. The % adsorption was minimum (53.4) at pH 2.0. This was because the H_3O^+ ions were competing with the metal ions for the exchangeable sites on the mangrove roots. The H_3O^+ ions were preferentially adsorbed rather than the lead ions. At higher pH values, the numbers of H^+ ions were few hence the surface was negatively charged. Consequently, the attraction of the cations was enhanced. However, when the pH was increased above 6.0, the Pb (II) ions get precipitated due to the hydroxyl ion forming insoluble lead hydroxide precipitate (Feng *et al.*, 2011). Metal speciation in solution is also pH dependent. The results suggest that at pH below 7.0 the predominant species are positively charged metal ions. At pH values higher than 7.0 insoluble hydroxides are formed. Similar results were reported in the literature (Aravind *et al.*, 2013). This implies that the optimal conditions for adsorption of Pb (II) ions onto mangrove roots are weakly acidic conditions.

Kongsuwan *et al.* (2006) demonstrated that the optimum pH for the adsorption of Cu and Pb were about 5 which was rather acidic. At low pH (< 3), there was excessive protonation of the active sites at mangrove roots surface and this often reduces the formation of links between metal ion and the active site. At moderate pH values (3-6), linked H^+ is released from the active sites and adsorbed amount of metal ions is generally found to increase. At higher pH values (> 6), the precipitation is dominant or both ion exchange and aqueous metal hydroxide formation (not necessarily precipitation) may become significant mechanisms in the metal removal process. This condition is often not desirable as the metal precipitation could lead to a misunderstanding for the adsorption capacity. Consequently, in practice metal precipitation is generally not a stabilized form of heavy metal as the precipitation can sometime be very small in size, and upon the neutralization of the effluent from the wastewater treatment plant, the solubility of the metals increases resulting in a re-contamination of the waste outlet stream.

4.5.6 Adsorption Isotherm Studies for Pb (II) ions.

The Pb (II) ions uptake capacity of mangrove roots was evaluated using different concentrations of the metal ions on a fixed mass of adsorbent. Figures 52 and 53 below illustrate the results obtained and the constants calculated.

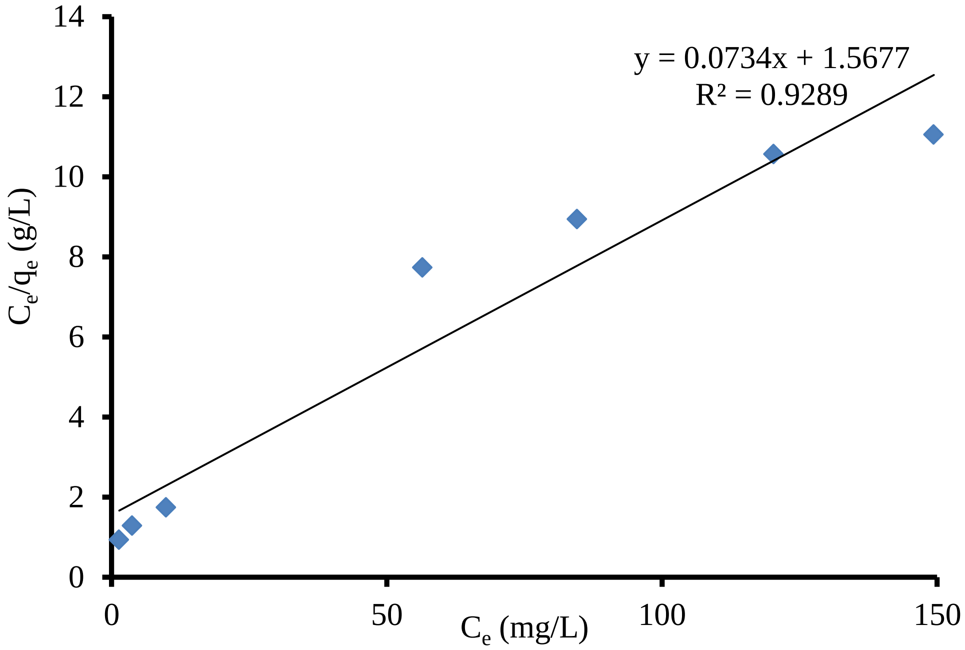

Figure 52: Linearized Langmuir Isotherm for Adsorption of Pb (II) ions by 1.0g Mangrove Roots.

