BIOSORPTION OF HEAVY METALS USING WATER HYACINTH *Eichhornia crassipes* (Mart.) Solms- Laubach: ADSORPTION PROPERTIES AND TECHNOLOGICAL ASSESSMENT

BY

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DECLARATION

This is my original work and has not been submitted for examination for a degree in any other university.

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DEDICATION

To my beloved uncle Late Mugwang'a Emile for showing us the way,

My mum for standing with me in my pursuit of education.

My sister Ann and brother Dennis.

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LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations	**Nomenclature**
% P	Percentage purity of the salt used
°C	Degrees centigrade
ATSDR	Agency for Toxic Substances and Disease Registry
AW	Atomic weight of the metal (g mol^{-1})
B	Langmuir isotherm constant *($dm^3\ mg^{-1}$)*
B_{DR}	Dubinin –Radushkevich isotherm constant
Cd^{2+}	Cadmium (II) ions
CDC	Center for Disease Control
C_e	Equilibrium concentration (mg L^{-1})
C_0	Adsorbate initial concentration (mg L^{-1})
Cu^{2+}	Copper (II) ions
DNA	Deoxyribonucleic acid
EDS	Energy Dispersive Spectroscopy
g	Gram
IAEA	International Atomic Energy Agency
K_F	Freundlich adsorption capacity constant (mg/g)
k_1	Pseudo first order rate constant of adsorption (min^{-1})
k_2,	Pseudo second order rate constant of adsorption (mg/g min^{-1})
K_F	Freundlich isotherm constant (mg/g) (dm3/g)
K_L	Langmuir adsorption capacity constant (mg/g)
mg g^{-1}	Milligram per gram
mg L^{-1}	Milligram per litre
mL	Milliliter
MW	Molecular weight of salt used (g mol^{-1})
n	Adsorption intensity

NEMA	National Environmental Management Authority
Pb^{2+}	Lead (II) ions
ppm	Parts per million
$q_{e, calc}$	Calculated concentration at equilibrium (mg/g)
q_e	Measured adsorbate concentration at equilibrium (mg/g)
Q_e	Mass of metal ions adsorbed at equilibrium (mg/g)
Q_{max}	Adsorption capacity (mg/g)
Q_t	Mass of Cu^{2+} ions adsorbed at time, t (min)
R	Universal gas constant (8.314J mol^{-1} K^{-1})
R^2	Correlation coefficient
rpm	Rotations per minute
SEM	Scanning Electron Microscopy
TDS	Total Dissolved Solids
USEPA	United States Environmental Protection Agency
UV-Vis	Ultraviolet-Visible
W	Equivalent weight of the salt used
WHO	World Health Organization
Zn^{2+}	Zinc (II) ions

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ABSTRACT

The adsorption of heavy metal ions (Cd^{2+}), Cu^{2+}), Pb^{2+}) and Zn^{2+}) by untreated water hyacinth *Eichhornia crassipes* obtained from Lake Victoria, Kenya was investigated under batch mode. The effects of sample part, particle size, contact time, solution pH, and temperature, shaking speed, adsorbent dosage and initial metal ion concentration of aqueous solutions were investigated. The roots showed highest ability for the uptake of heavy metals (Cu, Zn, Cd and Pb) from aqueous solutions, therefore were used for all subsequent sorption studies in this research. Maximum removal of metal ions took place at a pH of 4-6. 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 400 rpm led to a decrease in percentage adsorption. Increase in temperature led to a decrease in the percentage adsorption. Heavy metals adsorption was considered a fast process with almost all the adsorption taking place in the first 5 minutes upon contact of the adsorbent with the aqueous solutions of metals. Twenty minutes of equilibration time was found to be adequate for adsorption of the metal ions, yielding 100 % adsorption at low concentration of metal ions.

In order to understand the mechanism of adsorption, Fourier Transform Infra Red (FT-IR) analysis and ion exchange experiment were carried out. Ion exchange accompanied by the release of light metal ions (K^+, Na^+, Mg^{2+} and Ca^{2+}) was observed to be the main mechanism of heavy metal adsorption. Complexation also occurred as demonstrated by FTIR spectra involving hydroxyl, caboxylate, phosphate, ether and amino functional groups.

The equilibrium data were correlated with Langmuir and Freundlich Isotherm models. Based on the Langmuir model the maximum adsorption capacities were found to be 3.200, 17.568, 16.166 and 12.820 mg g^{-1} for cadmium, copper, lead and zinc respectively. The correlation with Langmuir showed that uptake of the heavy metals in aqueous systems occurred by monolayer sorption with the eventual formation of a plateau of saturation. Several kinetic models were applied to the adsorption data and it was found that pseudo-second order fitted well with the adsorption data.

These results indicated that *Eichhornia crassipes* can be used as a low cost adsorbent for the removal of heavy metals from aqueous solutions.

CHAPTER ONE

1. INTRODUCTION

1.1 Background Information

Saving water to save the planet and to make the future of mankind safe is what we need now. With the growth of mankind, society, science and technology, our world is reaching to new high horizons but the cost which we are paying or will pay in near future is surely going to be too high. Among the consequences of this rapid growth is environmental disorder with a big pollution problem which is likely to slow down the attainment of the millennium development goals (MDG's) particularly MDG 7 target 10 which concerns sustainable access to safe drinking water and sanitation and the Kenya's Vision 2030 objectives. Besides other needs the demand for water ('Water for People Water for Life'United Nations World Water Development Report UNESCO) has increased tremendously with agricultural, industrial and domestic sectors consuming 70, 22 and 8% of the available fresh water, respectively and this has resulted in the generation of large amounts of wastewater containing a number of 'pollutants.' One of the important classes of the pollutants is heavy metals. Pollution by heavy metals is a serious threat to aquatic ecosystems because some of these metals are potentially toxic, even at very low concentrations. Additionally, heavy metals are not biodegradable and tend to accumulate in living organisms, and they can cause severe problems to both human health and wildlife (Crini, 2005).

Heavy metals in water have been a major preoccupation for researchers for many years due to their toxicity towards aquatic life, human beings and the environment. As they do not degrade biologically like organic pollutants, their presence in industrial effluents and drinking water is a public health problem (Ibrahim *et al.*, 2010).

Natural processes and human activities have polluted and reduced the quality of water resources in Kenya. Groundwater and surface water have been contaminated in various ways; e.g. by mining wastes including cyanide and toxic heavy metals, by agricultural chemicals, industrial and domestic sewage that is sometimes discharged without treatment into waterways and by natural trace elements (e.g. arsenic).

Since it is important to eliminate or reduce the concentration of heavy metals in the aquatic ecosystems, various methods and technologies are commonly applied in removing metal ions from aqueous solution, mainly consisting of physical, chemical and biological technologies. Conventional methods for removing metal ions from aqueous solution have been suggested, such as chemical precipitation, filtration, ion exchange, electrochemical treatment, membrane technologies, and adsorption on activated carbon. However, the application of some of these methods may be impractical due to economic constraints or may be insufficient to meet strict regulatory requirements. Furthermore, they may generate hazardous products or products which are difficult to treat (Gavrilescu, 2004; Reddad *et al.*, 2002).

The traditional coagulation and flocculation processes use inorganic coagulants such as aluminium hydroxides in drinking water treatment. Metal coagulants can be used to partially remove heavy metal from wastewater (Eilbeck and Mattock, 1987), but, the use of metal coagulants is not 100% effective for removing metal cations from water at pH 7 (Bell and Saunders, 2005).

Among these methods, adsorption has been shown as the most appealing in terms of economic and an environmental friendly procedure to remove heavy metals in wastewater. For heavy metal ions of low concentrations (<100mg L^{-1}), adsorption is a much preferable technique to remove heavy metals in wastewater. The high cost of adsorbents such as activated carbon and some ion-exchange resins used for the treatment of water and wastewater have triggered the need for new more effective and cheaper adsorbents. Natural materials that are available in large quantities or industrial waste products can also be used as adsorbents. Biosorbents are cheaper, more effective alternatives for the removal of metallic elements, especially heavy metals from aqueous solutions. Biosorbents are selective and regenerable and the process is highly effective in the treatment of dilute effluents (Chojnacka, 2010).

Seaweeds have a high bonding affinity with heavy metals. Since their cell walls have different functional groups (such as carboxyl, hydroxyl, phosphate or amine) that can bind to metal ions, they are much more efficient than active carbon and natural zeolites.

Currently Lake Victoria experiences negative effects which are a result of proliferation of *E. crassipes*. The *E. crassipes* is an environmental menace. The use of its biomass as a low cost alternative for the removal of heavy metals from municipal and industrial effluents will help reduce the effects of the water weed which is threatening the livelihoods of the riparian populations in the East African community. This will go a long way in helping the country to achieve the Vision 2030 objectives and in turn the Millennium Development Goals.

1.2 Statement of the problem

Due to the discharge of large amounts of metal contaminated wastewater, industries producing effluents containing heavy metals such as Cd, Cu, Pb, Zn, As, Ni and Cr are the most hazardous among the chemical-intensive industries. Given that the heavy metals cause serious health effects, including reduced growth and development of cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some metals, such as mercury and lead, may also cause development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, nervous system, and damaging of the fetal brain. It is therefore necessary to treat metal contaminated wastewater prior to its discharge into the environment in order to comply with the stringent environmental regulations and also safeguard the present and future generations (UNEP, 2008).

Heavy metal removal from inorganic effluent can be achieved by conventional treatment processes such as chemical precipitation, ion exchange, reverse osmosis, membrane filtration, evaporation and electrochemical removal.

These processes have significant disadvantages, which includes high capital and operational cost, incomplete removal, high-energy requirements, and production of toxic sludge which is more difficult to treat and dispose (Eccles, 1999). Adsorption has become one of the alternative treatments but activated carbon as an adsorbent is expensive; hence the search for low-cost adsorbents that have metal-binding capacities (Leung *et al.*, 2000). The adsorbents may be of mineral, organic or biological origin, zeolites, industrial by-products; agricultural wastes, biomass, and polymeric materials (Kurniawan *et al.*, 2005). The biosorbents are the most promising as they are abundant in supply and cost effective. Biosorption plays an important role in the elimination of metal ions from aqueous solutions in water pollution control (Veglio *et al.*, 1997). The main advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time, and no production of secondary compounds which might be toxic and possibility of metal recovery and reuse.

1.3 Justification

This project contributes towards the mitigation of the effects of heavy metals in the environment. It strives to come up with an innovative solution to the rising costs of treatment of wastewaters containing heavy metals before discharge into the environment. The project utilizes biological material that is readily acquired from the environment, with minimum or no further treatment the material is able to help towards the attainment of the MDG's particularly the goal of environmental conservation and sustainability. The source of the biosorbent is renewable and the method also helps in the using of what has otherwise been condemned. This being a locally available raw material helps in the saving of foreign exchange that would have been used to import technology and materials for pollution control.

1.4 Objectives

1.4.1 Overall objective

To develop cost effective and affordable water decontaminant for removal of heavy metals from polluted water streams and determines the optimum conditions for the working of the decontaminant using plant biomass material from water hyacinth

1.4.2 Specific objectives

(i) To study the effect of pH, contact time, temperature, and adsorbent and adsorbate dose, initial concentration of selected metal ions (Cu, Pb, Cd and Zn), shaking speed and particle size on removal of the respective metal ions from aqueous solutions.

(ii) To investigate the equilibrium removal conditions of the selected metal ions in terms of adsorption isotherms. Langmuir and Freundlich adsorption models to fit experimental data obtained.

(iii) To determine the sorption capacity of *Eichhornia crassipes* for selected metal ions.

(iv) To investigate the kinetics of selected metal ions removal from aqueous solutions by fitting the pseudo first order and pseudo- second- order reactions.

(v) To evaluate adsorption findings and technological assessment of findings for commercialization implications and options of proposed technology.

CHAPTER TWO

2. LITERATURE REVIEW

2.1 Water hyacinth ecology

The water hyacinth shown in Figure 1 is the most important of the world's noxious fresh-water plants. Its seven species comprise the genus *Eichhornia* (*E. azurea*- Anchored water hyacinth, *E. crassipes* - Common water hyacinth, *E. diversifolia*-Variable leaf water hyacinth, *E. paniculata*-Brazilian water hyacinth e.t.c). Water hyacinth is a free-floating perennial aquatic plant native to tropical South America. With broad, thick, glossy, ovate leaves, water hyacinth may rise above the surface of the water as much as 1m in height.

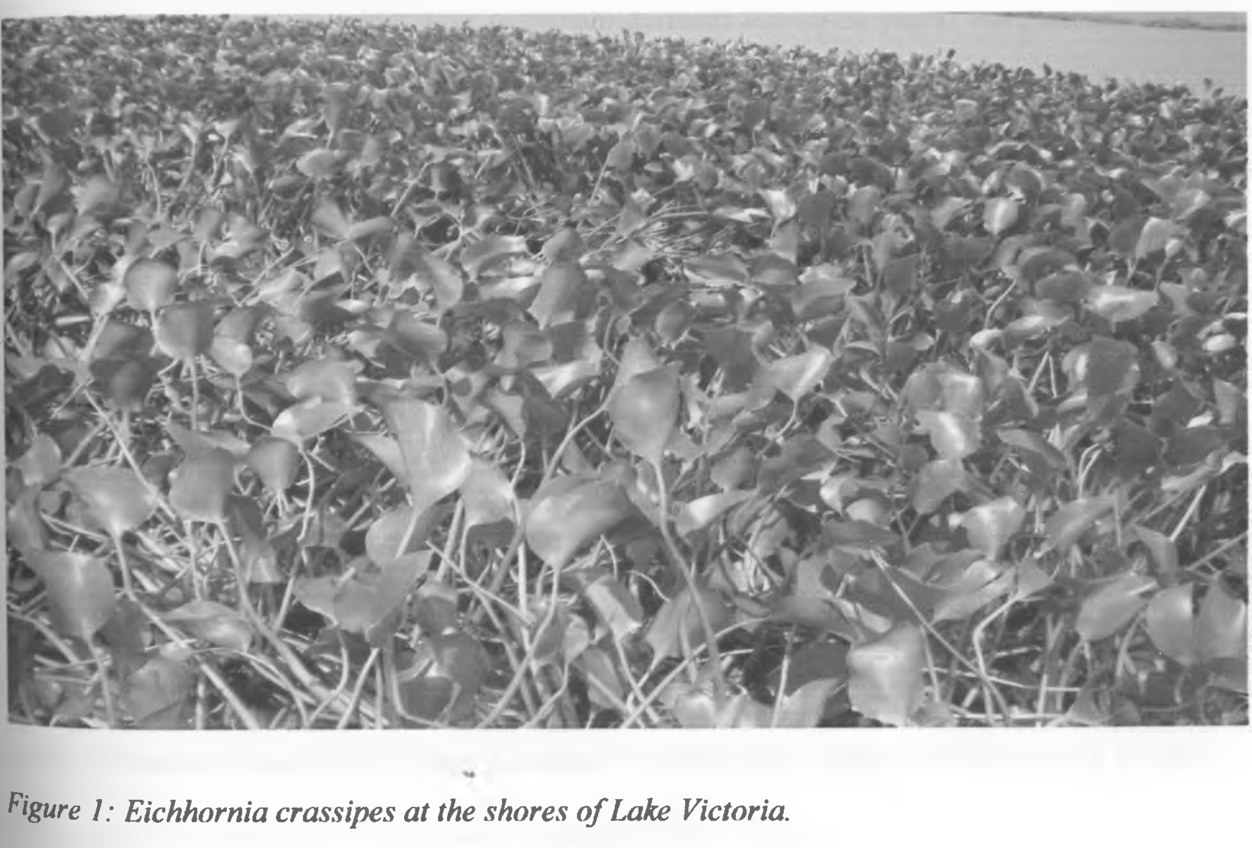

Figure 1: Eichhornia crassipes at the shores of Lake Victoria.

The leaves are 10-20 cm across, and float above the water surface. They have long, spongy and bulbous stalks. The feathery, freely hanging roots are purple black. An erect stalk supports a single spike of 8-15 conspicuously attractive flowers, mostly lavender to pink in colour with six petals. One of the fastest growing plants known, water hyacinth reproduces primarily by way of runners or stolons which eventually form daughter plants. It also produces large quantities of seeds, and these are viable up to thirty years. The common water hyacinth (*Eichhornia crassipes*) is a vigorous grower known to double its population in two weeks. Water hyacinth reproduces sexually by seeds and vegetatively by budding and stolon production(Das, 1969). Daughter plants sprout from the stolons and doubling times have been reported of 6-18 days. The seeds can germinate in a few days or remain dormant for 15-20 years. They usually sink and remain dormant until periods of stress (droughts). Upon reflooding, the seeds often germinate and renew the growth cycle (Barrett, 1980).