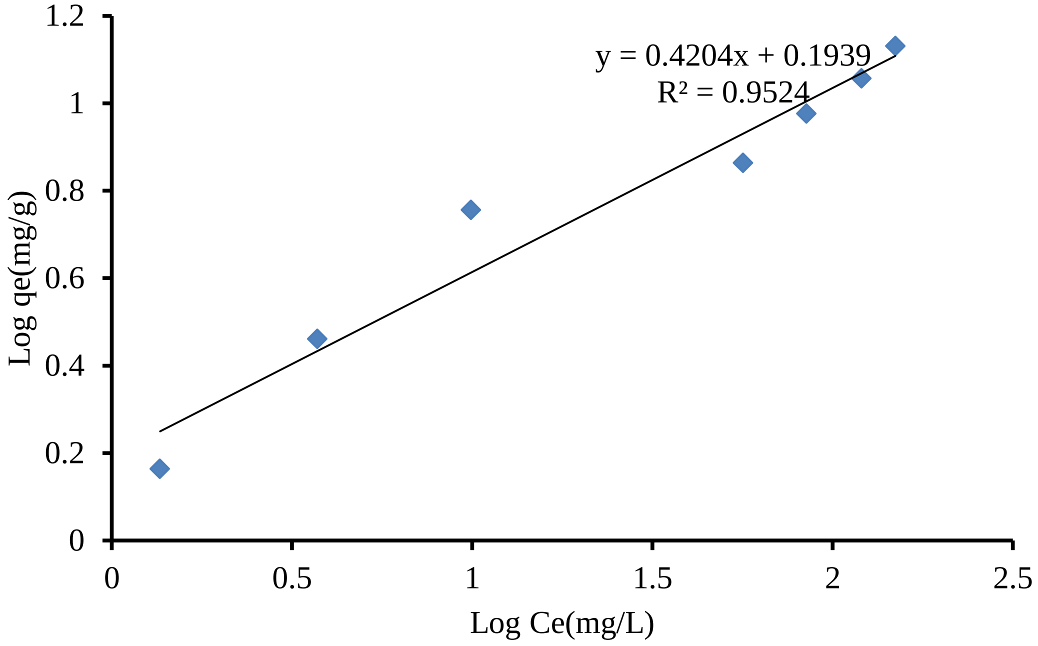

Figure 53: Freundlich Isotherm Plot for the Adsorption of Pb (II) onto 1.0g Mangrove Roots.

Table 9: Langmuir and Freundlich Isotherm Constants and their Correlation Coefficients for Pb (II) ions Adsorption using 0.5g Mangrove Roots.

Langmuir			**Freundlich**		
Q_{max}(mg/L)	***b*(L/mg)**	**R^2**	**K_F(mg/g)**	***n***	**R^2**
13.698	0.047	0.928	1.56	2.381	0.952

The correlation coefficient (R^2) was found to be 0.952 for Pb (II) adsorption using Freundlich model. The high value indicated that the equilibrium data fitted well to the Freundlich model, which means that adsorption of the metal ions onto the mangrove roots took place at the binding sites on the surface of the biomass by multilayer adsorption.

The adsorption capacity was found to be 1.56 mg of Pb (II) per gram of the adsorbent material. The value of n was found to be 2.381 which mean that the value of 1/n is in the range of 0 to 1 which indicates favorable adsorption under the conditions of study.

4.5.7 Adsorption Kinetics of Pb (II) ions

Adsorption kinetics involves the search for a best model that well represents the experimental data. In this study, the adsorption equilibrium data were analyzed using pseudo-first-order and pseudo-second-order models. The prediction of adsorption rate gives important information for designing batch adsorption systems. Figure 54 show the plot between amounts adsorbed, Q_t (mg/g) versus time t (min) for different initial concentrations.

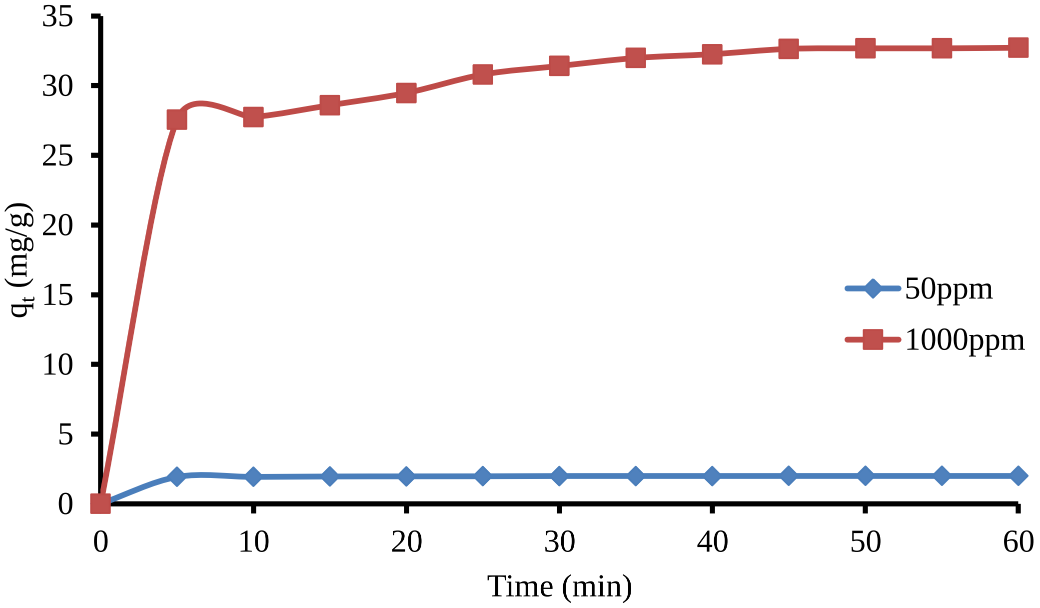

Figure 54: Effect of Contact Time on Uptake of Pb (II) ions by Mangroves Roots.

It is evident that metal ions adsorption increased insignificantly as equilibrium was reached. The adsorption at the initial stage could be explained by the availability of a number of vacant active sites on the adsorbent surface. Thus metal ions accumulated on the adsorbent surface rapidly within the first 5 minutes. In the later stage, adsorption was an attachment controlled process due to less available sorption sites.

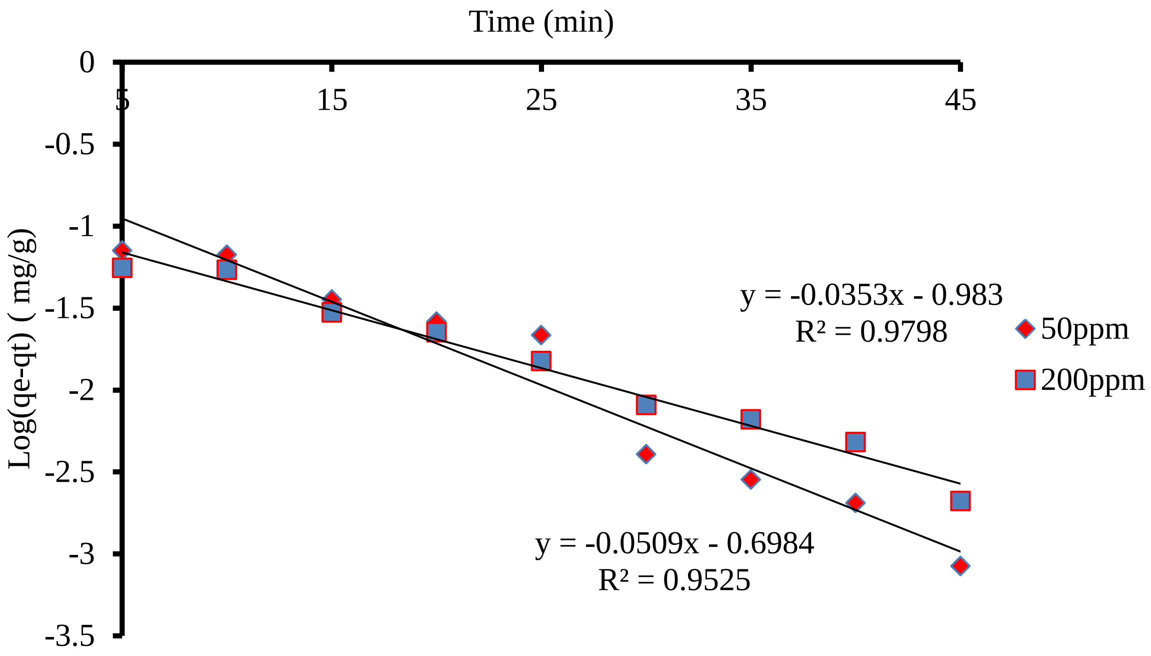

Figure 55: Pseudo-First Order Plot of Pb (II) Adsorption onto 0.5g Mangrove Roots.

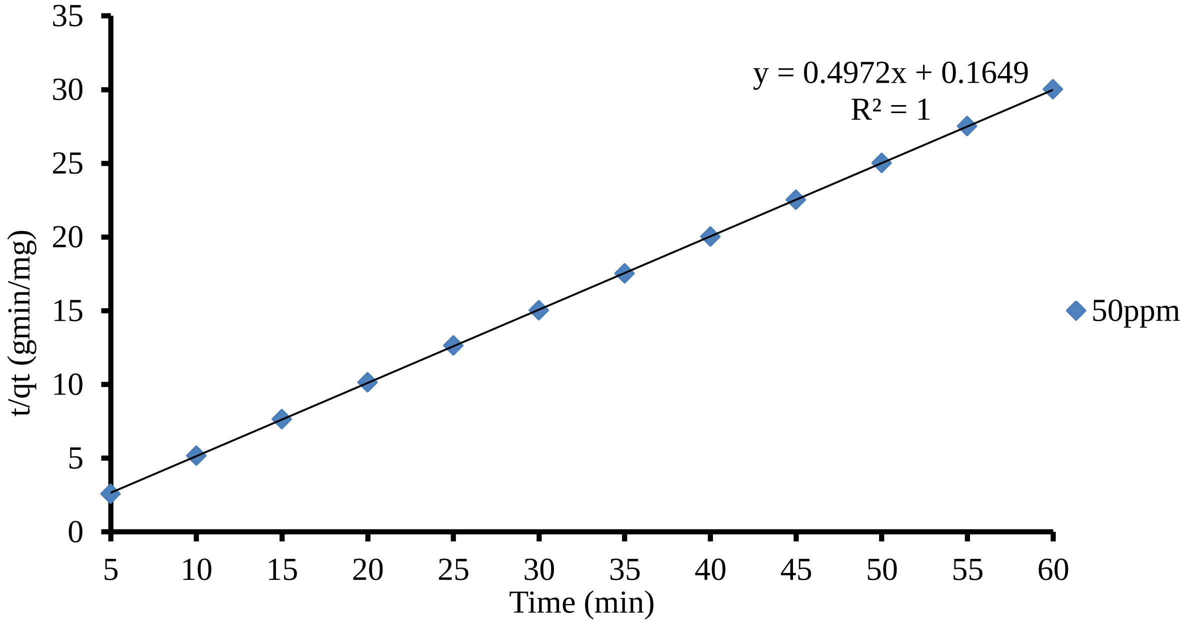

Figure 56: Pseudo-Second-Order Plots for 50ppm Pb (II) ions by 0.5g Mangrove Roots.