Water hyacinth grows over a wide variety of wetland types from lakes, streams, ponds, waterways, ditches, and backwater areas. They obtain their nutrients directly from the water. They prefer and grow most prolifically in nutrient-enriched waters. New plant populations often form from rooted parent plants and wind movements and currents help contribute to their wide distribution. Linked plants form dense rafts in the water and mud. In the Pacific Northwest, Water hyacinth is planted outdoors in ponds and in aquaria, but it is not considered winter hardy, except under special conditions. Leaf blades and petioles are occasionally used by coots. However, whatever benefits this plant provides to wildlife are greatly overshadowed by the environmental invasiveness of this noxious species (LVBC, 2008).

Water hyacinth affects the riparian population in many negative ways. There are economic impacts when the weed blocks boat access. The effects on transportation and fishing are immediately felt. Where the weed is prolific, there is a general increase in several diseases, as the weed creates excellent breeding areas for mosquitoes and other insects. There are increased incidents of skin rash, cough, malaria, encephalitis, gastro intestinal disorders, and Schistosomiasis (bilharzias). Water hyacinth also interferes with water treatment, irrigation, and water supply. It can smother aquatic life by deoxygenating the water, and it reduces nutrients for young fish in sheltered bays. It can also block supply intakes for the hydroelectric plant, interrupting electrical power for cities. The weed also interrupts local subsistence fishing, blocking access to the beaches (Mailu, 2001).

The use of herbicides to control water hyacinth is common. Excellent control of Water hyacinth by the use of the aquatic herbicides 2, 4-D or diquat has been reported (Mailu, 2001). Mechanical controls such as harvesting have been used for nearly 100 years in Florida, but are ineffective for large scale control, very expensive, and cannot keep pace with the rapid plant growth in large water systems. Three insects have been released for the biological control of water hyacinth in Lake Victoria. These include two weevil species (*Neochetina* spp.) and a moth (*Sameodes albiguttalis*). Unfortunately large scale reductions in water hyacinth populations did not occur. Instead insect predation reduced plant height, decreased the number of seeds produced, and decreased the seasonal growth of the plants. This, in turn, allowed better boat access into plant mats, reduced use of herbicides, and resulted in less plant problems. In Louisiana, the seasonal growth of water hyacinth was reduced from a high of over 400,000 hectares per year to lows of only about 80,000 hectares (LVBC, 2008).

Besides heavy metals, *Eichhornia crassipes* can also remove toxins, such as cyanide, a process which is environmentally beneficial in areas that have endured gold mining operations. *E.*

crassipes is also observed to enhance nitrification in waste water treatment cells of living technology. Their root zones are superb micro-sites for bacterial communities.

2.2 Applications of water hyacinth

Water hyacinth has a wide range of applications which depend on its physical, chemical and biological properties. The principal areas are agriculture, drinking water and waste water treatment, fibers and textiles, paper technology and energy.

2.3 Effects of heavy metals

"Heavy metals" is an inexact term used to describe more than a dozen elements that are metals or metalloids. They are toxic at low concentrations. Although heavy metals are natural components of the Earth's crust, their concentrations in an aquatic environments have increased due to mining and industrial activities and geochemical processes. Heavy metals are common in industrial applications such as the manufacture of pesticides, batteries, mining operations, alloys, metal plating facilities, textile dyes, tanneries, etc (CIS, 1999).

Living organisms require trace amounts of some heavy metals, e.g., iron, copper, and zinc, as they are essential to maintain their metabolism, but, at higher concentrations these metals can lead to poisoning and other hazards because they cannot be degraded or destroyed, and tend to bioaccumulate (Crini, 2005). They are therefore persistent in the environment. Some of the heavy metals are poisonous even in very small quantities for example cadmium and mercury.

Heavy metals enter a water source by:

- Direct discharge from industrial and municipal waste,
- Percolation of contaminated soils,

- Leaching of wastes from landfills,
- Naturally since some heavy metals, toxic levels can be just above the background concentration found in nature,
- Acidic rain breaking down soils and releasing heavy metals into streams, rivers, lakes and ground water.

Heavy metals become toxic when they are not metabolized by the body and accumulate in soft tissues. They therefore have negative effects on human and environmental health. Heavy metals can enter the bodies of human beings via the food chain, drinking water, air or absorption through the skin (CIS, 1999). Lead is a heavy metal that is toxic at very low exposure levels and has acute and chronic effects on human health. It is a multi-organ system toxicant that can cause neurological, cardiovascular, renal, gastrointestinal, haematological and reproductive effects (Volesky, 2007).

Copper can be found in many kinds of food, in drinking water and in air. Because of that, we absorb 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. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhea (Odell and Campbell, 1971). However, excessive intake of copper can cause serious health problems such as damage to heart, kidney, liver, pancreas, and brain, intestinal distress, and anemia (Abu Al-Rub *et al*. 2006). Industrial exposure to copper fumes, dusts, or mists may result in metal fume fever with atrophic changes in nasal mucous membranes. Chronic copper poisoning results in Wilson's disease. This is characterized by hepatic cirrhosis, brain damage, demyelization, renal disease, and copper deposition in the cornea (UNEP, 2008, 2009).

Cadmium is not essential for the body. However, cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects (Anayurt, 2009) and is a carcinogen. Symptoms of acute cadmium exposure are nausea, vomiting, abdominal pain, and breathing difficulty. Chronic exposure to cadmium can result in chronic obstructive lung disease, renal disease, and fragile bones. Children should be protected by carefully storing products containing cadmium, especially nickel-cadmium batteries. Symptoms of chronic exposure could include alopecia, anemia, kidney proteinuria, arthritis, learning disorders, migraines, growth impairment, emphysema, osteoporosis, loss of taste and smell, poor appetite, and cardiovascular disease. Some cadmium compounds are relatively water soluble, mobile in soil and bioavailable, depending on the water and soil chemistries. It tends to bioaccumulate in organs such as the kidney and liver of vertebrates, but aquatic invertebrates and algae can also build up relatively high concentrations. Effects on birds and mammals are mainly due to kidney damage. In sea birds and marine mammals in particular, cadmium accumulates to relatively high levels (UNEP, 2008).

Zinc can cause eminent health problems such as stomach cramps, skin irritations, vomiting, nausea and anaemia. Very high levels of zinc can damage the pancreas and disturb protein metabolism and cause arteriosclerosis.

2.4 Adsorption

Adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and chemical interactions (Kurniawan and Babel, 2003b). It 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). The exact nature of the bonding (ionic, covalent, or metallic) depends on the properties of the species involved, but the adsorbent is classified as exhibiting physisorption, chemisorption or electrostatic sorption (Ruthven, 1984).

2.4.1 Physisorption

In this type of adsorption, the molecules of adsorbate are held by Van der Waal's forces. This type of adsorption is characterized by:

- Low heat of adsorption (<2 or 3 times the latent heat of evaporation).
- Relatively low temperature, always under critical temperature of the adsorbate.
- Non- specific.
- Adsorption takes place in monolayer or multilayer.
- No dissociation of the adsorbed species.
- Rapid, non-activated, reversible.
- Low activation energy.
- No electron transfers although polarization of sorbate may occur.

2.4.2 Chemisorption

Unlike physical adsorption, chemisorption involves the formation of a chemical linkage between the adsorbed molecule and the surface of adsorbate thus it is highly selective. This type of adsorption is characterized by:

- High heat of adsorption (> 2 or 3 times the latent heat of evaporation).
- High temperatures.
- Strong covalent bond formed between the adsorbate and the surface.
- Adsorption takes place only in monolayer.
- High activation energy.
- Increase in electron density in the adsorbent- adsorbate interface.
- Reversible only at high temperature.

Adsorption phenomena are mainly utilized in performing bulk separation or purification. Adsorption separation processes are applied at an industrial level. However before an adsorption process is scaled up to commercial scale, a suitable adsorbent must be available in abundance at a low price.

A proper understanding of the adsorption process and design of adsorption equipment requires knowledge of equilibrium isotherms and adsorption kinetics.

2.5 Adsorption Equilibrium

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 and the amount remaining in solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration the bulk of the solution in a dynamic balance with the interface concentration (Kumar *et al.,* 2006); Ghiaci *et al*., 2004). The adsorption isotherms describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, an expression of surface properties and capacities of adsorbents, and effective design of adsorption systems (El-Khaiary, 2008). Equations that are commonly used to describe the experimental adsorption data are those developed by Langmuir (1916), Freundlich (1906) and Dubinin-Radushkevich (1947).

2.5.1 The Freundlich Isotherm

This isotherm developed by Freundlich (1906) describes the equilibrium on heterogeneous surfaces and does not assume monolayer capacity. The Freundlich equation is

$q_e = K_F C^{1/n}$ (nonlinear form) eq.1

$\log q_e = \log K_F + \frac{1}{n} \log C_e$ (linear form) eq.2

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg g^{-1}), C_e the equilibrium concentration of solute in the bulk solution (mg L^{-1}), K_F a constant indicative of the relative adsorption capacity of the adsorbent (mg g^{-1}) and the constant $\frac{1}{n}$ indicates the intensity of the adsorption. n is considered as the heterogeneity of the adsorbent and its affinity for the adsorbent (Foo and Hameed, 2010). A higher value of n (or a smaller value of $\frac{1}{n}$) indicates a stronger bond between the adsorbate and the adsorbent.

2.5.2 Langmuir isotherm

In its formulation, this empirical model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), adsorption can only occur at finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites (Vijayaraghavan *et al.*, 2006). The Langmuir adsorption isotherm describes the surface as homogeneous assuming that all the adsorption sites have equal adsorbate affinity and that adsorption at one site does not affect adsorption at an adjacent site (Langmuir, 1918; Weber, 1972). The Langmuir equation may be written in the linear or non-linear form as shown in equation 3 and 4;

$$q_e = \frac{Q_0 b C_e}{1 + bC_e} \text{.(non linear form)} \ldots\ldots\ldots\ldots\ldots\ldots \text{eq.3}$$

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} b} + \frac{1}{Q_{max}} C_e \ (linear\ form) \ldots\ldots\ldots\ldots\ldots\ldots . eq. 4$$

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

From the linear plots of C_e/q_e against C_e, the value of Q_{max} and *b* can be calculated from the slope and intercept respectively.

2.6 Kinetic sorption mechanisms

Metal sorption kinetics are influenced by sorption reactions and the mass transfer steps that govern the transfer of metal ions from the bulk of the solution to the sorption sites on the surface and inside adsorbent particles. The mechanisms of adsorption depend on the physical form of the biomass, the intrinsic structure of the *E. crassipes*, the nature of the adsorbate solutions, as well as the process conditions such as temperature and pH. The kinetics of heavy metal adsorption onto the *E. crassipes* biomass can be predicted using pseudo-first-order and pseudo-second-order models.

The kinetics of an adsorption process can be studied by carrying out a separate set of adsorption experiments at constant temperature to follow adsorption with time. The rate of adsorption can be determined quantitatively and tested by pseudo-first-order and pseudo-second- order models. This information is useful for further systems design in scale up experiments.

2.6.1 The Pseudo-First-order Equation

Pseudo-first-order model is used to describe the reversibility of the equilibrium between solid and liquid phases (Vijaya *et al.*, 2008). Assumes that the metal cation binds only on one sorption site on the sorbent surface.The pseudo-first-order model of Lagergren can be expressed by equation shown below (Wan Ngah and Hanafiah, 2008a).

$$log(q_e - q_t) = log\ q_e - \frac{k_1}{2.303} t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots. eq. 5$$

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_l is the rate constant of the pseudo-first-order adsorption process (min^{-1}). Linear plots of $log(q_e-q_t)$ versus t was used to predict the rate constant (k_1) and adsorption at equilibrium (mg g^{-1}), which are obtained from the slope and intercept respectively.

According to Gerente *et al.* (2007), the main disadvantages of this model are:

- The linearized equation does not give theoretical q_e values that agree with experimental q_e values, and
- The plots are only linear over approximately the first 30 minutes. Beyond this initial 30 minute period, the experimental data and theoretical results do not correlate well.

In some cases the pseudo-first-order model fits experimental data well and allows for the evaluation of the rate constant.

2.6.2 Pseudo-Second-order Equation

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .. eq. 6$$

Where k_2 is the rate constant of the pseudo-second-order adsorption (g mg^{-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 contant (k_2).

2.7 Adsorbents for heavy metal removal

2.7.1 Zeolites

Natural zeolites gained a significant interest mainly due to their ion exchange capability. Zeolites are aluminosilicates with Si/Al ratios between 1 and infinity. They have crystalline, hydrated aluminosilicates of alkali and alkaline earth cations, having infinite, three-dimensional structures (Mampton, 1997; Townsend *et al.*, 1991). An aluminosilicate tetrahedron connected to an oxygen atom, has charge balancing cations that counter balance the negative charge localised on the aluminosilicate framework (Keane, 1998). There are 40 natural and over 100 synthetic zeolites. Only seven (mordenite, clinoptilolite, chabazite, erionite, ferrierite, phillipsite, and analcime) occur in sufficient quantity and purity to be considered exploitable (Kesraoui-Ouki *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 (i.e. water softeners), catalytic applications in the petroleum industry, separation process (i.e. molecular sieves) 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). Cinoptilolite was reported to have effectively removed heavy metals from aqueous solutions (Can *et al.*, 2010). Among the minerals that posses adsorbent properties, zeolites appear as the most promising for metal purification therefore they have received increasing attention for pollution control. The zeolites can be regenarated using sodium chloride with a regeneration efficiency of more than 90% (Kurniawan, 2002).

2.7.2 Nano-technology

Nanoporous materials are defined as those materials having pore diameters less than 100 nm. Nanoporous materials, a subset of nanostructured materials possess unique surface, structural and bulk properties that underline their important uses in various fields such as ion exchange, separation, catalysis, sensor, biological molecular isolation and purifications (Lu and Zhao, 2004). This is a new functional material, which has attracted much attention due to its special properties. Most of the atoms on the surface of the nanoparticles are unsaturated and can easily bind with other atoms. Nanoparticles have high adsorption capacity. Besides, the operation is simple, and the adsorption process rapid. So there is a growing interest in the application of nanoparticles as adsorbents. During the last decade, considerable effort has been made in the synthesis, characterization, functionalization, molecular modeling and design of nanoporous materials due to their extremely small size and large specific surface area. Modified nano partcles and also composite nano materials have been reported to have good adsorbent properties (Afkhami *et al.*,2010; Rahmani *et al.*, 2010). Maghemite nanoparticles were used for six-successive adsorption–desorption cycles.

2.7.3 Industrial by-products

Industrial by-products such as fly ash, waste iron, slag and hydrous titanium oxide can be chemically modified to enhance their efficacy for removal of heavy metals from water and wastewater (Barakat, 2010). Widespread industrial activities generate huge amount of solid waste materials as by-products. Some of this material is being put to use while others find no proper utilization and are dumped elsewhere. The industrial waste material is available almost free of cost and causes major disposal problem. If the solid wastes could be used as low-cost adsorbents, it will provide a two-fold advantage to environmental pollution. Firstly, the volume of waste materials could be partly reduced and secondly the low-cost adsorbent if developed can reduce the pollution of wastewaters at a reasonable cost. In view of the low cost of such adsorbents, it would not be necessary to regenerate the spent materials. Thus, a number of industrial wastes have been investigated with or without treatment as adsorbents for the removal of pollutants from wastewaters. This includes fly ash, steel indusry waste (blast furnace slag and sludge) , aluminium industry sludge, fertilizer waste leather sludge and paper industry sludge. Like agricultural waste, industrial by-products are inexpensive and abundantly available. As a whole, adsorbents from industrial by-products such as iron/steel slag have some advantages for metal removal. In addition to having a wide pH range (pH 1.5–9.0) effective for metal removal, such adsorbents can be employed to treat inorganic effluent with metal concentration of less than 20 mg L^{-1}, in the range of 20-100 mg L^{-1}or higher than 100 mg L^{-1} (Volesky, 2007).