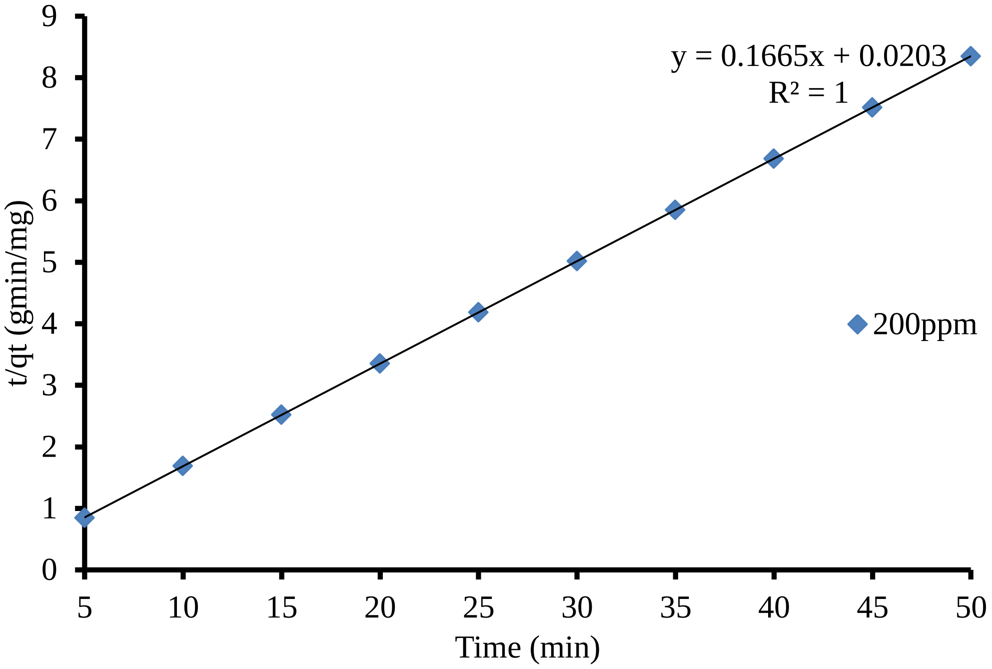

Figure 57: Pseudo-Second-Order Plots for 200ppm Pb (II) ions by 0.5g Mangrove Roots.

The pseudo first-order and pseudo second- order model equations were applied to the adsorption data. The results of Figures 55, 56 and 57 are summarized in Table 10. The conformity between experimental data and the model predicted values were expressed by the correlation coefficients R^2 (R^2 values close or equal to 1). Relatively high R^2 values indicated that the model successfully described the adsorption kinetics. The R^2 value of pseudo second–order was higher compared to R^2 value of pseudo first order mode.

Table 10: Comparison of Pseudo-First-Order and Pseudo-Second Order at Different Pb (II) ions Concentrations

Pseudo-first order				**Pseudo-second order**		
[Pb] mg/L	**Q_e (mg/g)**	**constant (min^{-1})**	**R^2**	**Q_e (Mg/g)**	**constant (min^{-1})**	**R^2**
50	0.104	0.0806	0.936	2.012	1.506	1
200	0.2004	0.115	0.981	6.024	1.377	1

These findings revealed that the pseudo second-order kinetic model provided a good correlation for the adsorption of Pb (II) onto mangrove roots compared to pseudo first order kinetic model. Therefore, the data show a good compliance with the pseudo equation which is based with equilibrium chemical adsorption (Seey and Jain, 2012). Anirudhan and Sreekumari (2011) reported pseudo second –order kinetics for adsorption of heavy metal ions from industrial effluents using activated carbon derived from waste coconut buttons.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The findings in this study revealed that mangrove roots can be effectively be employed as an eco-friendly adsorbent for the removal of Pb (II), Cd (II), Cu (II) and Zn (II) ions form aqueous solutions. The adsorption capacities for mangrove roots were found to be 13.698mg/g for lead, 5.494mg/g for cadmium, 6.211mg/g for zinc and 11.36mg/g for copper.

The data from the batch adsorption studies provided essential information in terms of optimum pH, shaking speed, particle size, temperature, adsorbent dose and the effective equilibrium time for the removal of heavy metal ions from aqueous solutions.

The removal of metal ions was affected by parts of mangroves biomass (roots, leaves and bark) and particle size. The adsorbent which was finely divided to less than 300µm gave the highest % adsorption because of an increase in the surface area which in turn increases the number of the binding sites. Mangrove roots showed a relatively higher ability to adsorb copper (II) ions in single component aqueous systems compared to the tree bark and leaves ground to the same particle size.

The removal of metal ions increased with increase in pH values. The highest adsorption was attained at a pH value of 6. At low pH (< 3), there was excessive protonation of the active sites at mangrove roots surface and this often prevents the formation of links between metal ion and the active site. At moderate pH values (3-6), linked H^+ was released from the active sites and adsorbed amount of metal ions was generally found to increase. At higher pH values (> 6), aqueous metal hydroxide precipitation could have been the significant mechanisms in the metal removal process.

The findings in this study revealed that removal of metal ions from aqueous solutions decreased with increase in particle size but increased with increase in adsorbent mass for all the particle sizes. The increase in the adsorption was due to the availability of more binding sites for metal ions. The smaller the particle size the larger the surface area exposed to interact with the metal ions in solution. Increase in particle size had the reverse effect of decreasing surface area, reducing number of binding sites hence decreasing the % adsorption.

The highest % adsorption was achieved at a shaking speed of 500rpm and equilibrium metal removal was attained in less than 30 minutes for all metals. Adsorption was also found to increase with increase in temperature.

The data obtained in the study was described by Langmuir and Freundlich isotherm. Langmuir adsorption isotherm fitted best implying that there was monolayer coverage of the metal ions on the surface of the adsorbent, homogenous distribution and that the surface was uniform. The adsorption data also fitted well for pseudo-second-order model.

Mangroves provide a conducive environment for breeding of aquatic life like fish that are important source of food security. The aquatic life is under threat of accumulation of heavy metals in the marines. The findings of this study show that mangrove roots are very effective in adsorption of heavy metals from aqueous solutions. Therefore, conservation of mangroves will boost the economy mainly through food security and income.

The investigation clearly indicated that mangrove roots are an effective, low-cost adsorbent that can be used to remove heavy metals from aqueous solutions. Given that the species is abundantly available, the plant root biomass can therefore be used as an alternative adsorbent in water treatment as it is cheap readily available and requires minimal processing for use in removal of water pollution.

5.2 RECOMMENDATIONS

The following recommendations are therefore made:

1. Since the mangrove roots have proved successful as an adsorbent for copper, lead, zinc and cadmium in the laboratory, a pilot project could be set up so as to assess the practicality of adsorption of these metals using the mangrove roots in the real life situation.
2. A multi-component study should be done using binary and ternary systems to establish the effect of metal ions on adsorption of other metal ions.

3. More studies be conducted on the mechanisms of adsorption by use of SEM and EDS in order to understand how the adsorption takes place
4. Detailed study should be carried out to determine the chemical composition of mangrove roots system and its surface area.
5. Modification of the plant biomass using the various modifying agents be done to study the influence on adsorption capacity of the plant material
6. Activated carbon to be developed from the mangrove roots biomass material and its adsorption studied.

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APPENDICES

APPENDIX I

Effect of Particle Part on Adsorption of Copper

	% Adsorption					
	0	0.125g	0.25g	0.5g	1g	2g
Bark	0	74.45	86.6	90.92	94.34	97.76
Leaves	0	72.55	82.14	86.22	94.1	97.2
Roots	0	81.3	88.96	95.82	97.66	98.22

APPENDIX II

Effect of Shaking on Adsorption on Adsorption of Copper

SPEED	% adsorption
0	85
100	93.77
200	97.13
300	98.53667
400	99.195
500	99.622
600	99.57333

APPENDIX III

Effect of Contact Time and Concentration on Adsorption of;

a) Copper

	% Adsorption		
Time(min)	50ppm	200ppm	1000ppm
0	0	0	0
5	96.18	56	46.1
10	96.26	56.66667	48.8
15	96.86	57	49
20	97.32	57.66667	49.6
25	97.42	60	50.3
30	97.76	62.33333	52.1
35	97.9	67.66667	54.4
40	98.1	79	56.4
45	98.1	84	57
50	98.58	84.33333	58.4
55	98.6	84.66667	59.1
60	98.6	84.66667	59.1

b) Lead

	% Adsorption		
Time(min)	50ppm	150ppm	1000ppm
0	0	0	0
5	96.4	95.94	68.9
10	96.6	96.04	69.375
15	98.16	97.66	71.5
20	98.64	98.14	73.7
25	98.86	98.64	77
30	99.74	99.1	78.533
35	99.8	99.2	79.966
40	99.84	99.32	80.65
45	99.9	99.5	81.6
50	99.94	99.62	81.7
55	99.94	99.64	81.7
60	99.94	99.64	81.8

c) Cadmium

	% Adsorption		
Time(min)	50ppm	200ppm	1000ppm
0	0	0	0
5	91.68	51	32
10	93.38	51.6	34.9
15	94.98	52.5	35.4
20	95.08	55	36
25	95.38	56.5	36.8
30	95.98	57.3	37.3
35	96.06	57.9	38
40	96.28	58.85	38.9
45	96.36	59.95	39.5
50	96.46	60.85	39.5
55	97.78	60.85	39.6
60	97.78	60.85	39.6

c) Zinc

	% Adsorption		
Time(min)	50ppm	200ppm	1000ppm
0	0	0	0
5	95	63.7	12.35
10	96.32	66	13.3
15	97.52	71	19
20	97.86	78.6	19.6
25	98.06	83.8	21.34
30	98.3	85.15	29.11
35	99.34	86.05	29.94
40	99.7	86.5	32.1
45	99.82	87.5	34
50	99.84	87.75	34.511
55	99.96	88.5	34.7
60	99.96	88.555	34.93

APPENDIX IV

Effect of Particle Size and Weight on Adsorption

a) Copper

Particle size(µm)	0	0.1	0.25	0.5	1
<300	0	97.68	98.98	99.76	99.88
>300<425	0	92.45	94.72	95.94	98.54
>425	0	76.78	85.6	92.5	97.96

b) Lead

	0	0.125	0.25	0.5	1
<300µm	0	97.96	98.98	99.76	99.88
>300<425µm	0	89.4	94.72	95.94	98.54
>425µm	0	57.6	78.68	92.5	97.96

c) Zinc

	0.125	0.25	0.5	1
<300µm	79.2	85.34	94.98	98.36
>300<425µm	72.48	79.14	92.66	96.32
>425µm	62.74	69.6	88.26	94.72

d) Cadmium

Particle size(µm)	0.125g	0.25g	0.5g	1.0g	2.0g
<300µm	47.2	64.8	84.14	97.32	97.4
>300<425µm	38	52.8	79.12	90.14	90.16
>425µm	31	49.8	65.2	81.92	82

APPENDIX V

Effect of Initial Concentration on Adsorption

a) Copper

	% Adsorption		
Concentration(ppm)	0.25g	0.5g	1.0g
50ppm	83.4	94.3	97.28
100ppm	76.1	86.3	96.28
200ppm	68.45	81.95	95.04
300ppm	65.73333	75.6	81.16667
400ppm	64.425	69.15	78.85
500ppm	64.16	67.8	75.94
600ppm	63.6	66.9	75.1

b) Lead

	% Adsorption		
Concentration(ppm)	0.25g	0.5g	1.0g
50ppm	98.84	99.72	99.94
100ppm	98.28	99.09	99.48
200ppm	92.395	98.945	99.595
300ppm	71.8	96.37	99.11
400ppm	61.65	94.115	98.85
500ppm	39.88	75.4	93.752
600ppm	30.08333	65.58333	91.26667

d) Zinc

	% Adsorption		
Concentration(ppm)	0.25g	0.5g	1.0g
0	100	100	100
50	70.4	90.74	97.12
100	54.8	75.8	92.55
200	32.2	54.4	78.2
300	27.4	40.33333	64.6
400	19	30.75	54.65
500	12.96	24	41.4
600	8.766667	17.25	33