2.7.4 Silica gel

Silica gels are classified into three types: regular, intermediate and low density gels. Regular density silica gel is prepared in an acid medium and shows high surface area (e.g. 750 m^2/g). Intermediate and low density silica gels have low surface areas (300–350 and 100–200 m^2/g, respectively). The gel is considered a good adsorbent and is used in many industries (Bhatnagar and Sillanpaa, 2010). Silica gel is a chemically inert, nontoxic, polar and dimensionally stable (< 400°C) amorphous form of SiO_2. 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, pickling, etc. These after treatment methods results in various pore size distributions. Modified forms of silica have also been widely explored for the removal of different pollutants (Wang *et al.*, 2009). Silica is used for drying of process air (e.g. oxygen, natural gas) and adsorption of heavy (polar) hydrocarbons from natural gas.

2.7.5 Activated carbon

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 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 et al., 2010). 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 can be manufactured from carbonaceous material, including coal (bituminous, sub-bituminous, and lignite), peat, wood, or nutshells (i.e., coconut). The manufacturing process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons, from the raw material, as well as to drive off any gases generated. The carbonization process is completed by heating the material at 400–600°C in an oxygen-deficient atmosphere that cannot support combustion. Activated carbon has been shown to have very effective sorption properties for cadmium, chromium, zinc and copper in sewage waters (Argo, 1972) which can be considered to be difficult matrix as wastewater from plating industry.

2.7.6 Biopolymers and hydrogels

Biopolymers are industrially attractive because they are, capable of lowering transition metal ion concentrations to sub-part per billion concentrations, widely available, and environmentally safe. Another attractive feature of biopolymers is that they possess a number of different functional groups, such as hydroxyls and amines, which increase the efficiency of metal ion uptake and the maximum chemical loading possibility. Among these biopolymers includes chitin and chitosan.

Chitin and chitosan are nitrogenous polysaccharides that are made up of acetyl glucosamine and glucosamine units. Chitin is the second most abundant polymer in nature. It occurs naturally as micro fibrils forming the structural components of exoskeleton of arthropods (Rangel-Mendez *et al.*, 2009). Its main source is seafood crustaceans such as crabs, shrimps, prawns and lobsters. Chitosan is a product of deacetylation of chitin and is a powerful chelating agent and interacts very efficiently with transition metals from waste water.

Hydrogels, which are cross-linked hydrophilic polymers, are capable of expanding their volumes due to their high swelling in water. Accordingly they are widely used in the purification of wastewater. Various hydrogels were synthesized and their adsorption behavior for heavy metals was investigated (Barakat, 2010).

2.7.7 Agricultural by-products and biological wastes

Agricultural materials particularly those containing cellulose shows potential sorption capacity for various pollutants. The basic components of the agricultural waste materials include hemicellulose, lignin, lipids, proteins, simple sugars, water, hydrocarbons, and starch, containing variety of functional groups. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable nature and low cost are viable option for water and wastewater remediation. Agricultural waste is a rich source for activated carbon production due to its low ash content and reasonable hardness, therefore, conversion of agricultural wastes into low-cost adsorbents is 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; Dakiky *et al.*, 2002;), coir pith (Parab, 2006; Unnithan *et al.*, 2004) , straw (Chun *et al.*, 2004), husks (Eromosele *et al.*,1996), leaf mould (Sharma and Forster, 1996), wheat bran (Dupont and Guilon, 2003), 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), bark (Sarin and Pant, 2006), wheat bran (Farooq *et al.*, 2010) and nut shells (Nasernajad *et al.*, 2005). 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). Another biomaterial *Luffa cylindrica* was found to be veyr effective in removal of cationic dye methylene blue from aques solutions (Agoi, 2010).

2.7.8 Clay minerals and oxides

Clay minerals and oxides are widespread and abundant in both aquatic and terrestrial environments. Finelly divided clay minerals and oxides exhibit large surface areas. Clay minerals and oxides adsorb cationic, anionic, and neutral metal species. They also take part in cationic and anionic exchange processes. Their sorption capacities, cation and anion exchange properties and binding energies vary widely. There are three types of clay: montmorillonite, bentonite and kaolinite. A number of studies on metal uptake using montmorillonite have been conducted. The adsorption of Cd(II), Cr(III), Cu(II), Ni(II) and Zn(II) ions on Na-montmorillonite 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. This material is valuable for its tendency to absorb water in the interlayer site. Chakir *et al.* (2002) studied the uptake of Cr(III) from simulated solution using bentonite and an expanded perlite. Surface complexation played major roles in Cr(III) removal. Kaolinite is the other clay, representing a layered alumino-silicate mineral with the structure of a tetrahedral (Si center) and octahedral (Al center). Kaolinite was used for Cu(II), Ni(II), Mn(II) and Co(II) removal from simulated solution. The metal sorption on kaolinite followed the Langmuir isotherm. Due to their small ionic radius, Cu(II) ions had the highest adsorption affinities compared to other. Other materials that have been investigated include glauconite, vermiculite (Sumathi and Naidu, 2005), wollastonite, titanium oxide and alumina. Natural clay rich in mica was found to be an excelent remover of heavy metal ions Cd^{2+}, Cr^{3+}, Pb^{2+} and Cu^{2+} in aqueous solutions (Attahiru, 2003).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1 Sampling site

Lake Victoria is the largest fresh water lake in Africa. It is the source of the longest branch of the River Nile, the White Nile, and has a water catchment area of 184,000 km^2 (71,040 sq miles). Lake Victoria is 68,800 km^2 (26,560 sq miles) in size, making it the second widest fresh water lake in the world in terms of surface area (third largest if one considers Lake Michigan-Huron as a single lake). The lake is relatively shallow, with a maximum depth of 84 m (276 ft) and a mean depth of 40 m (131 ft). Lake Victoria ranks as the seventh largest freshwater lake by volume, containing 2,750 cubic kilometers. It is a biological hotspot with great biodiversity. The lake lies within an elevated plateau in the western part of Africa's Great Rift Valley and is subject to territorial administration by Tanzania, Uganda and Kenya. Figure 2 shows the sampling sites (LVBC, 2008).

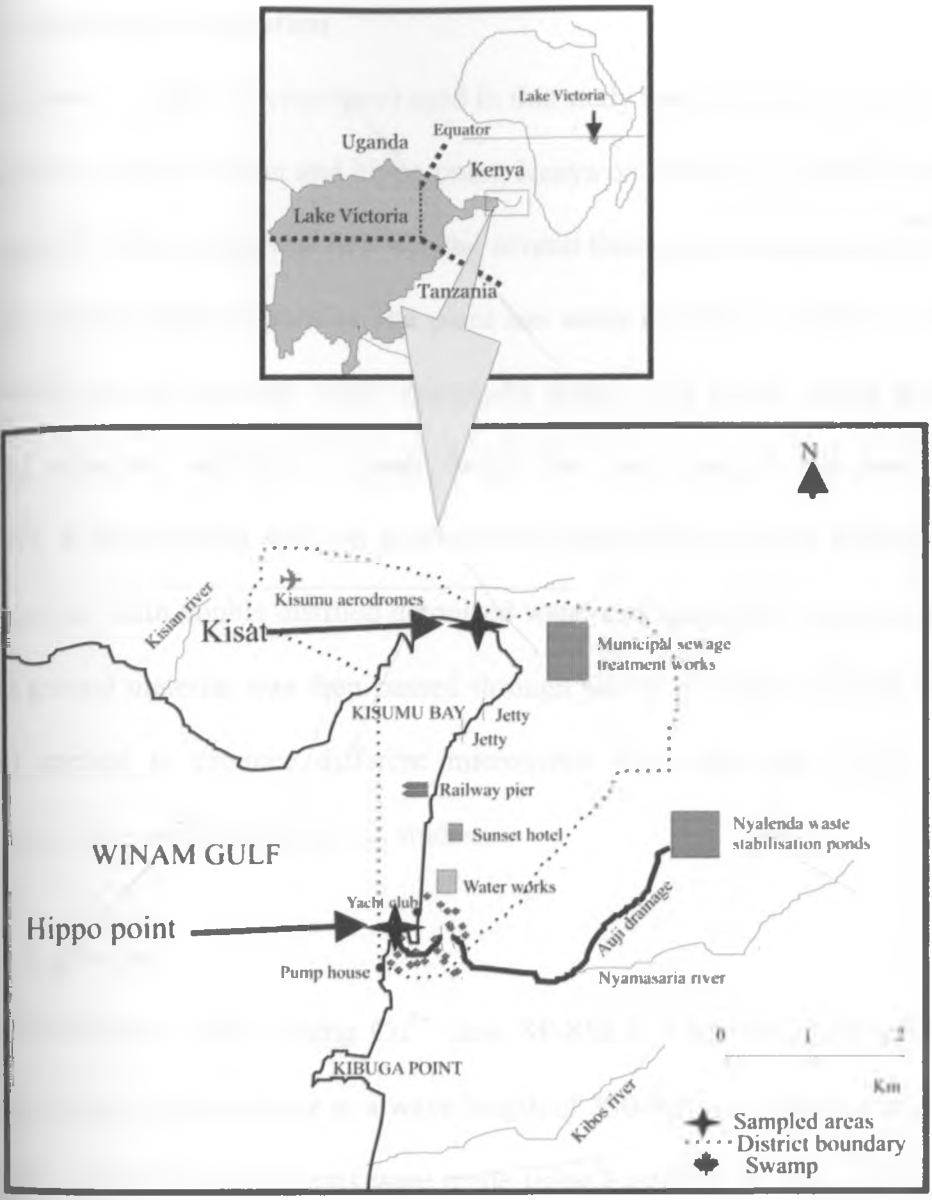

Figure 2: Sampling site in Kisumu bay where Eichhornia crassipes was collected

Source: KMFRI, Kisumu station

3.2 Adsorbent preparation

The water hyacinth *(E. crassipes*) used in this study was harvested from Lake Victoria in Winam gulf Kisumu bay at Kisat and hippo point, Kenya on 23rd August 2009 and 16th September 2009 (Figure 2). The sample was first washed several times with distilled water to remove any soil and other water soluble impurities.The plant has water content of 95.5% (LVBC, 2008). The plant material was divided into roots, stems and leaves. The leaves, stems and roots were then sun dried separately and kept in plastic bags. The dried material was then transported to Nairobi where it was ground using a mechanical grinder. The ground material were again washed thoroughly with double distilled deionised water and then dried in an oven for 48 hours at 60°C. The ground material was then passed through sieves of different mesh sizes (425, 300 and 75 μm) applied to produce different micrometer sized particles. These sieved samples were subsequently used for adsorption studies.

3.3 Apparatus

For preliminary studies using Cu^{2+} ions, SP-850 UV-Visible spectrophotometer was used for measurement of absorbance at a wave length of 330-900 nm equipped with a 10 mm path length cuvette. 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 Whatman filter paper number 4 for contact time experiment and 42). A stop watch was also used to monitor time. A mechanical grinder was used for grinding. Analytical balance (Fisher scientific A 160) was used for all weight measurements. Residual and initial concentrations were determined using a UV-Visible spectrophotometer (SP-850-Turner) for preliminary investigations and later Flame atomic absorption spectrophotometer (CTA 2000 AAS) and Varian Spectr AAS. Volumetric flasks (1000, 500, 250, 100, 50, 25 and 10 mL) were used in preparations and dilutions of the solutions. Propylene bottles were used for conducting the experiments and plastic filter funnels used during filtration. Glass plates were used for making of the thin films.

3.4 Reagents

All reagents used were of analytical grade. Working solutions were prepared by appropriate dilutions of the stock solutions. Cadmium sulphate ($3CdSO_4.8H_2O$), copper (II) sulphate ($CuSO_4.5H_2O$), lead (II) nitrate ($Pb(NO_3)_2$), and Zinc (II) sulphate ($ZnSO_4.7H_2O$) which were supplied by Sigma Aldrich. Stock solutions of 1000 mg L^{-1} were prepared by dissolving appropriate masses in double distilled deionised water as shown in Table 1.

Table 1. Amount of solute weighed to prepare stock solutions

Metal	Metal salt	MW	Amount weighed (g)	Volume of volumetric flask (mL)
Cadmium	$3CdSO_4.8H_2O$	769.56	3.4274	500
Copper	$CuSO_4.5H_20$	249.68	1.9746	500
Lead	$Pb(NO_3)_2$	331.20	0.8033	500
Zinc	$ZnSO_4.7H_20$	287.54	2.2100	500

Adjustments of pH were made using 0.1 M hydrochloric acid and 0.05 M sodium hydroxide. Sodium hydroxide (0.05 M) solution was prepared by dissolving in suitable amounts of double distilled de- ionized water. Hydrochloric acid (0.1 M) solution made by dissolving an appropriate amount of 12 M concentrated acid (Aldrich Company) in double distilled de-ionized water. The colour of copper (II) ions was intensified using 35% v/v ammonia solution supplied by Aldrich.

3.5 Adsorbent characterization

In order to understand the type of bioamass that was to be used for adsorption the biomass material had to be characterize by various methods, spectroscopic, qualitative, quantitative and even some data obtained from the literature.Some of the methods used are described below.

3.5.1 pH_{ZPC} and pH slurry

The pH of aqueous slurry was determined by soaking 1 g of *E. crassipes* in 50-mL distilled water, stirred for 24 h, filtered and the final pH was measured. The pH of zero-point charge or pH_{ZPC} was determined based on the previous method (Balistrieri and Murray, 1981). This was done by immersing 0.1 g of the *E. crassipes* biomass in 50 mL (0.01M) potassium nitrate solutions in which the initial pH values were adjusted from 2 to 9 and left for 24 h. The final pH of the solutions was determined after 24 h. The pH_{ZPC} was determined from the curve that cut the pHo (initial pH of the solutions) line of plot of ΔpH (the difference between initial and final pH) versus pHo (Hanafia *et al.*, 2009). The content of light metal ions (K^+, Na^+, Mg^{2+}, and Ca^{2+}) in *E. crassipes* was carried out according to dry ashing procedure (Isaac and Kerber, 1971).

3.5.2 FT-IR characterisation

The Fourier transform infrared (FT-IR) spectra of *E. crassipes* before and after copper, cadmium, lead and zinc adsorption were recorded with Fourier transform infrared spectrophotometer (Shimadzu, FT-IR System 8400 Model, Japan) in the range of 250 to 4,000 cm^{-1}. The proportion of biosorbent to potassium bromide (KBr) was 1: 300 mg.

3.5.3 Ion exchange experiment

The ion exchange experiment was done in order to investigate the mechanism of interaction between the biosorbent and the metal cations. This was done by quantitatively measuring the amount of cations released from blanks when *E.crassipes* was soaked in distilled water for 24 h. The amount of cations present in effluent after adsorption were also measured.

3.5.4 Other characteristics of *E. crassipes*

Data concerning other characteristics of *E. crassipes* was obtained from the literature .This included the content of light metal ions like Na^+, K^+, Mg^{2+} and Ca^{2+}. The percentage content of carbon, nitrogen, and sulfur and phosphorous in *E. crassipes* was obtained in the literature. The ash content analysis was caried out by combusting 1.0 g of E. *crassipes* in a furnace for 2 h.

3.6 Preparation of Stock Solution

A concentration 1000 mg L^{-1} of the metal ion solutions were prepared by dissolving appropriate amounts of metal salts in a given volume of distilled water as shown previously in table 1. The volume was then topped up to the mark. In the preparation of copper (II) solution for UV-Vis analysis 50 ml of ammonia solution (27%) was then added to intensify the blue color of copper (II) sulphate solution. The solution was then topped up to the mark using double distilled de-ionized water.

The formula below was used to calculate the amount of the salt weighed:

$$w = \frac{mw}{aw} \times \frac{100}{p} \times \frac{v}{1000} \quad \text{.......eq. 7}$$

where w is the weight of the salt used (g), aw is the atomic weight of the metal, mw is the molecular weight of the salt (g mol^{-1}), p is the percentage purity of the salt (%) and v is the volume of the stock solution to be prepared.

3.7 Working solutions

Working solution concentrations for the elements were prepared using the formula given below:

$$C_0V_0 = C_1V_1 \quad \text{.......e.q.8}$$

Where C_0 = Concentration of the stock solution, mg L^{-1}

C_1 = Concentration of the working standard solution, , 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

3.8 Operating conditions for AAS analysis

Table 2 shows the operating conditions for the atomic absorption spectrophotometer (AAS) during the analysis.