APPENDIX VI

Effect of temperature on adsorption

a) Copper

Temperature(°C)	% Adsorption
25	92.5
30	95.8
40	97.75
50	99.105
60	99.4
70	99.8

b) Lead

Temperature(°C)	%adsorption
25	92.5
30	94.6
40	96.54
50	97.38
60	97.93
70	98.85

c) Zinc

Temperature(°C)	% Adsorption
25	33
30	74
40	80
50	82.5
60	84
70	74.8

d) Cadmium

Temperature(°C)	% Adsorption
25	26
30	49.65
40	55.5
50	62
60	74
70	61

APPENDIX VI

Effect of pH on adsorption

a) Copper

pH	% Adsorption
2	92.86
4	94
6	95.4
8	96.14
10	98.12
12	98.68

b) Lead

pH	% Adsorption
2	53.4
4	60.8
6	76.4
8	83.4
10	90.88
12	98.8

c) Zinc

pH	% Adsorption
2	47.8
4	59.6
6	63.2
8	70
10	79.6
12	84.4

d) Cadmium

pH	% Adsorption
2	53
4	63
6	67.2
8	70.2
10	85.12
12	98.32

APPENDIX VII

Adsorption Isotherm Studies for:

a) Copper

1. Langmuir data

concentration	Ce(mg/l)	qe(mg/g)	Ce/qe(g/l)	Ce(mg/l)	Ce/qe(g/l)
50ppm	1.4	1.458	0.960219	1.4	0.960219
100ppm	3.7	2.889	1.28072	3.7	1.28072
200ppm	9.9	5.703	1.735928	9.9	1.735928
300ppm	56.5	7.305	7.734428	56.5	7.734428
400ppm	100	9	11.11111	100	11.11111
500ppm	165.4	10.038	16.47739	165.4	16.47739
600ppm	233	11.01	21.16258	233	21.16258

2. Freundlich data

Ce(mg/l)	qe(mg/g)	Log Ce(mg/l)	log qe(mg/g)
1.4	1.458	0.146128	0.163758
3.7	2.889	0.568202	0.460748
9.9	5.703	0.995635	0.756103
56.5	7.305	1.752048	0.86362
100	9	2	0.954243
165.4	10.038	2.218536	1.001647
233	11.01	2.367356	1.041787

b) Lead

1. Langmuir data

Concentration(ppm)	Ce(mg/l)	qe(mg/g)	Ce/qe(g/l)
50ppm	1.36	1.4592	0.932018
100ppm	3.72	2.8884	1.28791
200ppm	9.92	5.7024	1.739618
300ppm	56.5	7.305	7.734428
400ppm	84.6	9.462	8.941027
500ppm	120.3	11.391	10.56097
600ppm	149.4	13.518	11.05193

2. Freundlich Data

Ce(mg/l)	qe(mg/g)	Log Ce(mg/l)	Log qe(mg/g)
1.36	1.4592	0.133539	0.133539
3.72	2.8884	0.570543	0.570543
9.92	5.7024	0.996512	0.996512
56.5	7.305	1.752048	1.752048
84.6	9.462	1.92737	1.92737
120.3	11.391	2.080266	2.080266
149.4	13.518	2.174351	2.174351

c) Zinc

1. Langmuir Data

Concentration(ppm)	qe(mg/g)	Ce(mg/l)	Ce/qe(g/l)
50ppm	1.4568	1.44	0.988468
100ppm	2.7765	7.45	2.683234
200ppm	4.692	43.6	9.292413
300ppm	5.814	106.2	18.26625
400ppm	6.558	181.4	27.66087
500ppm	6.21	293	47.18196
600ppm	5.94	402	67.67677

2. Freundlich data

Ce(mg/l)	Log Ce(mg/l)	qe(mg/l)	Log qe(mg/g)	Log Ce(mg/l)	Log qe(mg/g)
1.44	0.158362	1.4568	0.1634	0.158362	0.1634
7.45	0.872156	2.7765	0.443498	0.872156	0.443498
43.6	1.639486	4.692	0.671358	1.639486	0.671358
106.2	2.026125	5.814	0.764475	2.026125	0.764475
181.4	2.258637	6.558	0.816771	2.258637	0.816771
293	2.466868	6.21	0.793092	2.466868	0.793092
402	2.604226	5.94	0.773786	2.604226	0.773786

d). Cadmium

1. Langmuir Data

Concentration(ppm)	Ce(mg/l)	qe(mg/g)	Ce/qe(g/l)
50ppm	1.68	1.449	1.15942
100ppm	13.5	2.595	5.202312
200ppm	76	3.72	20.43011
300ppm	176	3.72	47.31183
400ppm	248	4.56	54.38596
500ppm	334	4.98	67.06827
600ppm	415	5.55	74.77477

2. Freundlich Data

Ce(mg/l)	qe(mg/g)	Log Ce(mg/l)	Logqe(mg/g)
1.68	1.449	0.225309	0.161068
13.5	2.595	1.130334	0.414137
76	3.72	1.880814	0.570543
176	3.72	2.245513	0.570543
248	4.56	2.394452	0.658965
334	4.98	2.523746	0.697229
415	5.55	2.618048	0.744293

APPENDIX VIII

First order Kinetics data for 50 ppm Cu (II).

Concentraiton:50ppm						
Time	Mass	Volume	qt(mg/g)	qe(mg/g)	qe-qt(mg/g)	Log(qe-qt)(mg/g)
5	0.5	20	1.9236	1.972	0.0484	-1.31515
10	0.5	20	1.9252	1.972	0.0468	-1.32975
15	0.5	20	1.9372	1.972	0.0348	-1.45842
20	0.5	20	1.9464	1.972	0.0256	-1.59176
25	0.5	20	1.9484	1.972	0.0236	-1.62709
30	0.5	20	1.9552	1.972	0.0168	-1.77469
35	0.5	20	1.958	1.972	0.014	-1.85387
40	0.5	20	1.962	1.972	0.01	-2
45	0.5	20	1.962	1.972	0.01	-2
50	0.5	20	1.9716	1.972	0.0004	-3.39794
55	0.5	20	1.972	1.972	0	#NUM!
60	0.5	20	1.972	1.972	0	#NUM!

First order Kinetics data for 200 ppm Cu (II)

	Concentration:200ppm					
Time(min)	mass(g)	volume(mL)	qt(mg/g)	qe(mg/g)	qe-qt(mg/g)	log(qe-qt)(mg/g)
5	0.5	20	2.72	6.16	3.44	0.536558
10	0.5	20	2.8	6.16	3.36	0.526339
15	0.5	20	2.84	6.16	3.32	0.521138
20	0.5	20	2.92	6.16	3.24	0.510545
25	0.5	20	3.2	6.16	2.96	0.471292
30	0.5	20	3.48	6.16	2.68	0.428135
35	0.5	20	4.12	6.16	2.04	0.30963
40	0.5	20	5.48	6.16	0.68	-0.16749
45	0.5	20	6.08	6.16	0.08	-1.09691
50	0.5	20	6.12	6.16	0.04	-1.39794
55	0.5	20	6.16	6.16	0	#NUM!
60	0.5	20	6.16	6.16	0	#NUM!

Second order Kinetics data for 50 ppm Cu (II)

Time(min)	qt(mg/g)	t/qt(gmin/mg)
5	1.9236	2.599293
10	1.9252	5.194266
15	1.9372	7.743134
20	1.9464	10.27538
25	1.9484	12.83104
30	1.9552	15.3437
35	1.958	17.87538
40	1.962	20.38736
45	1.962	22.93578
50	1.9716	25.36011
55	1.972	27.89047
60	1.972	30.42596

Second order Kinetics data for 200 ppm Cu (II)

Time(min)	qt(mg/g)	t/qt(gmin/mg)
5	2.72	1.838235
10	2.8	3.571429
15	2.84	5.28169
20	2.92	6.849315
25	3.2	7.8125
30	3.48	8.62069
35	4.12	8.495146
40	5.48	7.29927
45	6.08	7.401316
50	6.12	8.169935
55	6.16	8.928571
60	6.16	9.74026

First order Kinetics data for 50 ppm Pb (II)

Time (mins)	Volume (mL)	Mass(g)	qt(mg/g)	qe(mg/g)	qe-qt(mg/g)	Log(qe-qt)(mg/g)
5	20	0.5	1.928	1.99884	0.07084	-1.14972
10	20	0.5	1.932	1.99884	0.06684	-1.17496
15	20	0.5	1.9632	1.99884	0.03564	-1.44806
20	20	0.5	1.9728	1.99884	0.02604	-1.58436
25	20	0.5	1.9772	1.99884	0.02164	-1.66474
30	20	0.5	1.9948	1.99884	0.00404	-2.39362
35	20	0.5	1.996	1.99884	0.00284	-2.54668
40	20	0.5	1.9968	1.99884	0.00204	-2.69037
45	20	0.5	1.998	1.99884	0.00084	-3.07572
50	20	0.5	1998.8	1.99884	-1996.8	
55	20	0.5	1.9988	1.99884	-0.00004	
60	20	0.5	1.99884	1.99884	0	

First order Kinetics data for 200 ppm Pb (II)

Time(mins	Volume(mL)	Mass(g)	qt(mg/g)	qe(mg/g)	qe-qt (mg/g)	Log(qe-qt)(mg/g)
5	20	0.5	5.9139	5.9946	0.0807	-1.09313
10	20	0.5	5.9391	5.9946	0.0555	-1.25571
15	20	0.5	5.9406	5.9946	0.054	-1.26761
20	20	0.5	5.9649	5.9946	0.0297	-1.52724
25	20	0.5	5.9721	5.9946	0.0225	-1.64782
30	20	0.5	5.9796	5.9946	0.015	-1.82391
35	20	0.5	5.9865	5.9946	0.0081	-2.09151
40	20	0.5	5.988	5.9946	0.0066	-2.18046
45	20	0.5	5.9898	5.9946	0.0048	-2.31876
50	20	0.5	5.9925	5.9946	0.0021	-2.67778
55	20	0.5	5.9943	5.9946	0.0003	-3.52288
60	20	0.5	5.9946	5.9946	0	

Second order Kinetics data for 50ppm Pb (II)

Time(min)	qt(mg/g)	t/qt(gmin/mg)
5	1.928	2.593361
10	1.932	5.175983
15	1.9632	7.640587
20	1.9728	10.13788
25	1.9772	12.64414
30	1.9948	15.0391
35	1.996	17.53507
40	1.9968	20.03205
45	1.998	22.52252
50	1.9988	25.01501
55	1.9988	27.51651
60	1.99884	30.01741

Second order Kinetics data for 200ppm Pb (II)

Time(min)	qt(mg/g)	q/qt(gmin/mg)
5	5.9139	0.845
10	5.9391	1.689
15	5.9406	2.52
20	5.9649	3.354
25	5.9721	4.186
30	5.9796	5.015
35	5.9865	5.849
40	5.988	6.682
45	5.9898	7.513
50	5.9925	8.344

First order Kinetics data for 50 ppm Cd (II)