Table 2. Optimum 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
Acetylene(C_2H_2) Flow(L min^{-1})	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	2-8	0.2-1.6	0.5-2	0.2-1.6

Source: AAS instruction manual/CTA-2000 and Spectr-AA

3.9 Investigations using UV-Vis Spectrophotometer and Atomic Absorption Spectrophotometer

3.9.1 Effect of weight and particle size

The dried sample was 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, >75<300 and <75 μm). Preliminary investigations were conducted to determine the appropriate particle size for the efficient adsorption of Cu^{2+} from aqueous solutions using water hyacinth. Two grams of each particle sizes group was weighed in polypropylene containers and mixed with 30 mL of 200 mg L^{-1} $CuSO_4$ solution. The mixtures were allowed to equilibrate on an orbital shaker rotated at 200 rpm for 30 minutes. The mixtures were then filtered and absorbance of the filtrates was measured using UV-Visible spectrophotometer. The absorbance of the blank was also taken and compared with that of the filtrates to determine the amount of Cu^{2+} ions adsorbed. The initial and residual concentrations were determined using UV-Visible spectrophotometer. For the studies that involved the use of AAS for analysis, 0.125 g, 75 μm particle size of *E. crassipes* was weighed into a 60 mL polypropylene container. To the material, 20 mL of 10 mg L^{-1} aqueous Cu^{2+} was added and the mixture equilibrated for 20 minutes under agitation at 200 rpm. The mixture was then filtered and the containers tightly closed awaiting determination of the residual concentration by AAS. The procedure was repeated using the same volume and concentration but different masses of 0.25, 0.50, 1.0 and 2.0 g of the *E. crassipes*. The procedure was repeated using *E. crassipes* of particle sizes; <300 μm, >300 μm and >425 μm. The whole procedure was repeated using Zn^{2+},

Cd^{2+} and Pb^{2+} in place of Cu^{2+} solution. The particle sizes <75, <300, >300 and >425 refer to <75 µm, >75 but <300 µm, >300 but <425 µm and >425 µm respectively. The particle size of <300 µm was found to give the highest percentage adsorption and therefore was used for all the subsequent adsorption experiments.

3.9.2 Effect of shaking speed on adsorption

An amount of 0.20 g of *E. crassipes* portions were weighed into several polypropylene containers whose shaking speed was indicated against them. The shaking speed was varied in the range of 100-600 rpm. After which 30 mL of 30 of mg L^{-1} were added to the containers and the mixtures allowed to equilibrate for 20 minutes at a given shaking speed separately. The mixture was then filtered and absorbance of the filtrate determined using UV-Vis. The absorbance of the Cu^{2+} ions solution before filtration was determined and compared to the absorbance of filtrate for determination of percentage adsorption.

3.9.3 Effect of plant part

An amount of 0.125g of <300 µm root sample was weighed in polypropylene containers and mixed with 20 mL of 320 mg L^{-1} 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 absorbance of the filtrate taken using UV-Visible spectrophotometer. The procedure was repeated using different weights of the same particle size of the root samples. The above procedure was also repeated using the shoot and leaves of the same particle size of < 300 µm. The residual concentrations were confirmed using Atomic absorption spectrophotometer.

3.9.4 Effect of contact time

An amount of 0.5g portions of *E. crassipes* were weighed into 12 different polypropylene containers. The mixtures in the polypropylene containers were to be equilibrated under mechanical shaking for 0 to 60 minutes at 5 minutes interval respectively. To each container, 20 mL of 200 mg L^{-1} Cu^{2+}solution was added. The first container carrying a zero time label was filtered immediately and the absorbance of the filtrate determined using UV-Visible spectrophotometer. The solutions were then filtered after the various equilibration times and the absorbance of the filtrates were determined using UV-Visible spectrophotometer. The procedure was done in duplicate for each of the Cu^{2+} aqueous solutions. For studies in which residual concentration was to be determined by FAAS Cu^{2+} ion solutions of different concentrations were prepared. An amount of 0.5 g of *E. crassipes* was weighed into 60 mL polypropylene containers. Then 20 mL of each of the Cu^{2+} ions were added to the different containers having the *E. crassipes* and the mixtures equilibrated for different times (0, 5, 10, 15, 20, 25, 30, 35, 40, 45 ,50, 55 and 60 minutes). This procedure was done in duplicate for each of the copper solutions. The mixtures were then filtered into poly propylene containers and the residual concentration of copper determined by AAS. The procedure was repeated using Cd^{2+} (80, 400 and 1000 mg L^{-1}), Zn^{2+} (20, 200 and 1000 mg L^{-1}) and Pb^{2+} (60, 150 and 1000 mg L^{-1}). Results are displayed in appendix (I).

3.9.5 Effect of temperature

For experiments in which residual concentration was determined by UV-Visible spectrometer, an amount of 0.5 g of the *E. crassipes* and 20 mL of 250 mg L^{-1} of Cu^{2+} ion solution were put in the incubator (Gallenkamp orbital incubator) and the two allowed to attain thermal equilibrium for about 30 minutes at the required temperature (25, 30, 40, 50, 60 and 70°C). After the duration the *E. crassipes* was mixed with the given volume of the Cu^{2+} solution and the mixture allowed to equilibrate under mechanical shaking for 20 minutes after which the mixture was filtered into a propylene container. The concentration of the filtrate was determined using the SP-Turner 850 Spectrophotometer. For experiments where AAS was used for determination of the residual concentration, 0.5 g of *E. crassipes* and 20 mL of a given concentration of the metal ions solutions were placed in an incubator for about 30 minutes for the temperature to be adjusted to the required temperature. Then the adsorbent and the metal ions solutions were mixed and the mixture equilibrated for 20 minutes under mechanical shaking at 80 rpm. 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+} (79 and 468 ppm), Cu^{2+} (50 and 400 mg L^{-1}), Pb^{2+} (70.9 and 500 mg L^{-1}) and Zn^{2+} (25 and 200 mg L^{-1}) ions. Results are displayed in appendix (III).

3.9.6 Effect of pH

To study the effect of pH on metallic ion adsorption capacity of the *E. crassipes*, experiments were conducted at different pH values. The experimental conditions are given in the table 3.

Table 3 . Parameters used to study the effect of pH on metal ions adsorption

Metal	Mass of *E.crassipes* (g)	Initial pH range	Concentration of metallic ion (mg L^{-1})
Cadmium	0.25	1-7	50, 200
Copper	0.25	1-7	50, 200
Lead	0.25	1-7	50, 200
Zinc	0.25	1-7	50, 200

The pH of the metal solutions were adjusted using 0.1 M HCl and 0.05 M NaOH.The pH was measured using Extik ® EC 250 pH/conductivity/TDS meter. Higher pH values were avoided due to precipitation.

Adsorption experiments were perfomed by mixing the adsorbent with 20 mL of a solution containing a single metallic ion. Batch experiments were conducted at room temperature using an agitation speed of 300 rpm for 20 minutes. At the end of desired time, the mixture was filtered, the filtrate was collected to determine the residual metal ion concentration. The concentration of heavy metals were determined by use of UV-Vis for Cu^{2+} ions in the preliminary study and later by atomic absorption for all the metals in the study. This is because the later intrument is more accurate and less subject to background interferances during determination and therefore improves the reliability of the data obtained for copper adsorption. However, the UV- Vis could not be used for determination of colourless ions hence use of AAS for determination of Pb^{2+}, Zn^{2+} and Cd^{2+} ions. Results are displayed in appendix (II).

3.9.7 Effect of weight of *E. crassipes*

An amount of 0.125g of the sample particle size >75<300 μm was weighed in polypropylene containers and mixed with 30ml of 200 mg L^{-1} $CuSO_4$ solution. The mixtures were allowed to equilibrate on an orbital shaker operated at 200 rpm for up to 1 h and mixtures filtered at time intervals of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 minutes, filtered and then absorbance of the filtrate determined using UV-Visible spectrophotometer. The procedure was repeated using different weights (0.25, 0.5, 1.0, 1.5, 2.0g) of the same particle size and different concentrations (200, 300, 400, 500, 600 and 700 mg L^{-1}) and the mixture equilibrated on a mechanical shaker for 20 minutes. For studies conducted using AAS for quantification; an aqueous solution of Cu^{2+} ions was prepared and concentration determined using AAS after which different weights of the *E. crassipes* were weighed into 60 mL polypropylene containers (0.125, 0.25, 0.5, 1.0, 2.0 g). Volumes of 20 mL Cu^{2+} ions of known concetration were then added to each of the containers separately and the mixture equilbrated on an orbital shake for 20 minutes. The mixtures were then filtered into 50 mL polypropylene containers and the concentration of copper later determined using AAS. The above procedure was repeated for Zn^{2+}, Cd^{2+}, and Pb^{2+} ions.

3.9.8 Effect of initial concentration of metal ions

A stock solution of 1000 mg L^{-1} copper (II) sulphate was prepared from which 8 different concentrations of Cu^{2+} ions solutions ranging from 30-600 mg L^{-1} were prepared. Absorbance of the different $CuSO_4$ solutions were taken as blanks using the UV-Visible spectrophotometer after which 30 mL of each Cu^{2+} solutions was added to 0.5g of sample particle size >300<425 µm. 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, 1.0 and 2.0 g) but same volume of sorbate and residual concentrations determined for each combination. For studies where AAS was used for quantification, the procedure above was used but the equilibration time was 20 minutes. After which the mixture was filtered into polypropylene containers and the residual concentration determined by use of atomic absorption spectrophotometer (CTA 2000 –AAS for copper and zinc and Varian spectr AA for cadmium and lead). The procedure used for AAS study is repeated using Cd^{2+}, Zn^{2+} and Pb^{2+}. See appendix (IV) for results.

3.9.9 Adsorption equilibrium

Adsorption equilibrium studies were perfomed by placing 0.125 g *E. crassipes* in contact with 20 mL of single metal ion solutions of different concentrations. The experiments were conducted at room temperature for each metalic ion until equilibrium was established. After the desired time the metallic ion solutions were filtered and the residual metal ion concentration determined by atomic absorption. The concentration range was between 20-1000 mg L^{-1}. Summarry of results are shown in appendix (V).

3.10 Adsorption kinetics in batch experiments

Kinetics studies for Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions were carried out. The experiments were performed at 3 initial concentrations (50, 300 and 1000 mg L^{-1} for Cu^{2+}, 69, 432, and 1540 mg L^{-1} for Cd^{2+}, 60, 150 and 1000 mg L^{-1} for Pb^{2+} and 20, 200 and 1000 mg L^{-1} for Zn^{2+} with a particle size of 300µm of *E. crassipes.*

An amount of (0.125- 2.0 g) adsorbent was mixed with 20 mL of a single metal solution for a total contact time of 1 h, at room temperature using an agitation speed of 200 rpm. The samples were filtered and the residual metallic ion content was determined by atomic absorption.

In order to evaluate the kinetics mechanism of the adsorption process, pseudo-first-order and pseudo-second-order models were tested with the experimental data. Summary of results displayed in appendix (VI).

3.11 Evaluation of experimental data

3.11.1 Adsorption capacity

The adsorption capacity, **q_e**, was calculated from the difference between the initial single metal concentration in aqueous solution, **C_o**, and the equilibrium concentration, **C_e** according to the formula:

$$q_e = \frac{(C_o - C_e)V}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{eq. } 9$$

Where **V** is the volume of aqueous solution (L) and **W** is the mass of *E. crassipes* (g)

3.11.2 Adsorption isotherms

In the endeavor to explore novel adsorbents in accessing an ideal adsorption system, it is essential to establish the most appropriate adsorption equilibrium correlation, which is indispensable for reliable prediction of adsorption parameters and quantitative comparison of adsorbent behavior for different adsorbent systems (or for varied experimental conditions). In the perspective, equilibrium relationships, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems. The adsorption data was therefore evaluated using the Langmuir and the Freundlich adsorption isotherms.

3.11.3 Adsorption kinetics

To identify the rate controlling mechanisms during adsorption of cadmium, copper, lead and zinc 3 steps were considered

- Mass transfer of the metallic ion from the bulk of the solution to the surface of the adsorbent
- Adsorption of the metallic ion onto sites , and
- Internal diffusion of the metallic ion onto *E. crassipes*.

Simplified models were applied to evaluate the experimental batch data for each metal. The goodness of the fit was estimated in terms of the coefficient of determination, $\mathbf{R^2}$.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1 Sorption characteristics of Cu (II) ions

4.1.1 FT-IR analysis

The Fourier Transform Infra-Red Analysis (FT-IR) was done in order to identify the binding sites of heavy metal adsorption available on the biosorbent. The spectra obtained were used to elucidate the mechanism of interaction between the metal cations in solution and the adsorbent. The FT-IR spectroscopy was used to obtain information about the possible adsorbent – metal interactions. The FT-IR spectra of the unloaded and the metal loaded biosorbent in the range of 250- 4000 cm^{-1} were therefore taken and results are displayed in appendix (VIII).

The FT-IR spectra of *E. crassipes* before and after adsorption displayed a number of absorption peaks indicating the complex nature of the examined adsorbent. The broad and strong peak ranging from 3000 to 3700 cm^{-1} represents the overlapping hydroxyl, silanol and amine stretching vibrations. The peak observed at 2926 cm^{-1} could be assigned to the asymmetric CH_2 aliphatic group. The strong peak at 1635 cm^{-1} was assigned to the caboxylate ($-COO^-$) group while the peaks in the region 1033 and 1095 cm^{-1} were assigned to C-O and C-N stretching vibrations respectively.

From the spectra it was clear that the intensity of heavy metal loaded *E. crassipes* was slightly lower than the spectra of *E. crassipes* before adsorption and there were some shifts in wave numbers after adsorption. For instance the wave number 3431 shifted to 3439 cm^{-1} suggesting a chemical interaction between the hydroxyl, silanol or amine group and the metal cations.

The carboxylic group also took part in the metal adsorption as the wave number shifted from 1635 to 1643 cm^{-1} after metal adsorption suggesting the involvement of caboxylate ion in metal adsorption. All the evidence from FT-IR pointed towards complexation as the mechanism of adsorption of the heavy metals onto the water hyacinth material. The metal cations bind themselves onto the negatively charged –OH, -NH, -COO-, POH and C-O-C binding sites. Similar results were reported by other studies (Sari and Tuzen, 2007; Wan Ngah *et al.*, 2008c, Sari *et al.*, 2007).

4.1.2 pH$_{ZPC}$ and pH of aqueous slurry

The zero point charge pH (pH$_{ZPC}$) is a very important parameter that determines the pH at which the adsorbent surface has net electrical neutrality. The pH$_{ZPC}$ was determined from the curve that cut the pH$_o$ (initial pH of the solutions) line of plot of ΔpH (the difference between initial and final pH) versus pH$_o$ (Wan Ngah and Hanafiah, 2008a). Figure 3 shows the plot of change in pH versus initial pH of *E. crassipes*. Actual data is shown in appendix (VII).

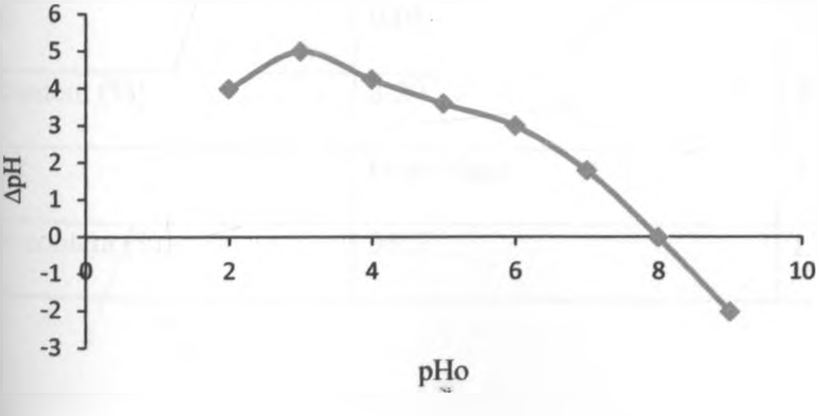

Figure 3: Plot of change in pH (ΔpH) versus the original pH (pH$_o$) for E. crassipes

The pH of aqueous slurry was found to be 7.80.Similar studies on water hyacinth from Chandola Lake, Ahmednabad, India returned a zero point charge pH value of 7.3 (Dave *et al.*, 2010) The other characteristics of *E. crassipes* were obtained and are summarised in table 4

Table 4. Characteristics of E. crassipes

Analysis	Value	Source
K^+(mg/L)	22.14	Wan Ngah *et al.*, 2009
Na^+(mg/L)	80.24	Wan Ngah *et al.*, 2009
Ca^{2+}(mg/L)	35.28	Wan Ngah *et al.*, 2009
Mg^{2+}(mg/L)	7.75	Wan Ngah *et al.*, 2009
pH_{slurry}	7.8	This thesis
pH_{ZPC}	8.00	This thesis
C (%)	44.52	Wan Ngah *et al.*, 2009
N (%)	1.2	Wan Ngah *et al.*, 2009
S (%)	0.04	Wan Ngah *et al.*, 2009
P (%)	0.05	Wan Ngah *et al.*, 2009
Ash content (%)	3.29	This thesis
Colour	Gray-black	This thesis
Water content (%)	95.5	LVBC, 2008

4.1.2 Absorption spectra of aqueous Cu^{2+} ions

In order to monitor the adsorption of Cu^{2+} ions from aqueous solution, the λ_{max} of Cu^{2+} solution was determined. Figure 4 shows the UV-Vis absorption spectra of copper (II) sulphate solution. For $CuSO_4$ solution, the absorption peak maximum (λ_{max}) appeared at 650 nm. The blue colour of Cu^{2+} solution results from the absorption of the yellow colour from white light upon which a blue colour is transmitted. The more concentrated the copper solution, the more the yellow light is absorbed and the deeper the resulting transmitted blue colour.

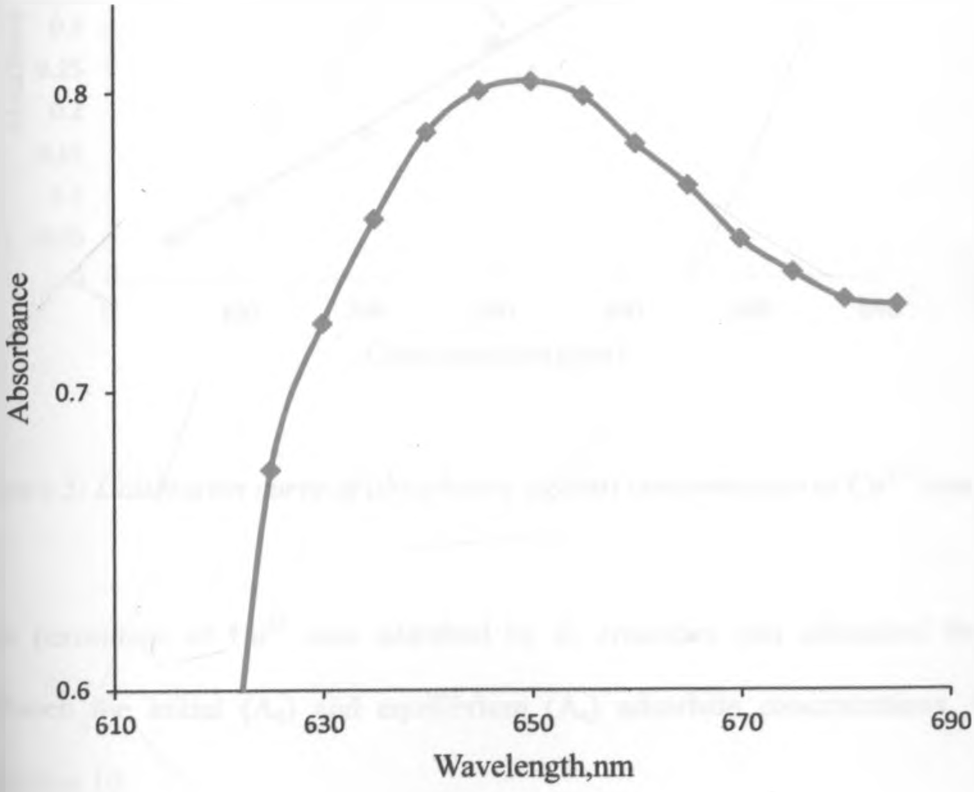

Figure 4: UV-Vis Absorption spectrum of Cu^{2+} ions solution.

4.1.3 Calibration curve

In all analytical analysis involving the use of a UV-Vis spectrophotometer, a calibration curve must be plotted in order to help in the determination of the residual concentration. The calibration curve of absorbance against copper sulphate solution concentrations was obtained using standard copper sulphate solutions of known concentrations. The experimental data were fitted with a regression line and a high correlation coefficient (0.997) was obtained (figure 5).

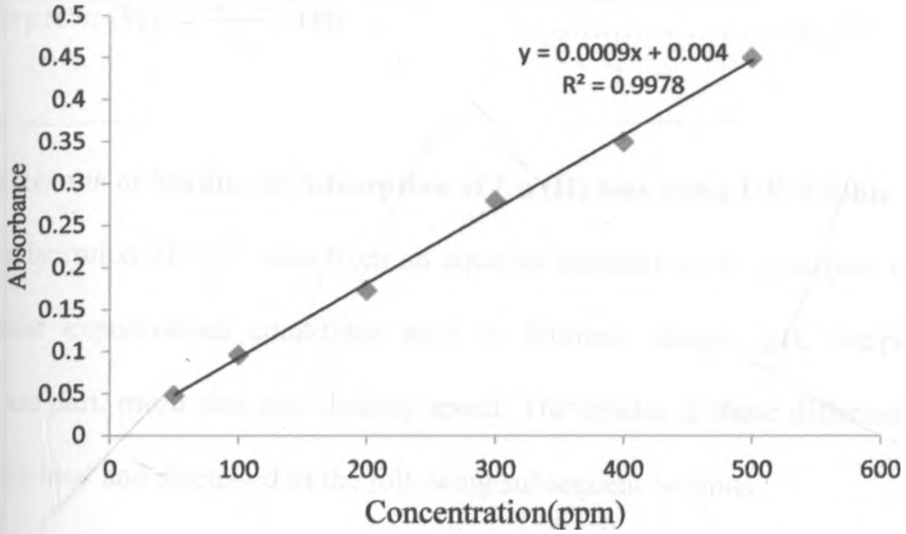

Figure 5: Calibration curve of absorbance against concentration of Cu^{2+} ions *solution.*

The percentage of Cu^{2+} ions adsorbed by *E. crassipes* was calculated from the differences between the initial (A_0) and equilibrium (A_e) adsorbate concentrations, which is given in Equation 10.

$$\text{Percentage adsorption} = \left(\frac{A_o - A_e}{A_0}\right) \times 100 \quad \text{..............................eq.10}$$

Where A_o is the initial absorbance of the solution and A_e is the final absorbance after adsorption.

The amount of heavy metal ions adsorbed was determined by using the following mass balance equation 11 below:

$$q_e = \frac{C_o - C_e}{m} V \text{ ....eq.11}$$

Where C_o and C_e are the metal concentrations (mg/L) before and after adsorption, respectively; V is the volume of adsorbate (L) and m is the weight of adsorbent (g).

The percentage adsorption of the metal ions was calculated from the following equation:

$$Adsorption\ (\%) = \frac{C_o - C_e}{C_o} \times 100 \text{ ....eq. 12}$$

4.1.4 Results of Studies of Adsorption of Cu (II) ions using UV-Visible

The adsorption of Cu^{2+} ions from an aqueous medium on *E. crassipes* was investigated under different experimental conditions such as biomass dosage, pH, temperature, contact time, biomass part, mesh size and shaking speed. The results of these different types of experiments are provided and discussed in the following subsequent sections.

4.1.4.1 Effect of plant part on adsorption of Cu^{2+} ions

Earlier studies have indicated that biosorbent dosage was an important parameter affecting biosorption capacity and removal efficiency (Yao and Ye, 2008; Acharya *et al.*, 2009; Li *et al.*, 2010). Therefore, the effect of plant part and mass of adsorbent was investigated and the results are displayed in the figure 6. From the results, it was observed that roots had the highest percentage adsorption of almost 100 (99.99% when 2.5 g of root sample was mixed with 320 mg L^{-1} of Cu^{2+} ions solution.

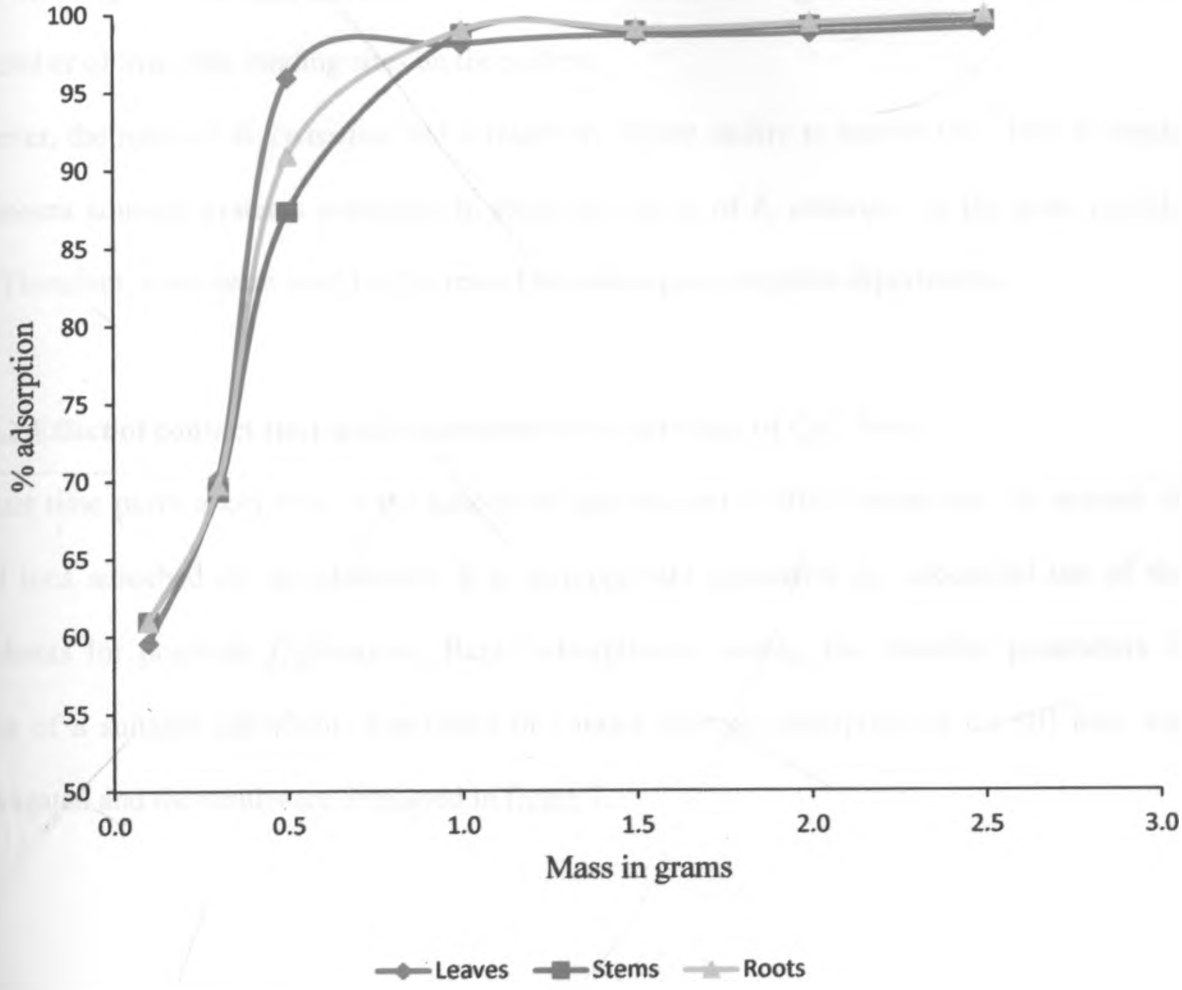

Figure 6: Effect of plant part and mass on the adsorption of 320 mg L^{-1} Cu^{2+} solution.

The roots were closely followed by the stems (99.54 %) and then the leaves (99.13 %). All the parts of the plant biomass have a high potential for the uptake of the metal ions from solution which implies that the whole plant can be utilized in the removal of heavy metal ions on a scaled up basis.

While observing the effect of dry weight of *E. crassipes* biomass on biosorption potential, it was noted that sorption potential increases with increased biomass weight. This is due to increase in the number of available binding sites on the sorbent.

However, the roots of *E. crassipes* had a relatively higher ability to adsorb Cu^{2+} ions in single component aqueous systems compared to stem and leaves of *E. crassipes* of the same particle size. Therefore, roots were used for the rest of the subsequent sorption experiments.

4.1.4.2 Effect of contact time and concentration on sorption of Cu^{2+} ions

Contact time plays a key role in the adsorption process and it often determines the amount of metal ions adsorbed on an adsorbent. It is an important parameter for successful use of the adsorbents for practical applications. Rapid adsorption is among the desirable parameters in choice of a suitable adsorbent. The effect of contact time on adsorption of Cu (II) ions was investigated and the results are displayed in figure 7.

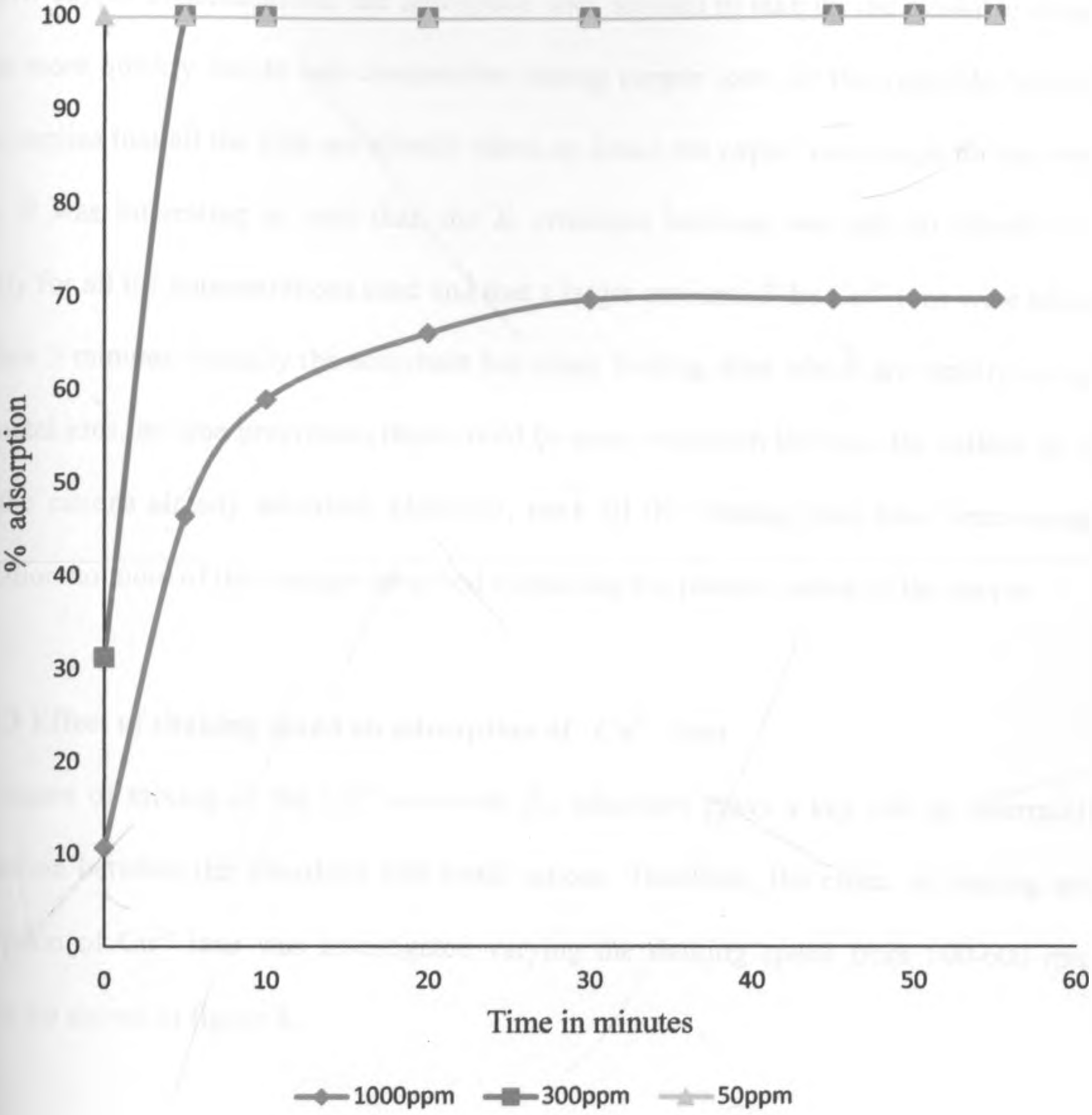

Figure 7: Effect of contact time on adsorption of 20 mL of Cu^{2+} ions onto 0.5 g of E. crassipes

The percentage of copper adsorbed was found to increase with increase in contact time. There is a rapid increase in the percentage of Cu^{2+} ions adsorbed for the first 5 min and thereafter the percentage adsorption remains relatively constant. For all the experiments conducted, about 20 minutes time was found adequate for equilibrium to be attained.