Time(min)	mass(g)	volume(mL)	qt(mg/g)	qe(mg/g)	qe-qt(mg/g)	Log(qe-qt)(mg/g)
5	0.5	20	1.8336	1.9556	0.122	-0.91364
10	0.5	20	1.8676	1.9556	0.088	-1.05552
15	0.5	20	1.8996	1.9556	0.056	-1.25181
20	0.5	20	1.9016	1.9556	0.054	-1.26761
25	0.5	20	1.9076	1.9556	0.048	-1.31876
30	0.5	20	1.9196	1.9556	0.036	-1.4437
35	0.5	20	1.9212	1.9556	0.0344	-1.46344
40	0.5	20	1.9256	1.9556	0.03	-1.52288
45	0.5	20	1.9272	1.9556	0.0284	-1.54668
50	0.5	20	1.9292	1.9556	0.0264	-1.5784
55	0.5	20	1.9556	1.9556	0	
60	0.5	20	1.9556	1.9556	0	

First order Kinetics data for 200 ppm Cd (II)

Time(min)	mass(g)	volume(mL)	qe(mg/g)	qe-qt(mg/g)	Log(qe-qt)(mg/g)
5	0.5	20	4.868	0.788	-0.13077
10	0.5	20	4.868	0.74	-0.17522
15	0.5	20	4.868	0.668	-0.32975
20	0.5	20	4.868	0.468	-0.45842
25	0.5	20	4.868	0.348	-0.54668
30	0.5	20	4.868	0.284	-0.62709
35	0.5	20	4.868	0.236	-0.79588
40	0.5	20	4.868	0.16	-1.14267
45	0.5	20	4.868	0.072	-1.154
50	0.5	20	4.868	0	#NUM!
55	0.5	20	4.868	0	#NUM!
60	0.5	20	4.868	0	#NUM!

Second order Kinetics data for 50ppm Cd (II)

Time(min)	qt(mg/g)	t/qt(gmin/mg)
5	1.8336	2.726876
10	1.8676	5.354466
15	1.8996	7.896399
20	1.9016	10.51746
25	1.9076	13.10547
30	1.9196	15.62826
35	1.9212	18.21778
40	1.9256	20.77275
45	1.9272	23.34994
50	1.9292	25.91748
55	1.9556	28.12436
60	1.9556	30.68112

Second order Kinetics data for 200ppm Cd (II)

Time(min)	qt(mg/g)	t/qt(gmin/mg)
5	4.08	1.22549
10	4.128	2.422481
15	4.2	3.571429
20	4.4	4.545455
25	4.52	5.530973
30	4.584	6.544503
35	4.632	7.556131
40	4.708	8.496177
45	4.796	9.382819
50	4.868	10.27116
55	4.868	11.29827
60	4.868	12.32539

First order Kinetics data for 50 ppm Zn (II)

Time(min)	mass(g)	Volume(mL)	qe(mg/g)	qt(mg/g)	qe-qt(mg/g)	Log(qe-qt)(mg/g)
5	0.5	20	1.9992	1.89	0.1092	-0.96177
10	0.5	20	1.9992	1.9	0.0992	-1.00349
15	0.5	20	1.9992	1.9264	0.0728	-1.13787
20	0.5	20	1.9992	1.9504	0.0488	-1.31158
25	0.5	20	1.9992	1.9572	0.042	-1.37675
30	0.5	20	1.9992	1.9612	0.038	-1.42022
35	0.5	20	1.9992	1.966	0.0332	-1.47886
40	0.5	20	1.9992	1.9868	0.0124	-1.90658
45	0.5	20	1.9992	1.994	0.0052	-2.284
50	0.5	20	1.9992	1.9964	0.0028	-2.55284
55	0.5	20	1.9992	1.9968	0.0024	-2.61979
60	0.5	20	1.9992	1.9992	0	#NUM!

First order Kinetics data for 200 ppm Zn (II)

Time(min)	mass(g)	volume(mL)	qtmg/g	qemg/g	qe-qt(mg/g)	Log(qe-qt)(mg/g)
5	0.5	20	3.1	7.0844	3.9844	0.60036
10	0.5	20	5.096	7.0844	1.9884	0.256333
15	0.5	20	5.28	7.0844	1.8044	0.147491
20	0.5	20	5.68	7.0844	1.4044	-0.09887
25	0.5	20	6.288	7.0844	0.7964	-0.41976
30	0.5	20	6.704	7.0844	0.3804	-0.56479
35	0.5	20	6.812	7.0844	0.2724	-0.6981
40	0.5	20	6.884	7.0844	0.2004	-0.7841
45	0.5	20	6.92	7.0844	0.1644	-1.07366
50	0.5	20	7	7.0844	0.0844	-1.19111
55	0.5	20	7.02	7.0844	0.0644	-1.11911
60	0.5	20	7.08	7.0844	0.0044	-235654

Second order Kinetics data for 50ppm Zn (II)

Time(min)	qt (mg/g)	t/qt(gmin/mg)
0	1.89	0
5	1.9	2.631579
10	1.9264	5.19103
15	1.9504	7.69073
20	1.9572	10.21868
25	1.9612	12.7473
30	1.966	15.25941
35	1.9868	17.61627
40	1.994	20.06018
45	1.9964	22.54057
50	1.9968	25.04006
55	1.9992	27.511
60	1.9992	30.012

Second order Kinetics data for 200ppm Zn (II)

Time(min)	qt(mg/g)	t/qt(gmin/mg)
0	3.1	0
5	5.096	0.981162
10	5.28	1.893939
15	5.68	2.640845
20	6.288	3.180662
25	6.704	3.729117
30	6.812	4.403993
35	6.884	5.084253
40	6.92	5.780347
45	7	6.428571
50	7.02	7.122507
55	7.08	7.768362
60	7.0844	8.469313