At low copper concentrations, the adsorption sites seemed to take up the available copper ions much more quickly due to less competition among copper ions for the available binding sites. That implies that all the ions are already taken up hence we expect no change for the rest of the time. It was interesting to note that, the *E. crassipes* biomass was able to adsorb Cu^{2+} ions rapidly for all the concentrations used and that a larger amount of the Cu^{2+} ions were adsorbed in the first 5 minutes. Initially the adsorbent has many binding sites which are rapidly occupied by the metal ions, as time progresses there could be some repulsion between the cations in solution and the cations already adsorbed. However, once all the binding sites have been occupied to saturation no more of the ions get adsorbed explaining the plateau nature of the curves.

4.1.4.3 Effect of shaking speed on adsorption of Cu^{2+} ions

The degree of mixing of the Cu^{2+} ions with the adsorbent plays a key role in determining the interaction between the adsorbent and metal cations. Therefore, the effect of shaking speed on adsorption of Cu^{2+} ions was investigated varying the shaking speed from 100-600 rpm. The results are shown in figure 8.

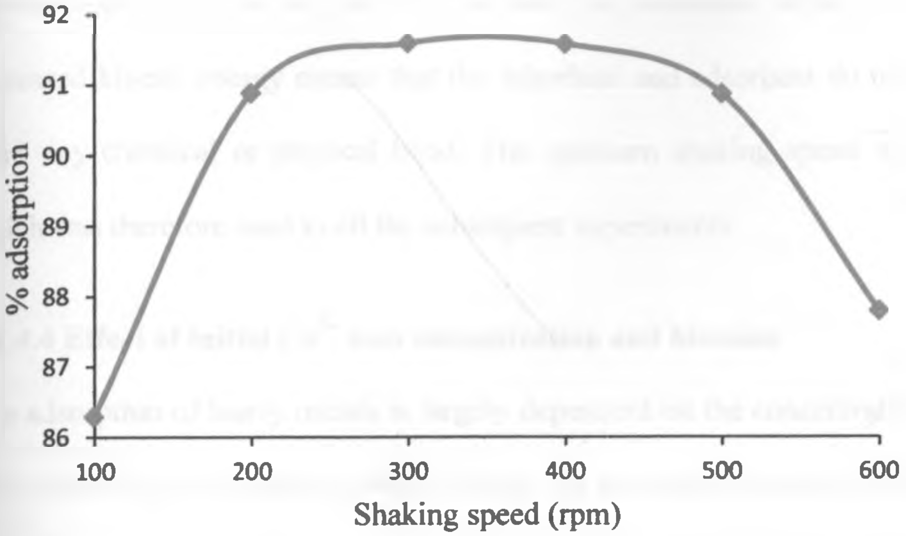

Figure 8: Effect of shaking speed on sorption of 200 mg L^{-1} Cu^{2+} on 0.2 g of E. crassipes biomass

From figure 8, it can be seen that an increase in shaking speed increases percentage adsorption from 86.3 to 91.6%. Increase in percentage adsorption is due to reduction in the boundary layer thickness around the adsorbent. However an increase in the shaking speed beyond 400 rpm leads to a reduction in the percentage adsorption.

The shaking speed determines the frequency of collisions between the adsorbent surface (*E. crassipes*) and the adsorbate (Cu^{2+} ions). The more the adsorbate touches the surface the more it is adsorbed. Increased shaking speed reduces the boundary layer thickness which ensures 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 400 rpm leads to a reduction in the percentage adsorption as the increased kinetic energy means that the adsorbate and adsorbent do not have sufficient time to form any chemical or physical bond. The optimum shaking speed was found to be 300 rpm which was therefore used in all the subsequent experiments.

4.1.4.4 Effect of initial Cu^{2+} ions concentration and biomass

The adsorption of heavy metals is largely dependent on the concentration of the adsorbate. This is because the concentration directly affects the adsorption capacity. The effect of concentration of Cu^{2+} ions on adsorption was investigated in batch and the results are displayed in figure 9.

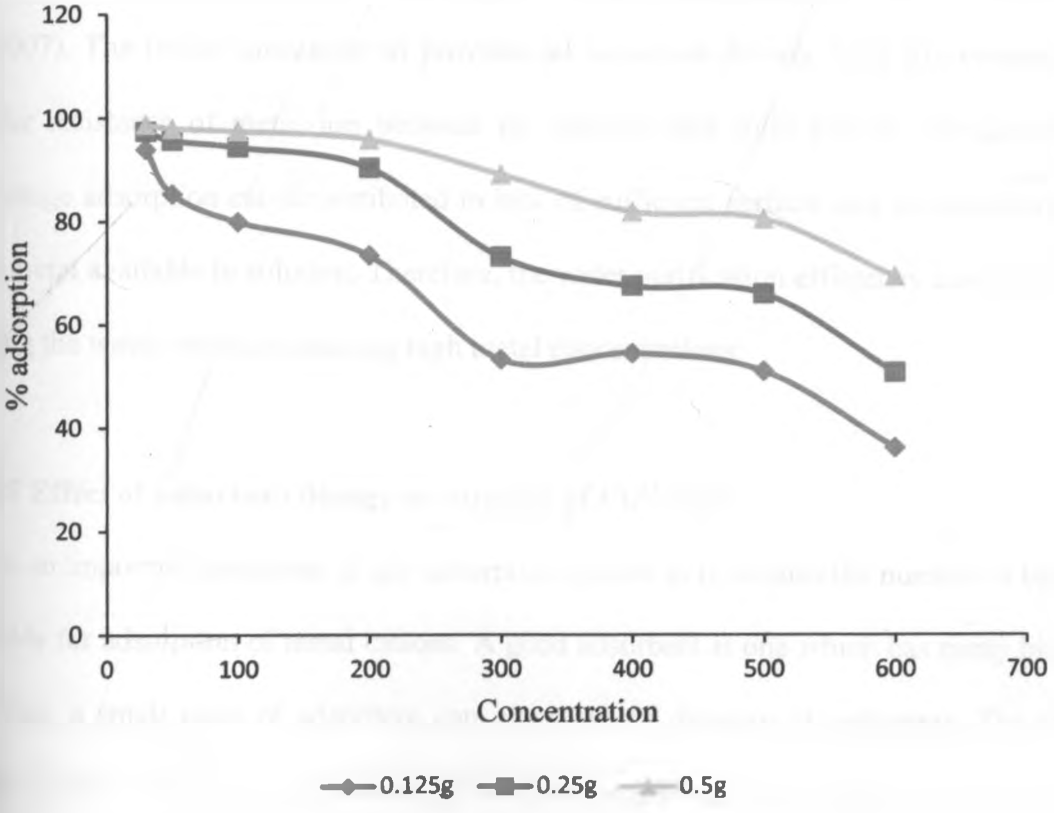

Figure 9: Effect of initial concentration of Cu^{2+} ions on the adsorption by E. crassipes.

As it can be seen from figure 9, an increase in initial concentration of Cu^{2+} ions resulted in decrease in percentage adsorption. However an increase of the biomass concentration of the biosorption system also results into increase in the percentage adsorption.

This was because at high initial concentrations, the number of moles of Cu^{2+} ions available to the adsorption sites available were high, so functional adsorption becomes dependent on the initial concentration. At lower concentrations, all the Cu^{2+} could interact with the binding sites and thus a higher percentage adsorption than higher Cu^{2+} concentrations. At higher concentrations, lower percentage adsorption is due to saturation of the adsorption sites. This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations (Hanif *et al.*, 2007). The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phases. The decrease in the percentage adsorption can be attributed to lack of sufficient surface area to accommodate much more metal available in solution. Therefore, the water purification efficiency can be improved by diluting the waste waters containing high metal concentrations.

4.1.4.5 Effect of adsorbent dosage on sorption of Cu^{2+} ions

This is an important parameter in any adsorption system as it dictates the number of binding sites available for adsorption of metal cations. A good adsorbent is one which has many binding sites such that, a small mass of adsorbent can adsorb a big quantity of pollutants. The biosorptive efficiency for Cu^{2+} ions as a function of biomass dosage was investigated. In this study several different adsorbent dosages were selected ranging from 0.125 to 2.5 g while the concentration was kept constant and the results are displayed in figure 10.

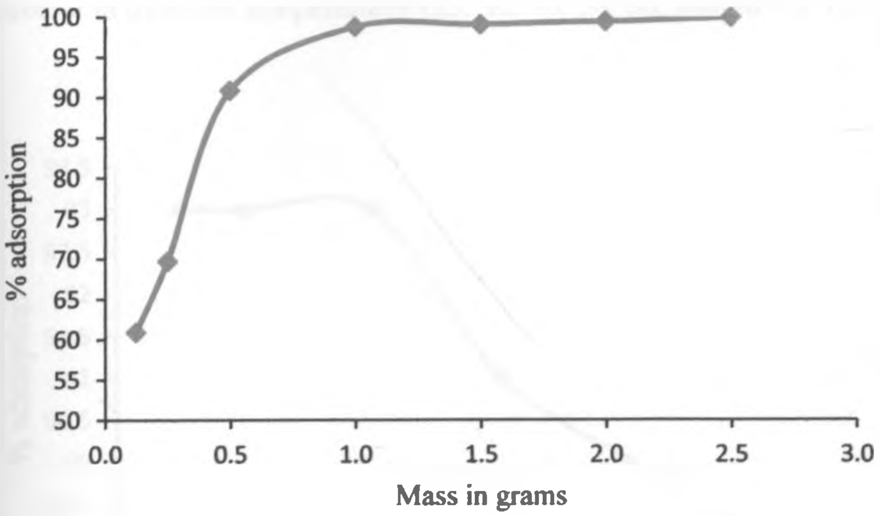

Figure 10: Effect of adsorbent dosage on adsorption of 320 mg L^{-1} Cu^{2+} ions by E. crassipes.

From the results it can be seen that the percentage of metal ions adsorbed on the *E. crassipes* biomass increased with increase in the adsorbent dosage and maximum removal recorded was 98.06 % while the lowest was 54 % after exposure for 30 minutes. The results in figure 10 clearly indicate that an increase in the mass of the biosorbent increases the number of available adsorption binding sites hence an increase in the percentage adsorption. It can be noted that a mass of a 1.0 g is adequate to adsorb all the ions present in 20 ml of 320 mg L^{-1} Cu^{2+} ions.

4.1.4.6 Effect of temperature on adsorption of Cu^{2+} ions

Temperature of a medium affects the removal efficiency of pollutants from aqueous solutions. This is partly because most pollutants have high solubility at higher temperatures. Removal of heavy metals from aqueous solutions by biosorption is often also affected by temperature. Several experiments were carried out with a mixture of the *E. crassipes* biomass incubated in an incubator at different temperatures (25, 30, 40, 50, 60, and 70°C). The results are shown in figure 11.

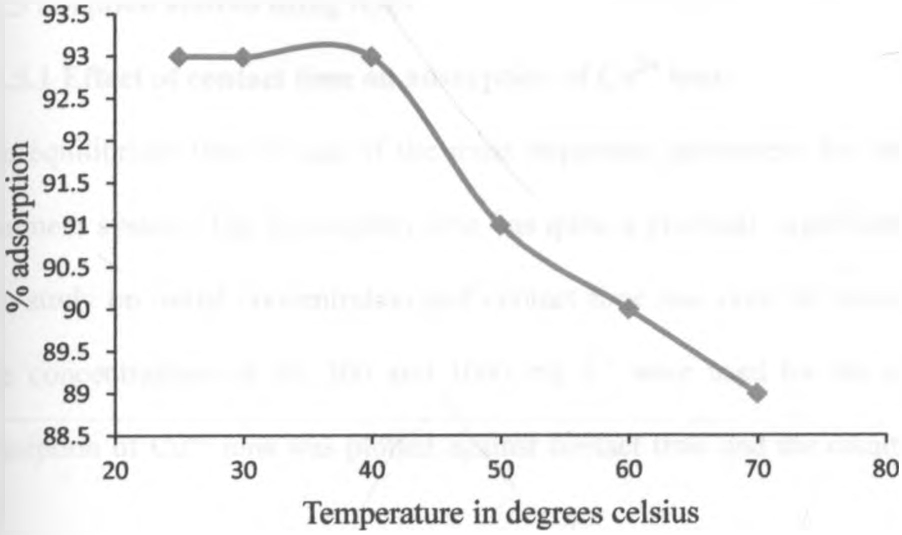

Figure 11: Effect of temperature on adsorption of Cu^{2+} ions by 0.5 g of E. crassipes.

It can be seen from the figure 11 that as the temperature increases the percentage adsorption of Cu^{2+} ions decreases from 93 % at 25 °C to 89 % at 70 °C.

This could be attributed to the following; a higher temperature destroys the binding sites on the adsorbent (Özer and Özer, 2003). An elevated temperature also increases the kinetic energy of the sorbate molecules which prevents them from binding onto the adsorbent thus increasing the tendency to desorb metal ions from the interface to the solution (Sari and Tuzen, 2007). This result indicated the exothermic nature of Cu^{2+} biosorption onto *E. crassipes.* From the results it can be concluded that increase in temperature is unfavorable for adsorption of aqueous copper ions hence the reaction is better done at room temperature of about 25°C. This is an advantage because the process does not involve use of extra energy in the form of heating and cooling hence economical.

4.1.5 Sorption studies using AAS

4.1.5.1 Effect of contact time on adsorption of Cu^{2+} ions

The equilibrium time is one of the most important parameters for an economical wastewater treatment system. The biosorption time has quite a practical significance (Zhang *et al.*, 2010). The study on initial concentration and contact time was done at room temperature, (25± 2°C). The concentrations of 50, 300 and 1000 mg L^{-1} were used for the study and the percentage adsorption of Cu^{2+} ions was plotted against contact time and the results are displayed in figure 12.

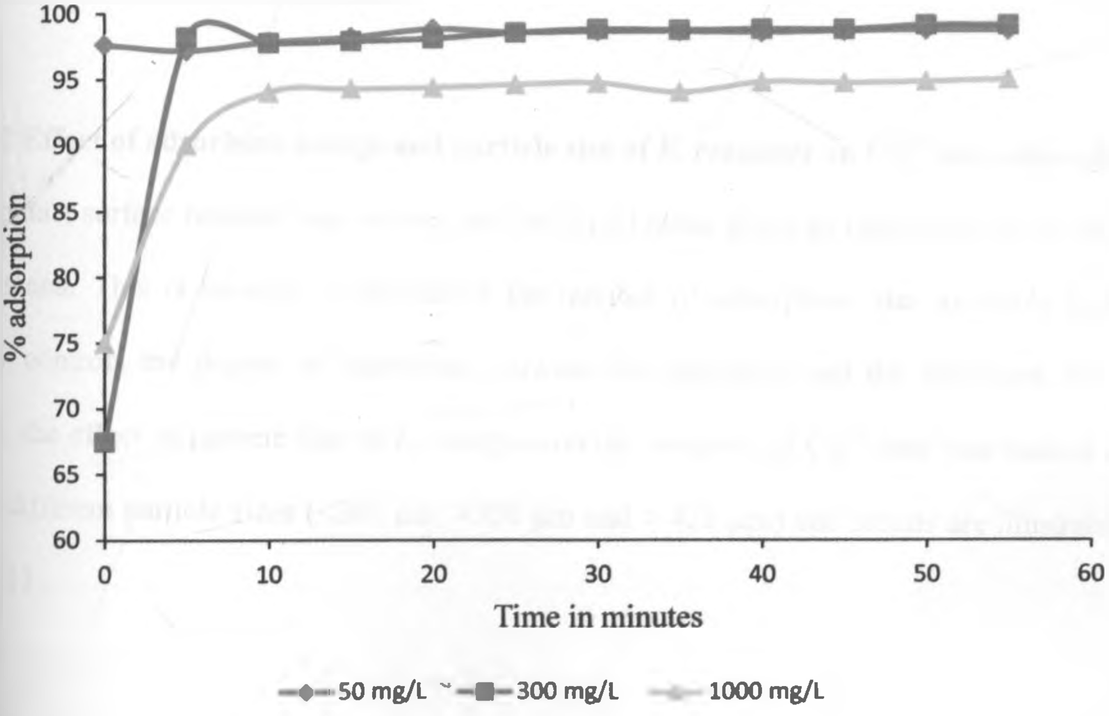

Figure 12: Effect of contact time on sorption of Cu^{2+} ions by 0.5 g of E. crassipes.

It can be observed from figure 12 that the percentage adsorption was decreases with increase in concentration with the lowest percentage adsorption at 20 minutes being 94.44% for a concentration of 1000 mg L^{-1} and the highest adsorption being 98.88 % for a concentration of 50 mg L^{-1}.

The adsorption process was found to be rapid with a higher percentage of adsorption noted immediately the metal ions come in contact with the adsorbent. However, the percentage adsorption slowed down and later remained constant after about 20 minutes of contact time. This can be attributed to the fact that all the binding sites have been occupied by the metal ions hence the plateau nature of all the three graphs in the figure above. The binding sites become saturated and cannot take any more of the metal ions or all the metal ions have been removed and there are no more ions to be adsorbed.

4.1.5.2 Effect of adsorbent dosage and particle size of *E. crassipes* on Cu^{2+} ions adsorption

The contact surface between any sorbent and the liquid phase plays an important role in sorption phenomena. This is because it determines the number of adsorption sites available hence it ideally controls the degree of interaction between the adsorbent and the adsorbate. For this reason, the effect of particle size of *E.crasippes* on the removal of Cu^{2+} ions was studied using three different particle sizes (<300 µm, >300 µm and > 425 µm) and results are illustrated in figure 13 .

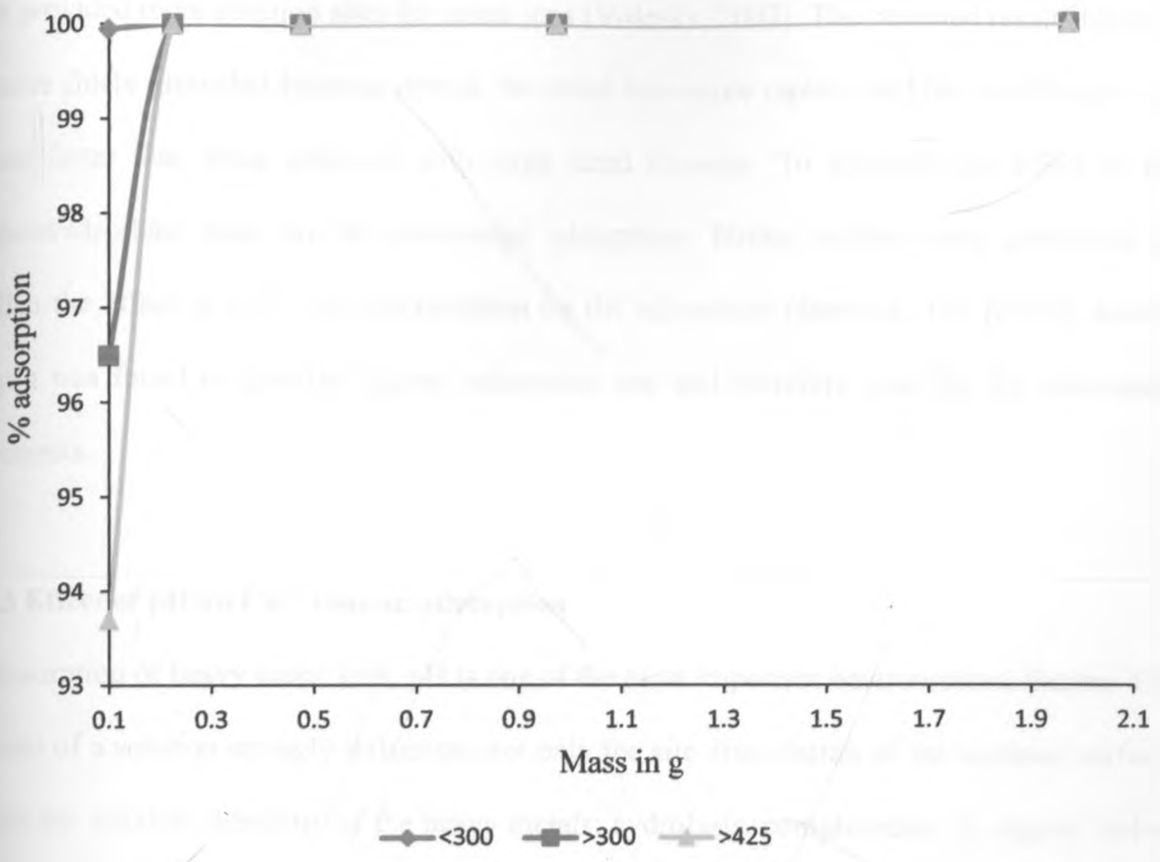

Figure 13: Effect of particle size and weight on adsorption of 10 mg L^{-1} Cu^{2+} ions

The results reveal that the copper uptake on *E.crassipes* decreases from 100 to 93.7% with increased particle size from <300 μm to >425 μm at an initial concentration of 10 mg L^{-1}. Decrease in particle size of the adsorbent increases the surface area, which in turn increases the adsorption capacity. Increased mass of the adsorbent also has an effect of increasing the adsorption sites.

This increase in percentage adsorption is due to increase in the number of binding sites which are able to sequester the metal ions available in the solution. The maximum adsorption was recorded with the smallest particle size. This was most probably due to increase in the total surface area, which provided more sorption sites for metal ions (Volesky, 2003). The obtained results indicate that more finely grounded biomass uptook the metal ions more rapidly and the equilibrium was attained faster than those achieved with large sized biomass. To ascertain the effect of the adsorbent/adsorbate ratio on the percentage adsorption, further studies were conducted to establish the effect of Cu^{2+} ion concentration on the adsorption observed. The particle size of <300μm was found to give the highest adsorption rate and therefore used for the subsequent experiments.

4.1.5.3 Effect of pH on Cu^{2+} ions on adsorption

For biosorption of heavy metal ions, pH is one of the most important environmental factors. 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 biosorption availability of the heavy metals (Esposito *et al.*, 2002; Wang, 2009., Li, 2010; Yao *et al.*, 2010).

Therefore the effect of pH on adsorption of Cu^{2+} ions was investigated using 50 mg L^{-1} of solution and a mass of 0.5 g of *E. crassipes* and the results are shown in figure 14, higher pH values were not considered due to precipitation.

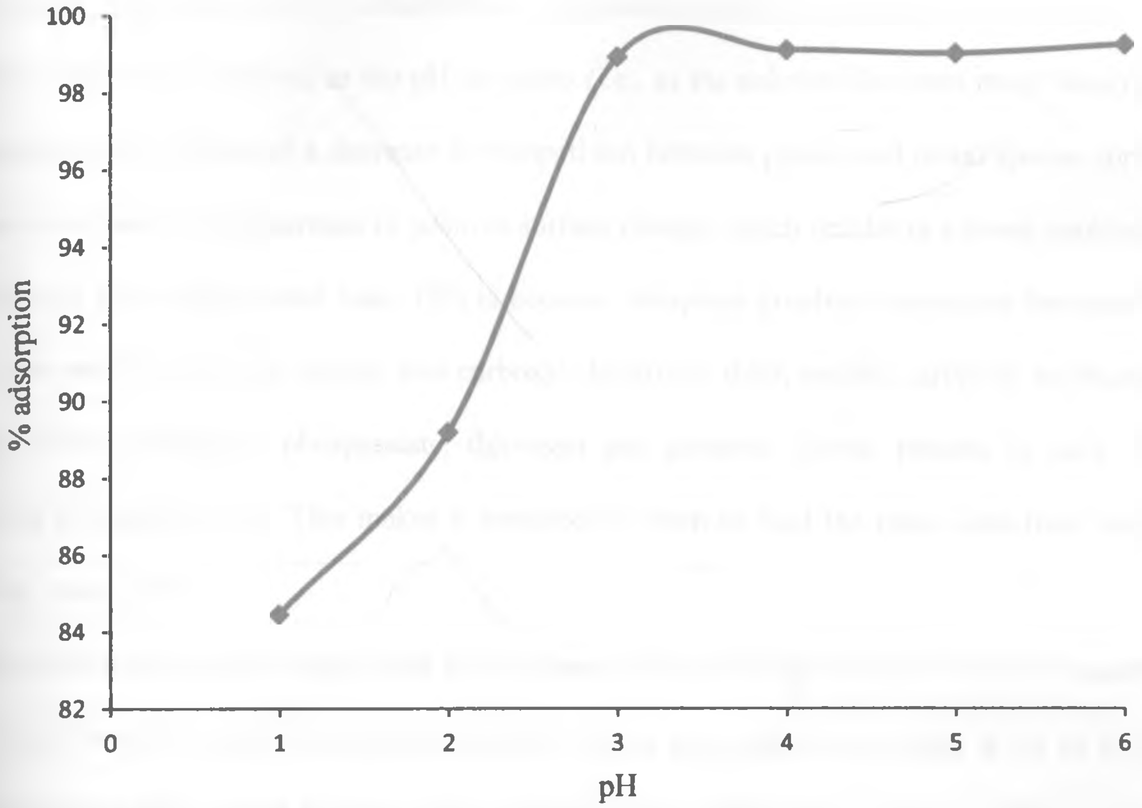

Figure 14: Effect of pH on the percentage adsorption Cu^{2+} ions by E. crassipes biomass.

It was observed that a sharp increase in the copper removal from 84.5 to 100% occurred when the pH values of the solutions changed from 2.0 to 5.0 and after 5.0 a plateau is obtained. The pH plays an important role in the adsorption process by affecting the surface charge of adsorbent, the degree of ionization and speciation of the adsorbate. 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^{2+} ions for the very charged adsorption sites of the *E. crassipes.* The surface bears a net positive charge which would impede the approach of the positively charged Cu^{2+} ions.

With the pH increasing, the H^+ concentration decreases leading to increased Cu^{2+} uptake. 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 coulombic repulsion of the sorbing metal ions. This is because adsoption involves interaction between the adsorbate and the funtional groups like carboxyl, hydroxyl, thiol, amido, carbonyl, sulphonate, amine, imine, imidazole, phosphonate, thio-ester and phospho diester present in such bio materials (Volesky, 2007). This makes it possible for them to bind the metal ions from waters (Farooq *et al.*, 2010).

On the other hand, experiements with pH > 6 were done, however, precipitation was observed and that is why the results presented in figure 6 show experiments only upto a pH of 6. For different biosorption system of metal ions, the optimal pH is different. There is a strong relation between the biosorption and the number of negative charges at the biomass surface which is itself related to the functional groups. In addition, the HCl was used to adjust the solution pH value. The Cl^- added may result in a decrease of the free Cu^{2+} species and an increase in the formation of the complex $CuCl^+$. This chloro complex has larger molecular size than the free Cu^{2+} and is adverse to the biosorption, leading to a decrease in copper uptake (Yao *et al.*, 2010).

4.1.5.4 Effect of temperature on Cu^{2+} ions adsorption

Given that temperature of the medium affects the efficiency of adsorption of aqueous solutions experiments were designed to investigate its influence on removal of heavy metals from solutions. Figure 15 shows the effect of temperature on adsorption of Cu^{2+} ions by *E. crassipes.*

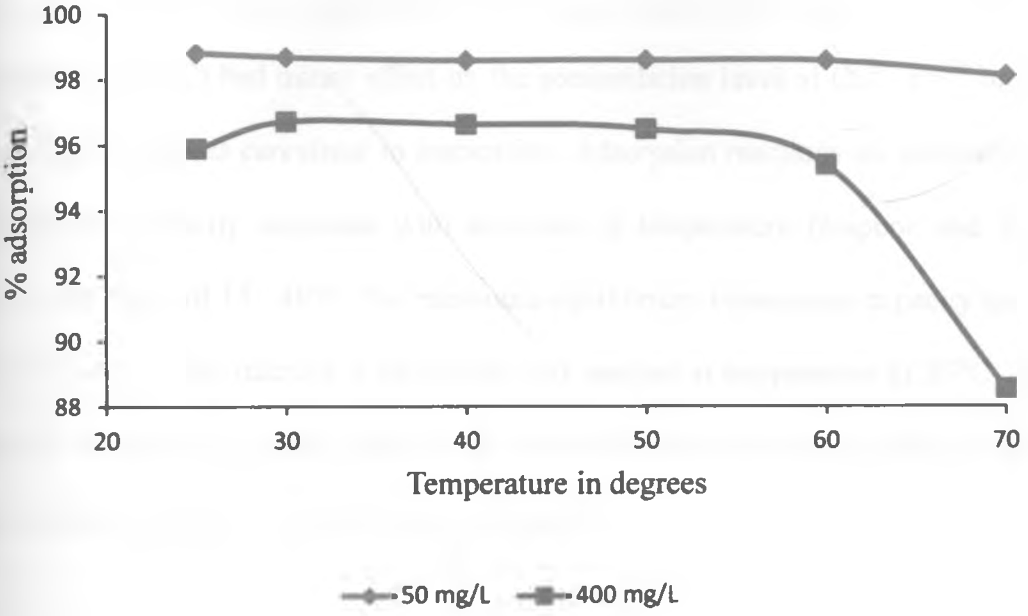

Figure 15: Effect of temperature on adsorption of Cu^{2+} ions by 0.5 g E. crassipes

It can be observed that the percentage adsorption is independent of temperature at the lower concentration of 50 mg L^{-1}. The percentage adsorption at 25 °C is 98.82 % while at a higher temperature of 60°C it is 98.6%. However at 70°C, the percentage adsorption drops slightly to 88.6%. This indicates that adsorption process is exothermic therefore favored by low temperatures. However for a higher concentration of 400 mg L^{-1} the increase in temperature has no effect between 30 to 50 °C, when the temperature goes to 70 °C there is a big drop in the percentage adsorption. This implies that reactions conducted at a higher concentration are more affected by temperature increase than those reactions done at a lower concentration.

Temperature has also an influence on the biosorption of metal ions, but to a limited extent under a certain range of temperature, which indicates that ion exchange mechanism exists in biosorption to some extent. Biosorption process is usually not operated at high temperature because it will increase the operational cost (Wang *et al.*, 2009). Brady *et al.* (1994) found that temperature (5–40°C) had minor effect on the accumulation level of Cu^{2+}, Co^{2+} or Cd^{2+} by free cells of *Saccharomyces cerevisiae* in suspension. Adsorption reactions are normally exothermic, so biosorption capacity increases with decrease of temperature (Kapoor and Viraraghavan, 1997). In the range of 15– 40°C, the maximum equilibrium biosorption capacity for Pb^{2+}, Ni(II) and Cr(VI) ions by the inactive *S. cerevisiae* was reached at temperature of 25°C. The decrease in capacity at higher temperature between 25 and 40°C revealed that the processes of biosorption for these metal ions by *S. cerevisiae* are exothermic.

The decrease of biosorption capacity at higher temperature may be due to the damage or inactivation of active binding sites in the biomass (Özer and Özer, 2003). However, metal biosorption by *S. cerevisiae* increases with increasing temperature in the range of 25–45°C, (Goyal *et al.*, 2003), higher temperature would lead to higher affinity of sites for metal or binding sites on the yeast. The energy of the system facilitates metal attachment on the cell surface to some extent. When the temperature is too high, there is a decrease in metal sorption due to distortion of some sites of the cell surface available for metal biosorption.This is due to the proteinous nature of the binding sites which then are denatured or deactivated by increased temperature.

In our study the results followed the previous reported facts that temperature increase beyond 50°C leads to a reduction in the degree of adsorption. The kinetic energy of the sorbate particles prevents most of them from binding onto the adsorbent sites. This could lead to desorption or cause the metal ions to bounce off the surface of the biosorbent instead of colliding and combining with it. Therefore, increase in temperature may be associated with decrease in the stability of metal ion-adsorbent complex and this will imply that adsorption process is exothermic. Generally, according to adsorption theory, adsorption decreases with increase in temperature and molecules adsorbed earlier on a surface tend to get desorbed from the surface at elevated temperatures (Aksu and Kutsal, 1991; Sari *et al.*, 2007).

4.1.5.5 Effect of initial concentration of Cu^{2+} ions on adsorption

Initial concentration is one of the key parameters that must be considered when setting up a sorption system. Adsorption experiments of Cu^{2+} ions with concentration from 50 to 600 mg L^{-1} with a fixed adsorbent doses for *E. crassipes* were therefore performed. The percentage Cu^{2+} ions removal range from 36.0 to 98.0% for mass of 0.125 g. Results are shown in figure 16.

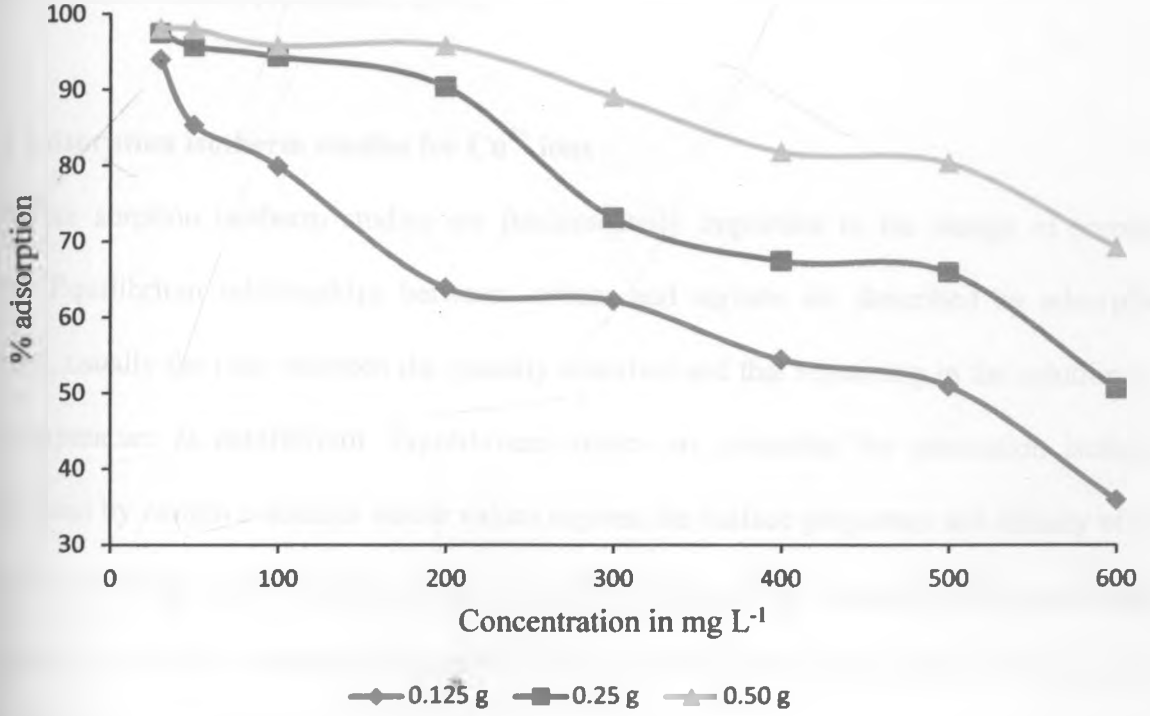

Figure 16: Effect of concentration on adsorption of Cu2+ ions by E. crassipes

As shown in Figure 16, the percentage of Cu^{2+} ions adsorbed decreased with increased in Cu^{2+} ions concentration. This can be attributed to the fact that the biosorbents have a limited number of active sites. Although lower percentage adsorption was observed, the equilibrium adsorption capacity of the biomass displayed an increasing trend with increased Cu^{2+} ions concentration. The initial concentration provides an important driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases, hence a higher initial concentration of metal ion may increase the adsorption capacity (Lalhruaitluanga *et al.*, 2010). However at lower concentrations, there are plenty of binding sites available on the biosorbent for the attachment of the metal ions. However, at higher initial concentrations there is competition for the binding sites. Similar results were reported in the literature using other biosorbents and sorbates (Semerjian, 2010).

4.1.5.6 Adsorption isotherm studies for Cu^{2+} ions

Equilibrium sorption isotherm studies are fundamentally important in the design of sorption systems. Equilibrium relationships between sorbent and sorbate 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, two important sorption isotherm models were selected to fit experimental data, which are namely; Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) and the results are displayed in figures 17 – 19.

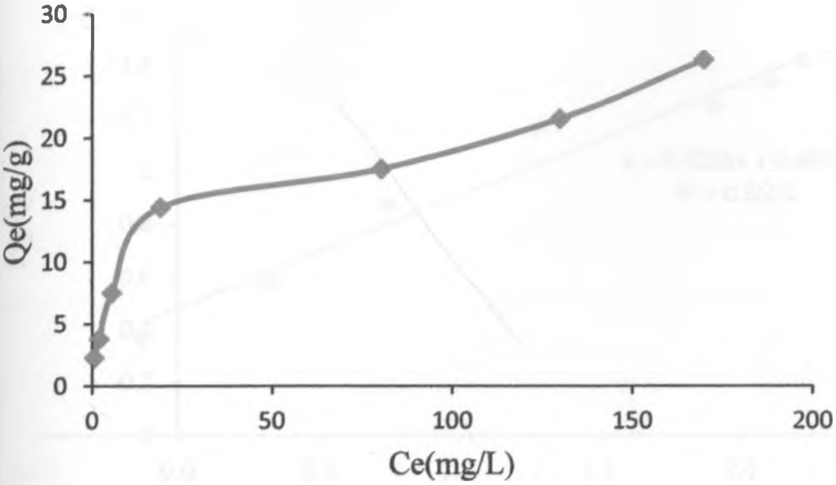

Figure 17: Langmuir non-linearized isotherm for Cu^{2+} ions adsorption on E. crassipes.

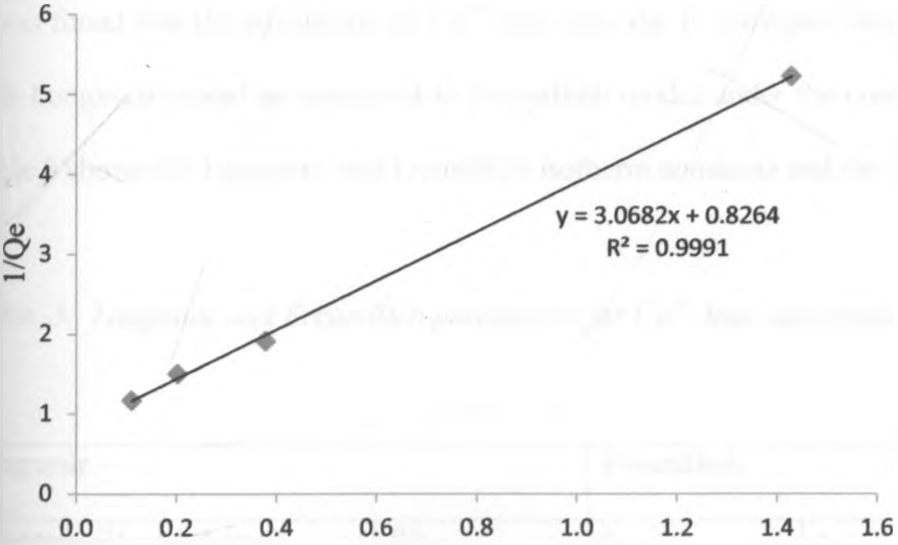

Figure 18: Langmuir linearized plot for Cu^{2+} ions adsorption onto E. crassipes.

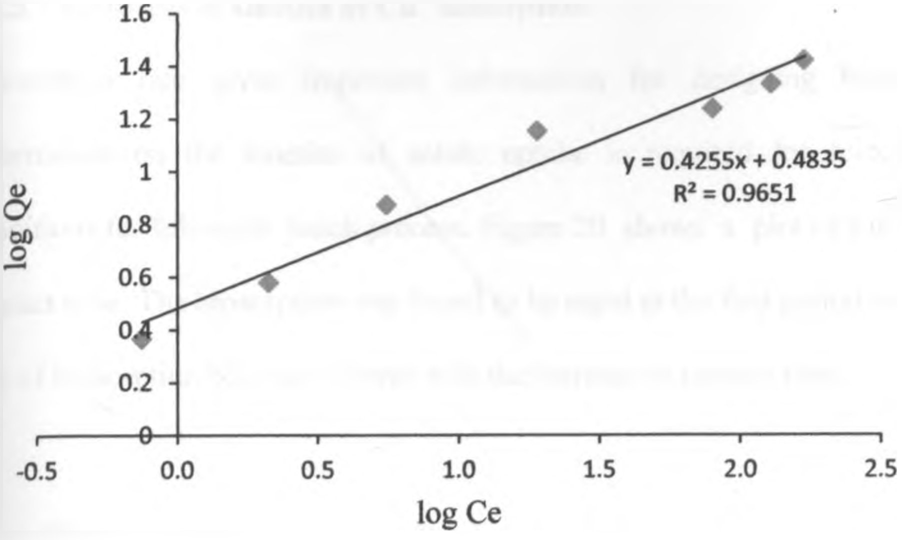

Figure 19: Freundlich plot for adsorption of Cu^{2+} onto E. crassipes

It was found that the adsorption of Cu^{2+} ions onto the *E. crassipes* biomass was correlated well with Langmuir model as compared to Freundlich model under the concentration range studied. Table 5 shows the Langmuir and Freundlich isotherm constants and the correlation coefficients.

Table 5. Langmuir and Freundlich parameters for Cu^{2+} ions adsorption.

Langmuir			Freundlich		
Q_{max}(mg g^{-1})	*b*(L/mg)	R^2	k_F	n	R^2
3.0682	0.8264	0.9991	3.044	2.3529	0.965

However, the value of n is between 0 and 1 which indicates favourable adsorption under the experimental conditions of the study.

4.1.5.7 Biosorption kinetics of Cu^{2+} adsorption

Biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Figure 20 shows a plot of Cu^{2+} ions biosorption versus contact time. The biosorption was found to be rapid at the first period of the process and then the rate of biosorption becomes slower with the increase in contact time.

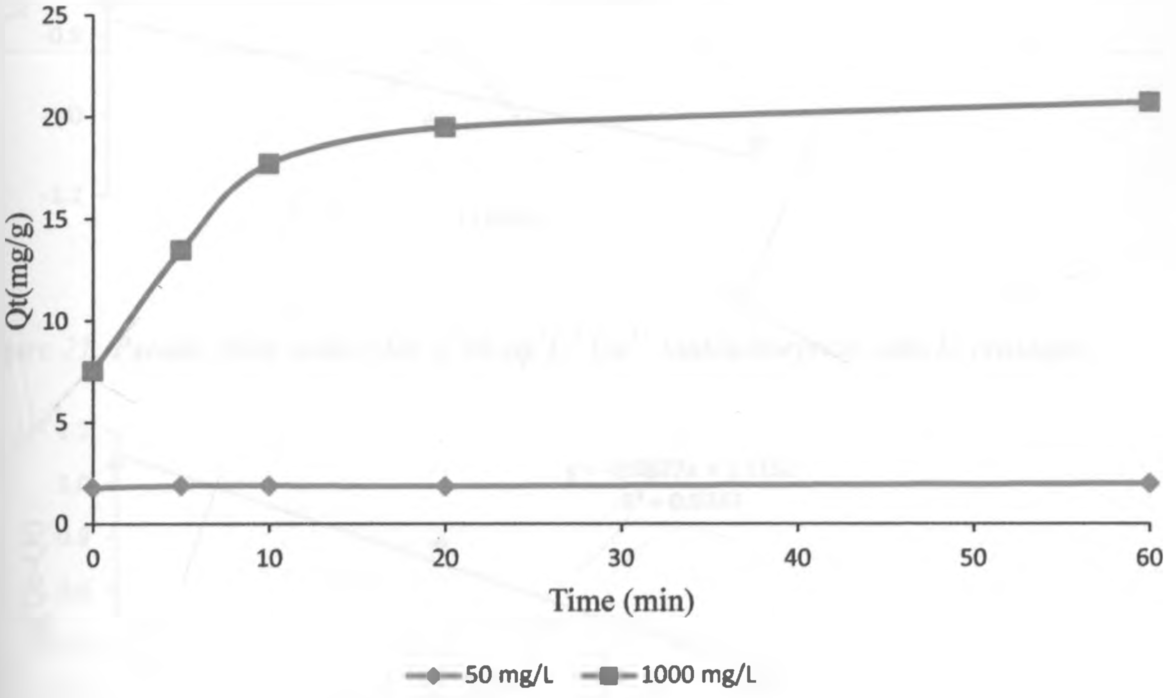

Figure 20: Effect of contact time on uptake of Cu^{2+} ions by E. crassipes.

The amount of copper adsorbed was found to increase with increase in copper concentration and time as shown in Figure 20. On changing the concentration of copper from 50 mg L^{-1} to 1000 mg L^{-1}, the amount adsorbed increased from 2.00 to 20.76 mg g^{-1}. This clearly demonstrates that *E.*

crassipes has plenty of adsorption sites that can sequester 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 modelling are displayed below in figure 21 to 23.

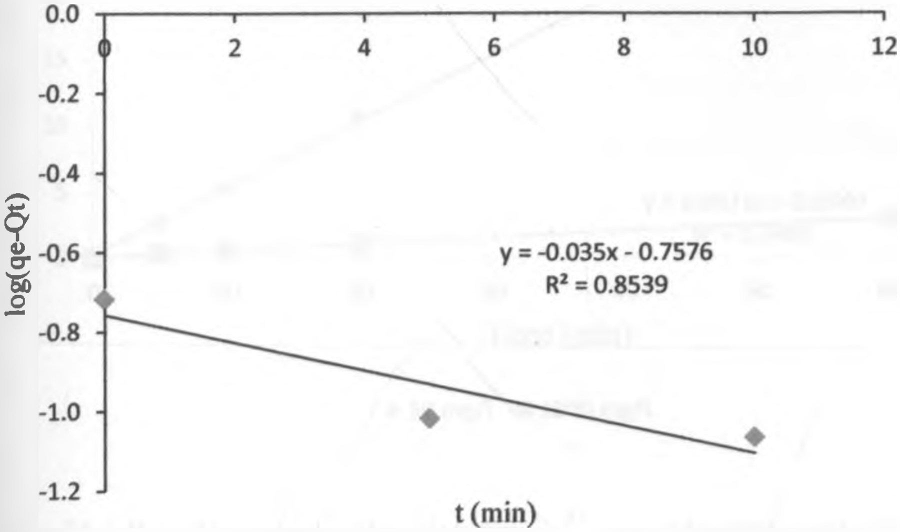

Figure 21: Pseudo -first-order plot of 50 mg L^{-1} Cu^{2+} ions adsorption onto E. crassipes.

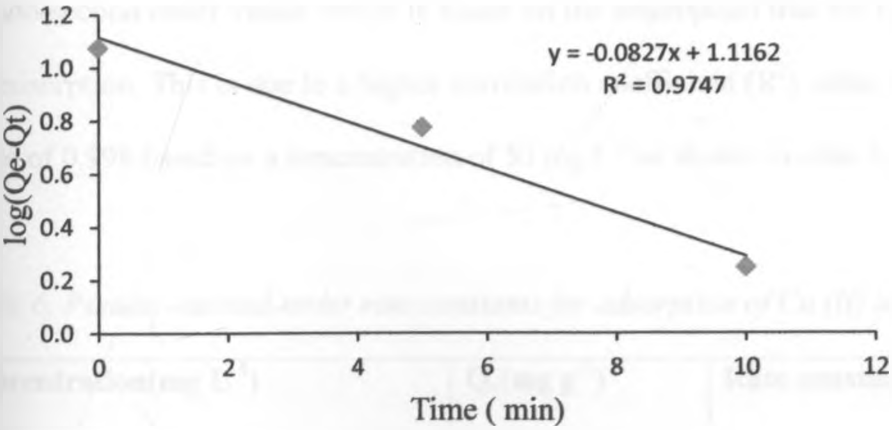

Figure 22:Pseudo-first -order plot for adsorption of 1000 mg L^{-1} Cu^{2+} ions onto E. crassipes.

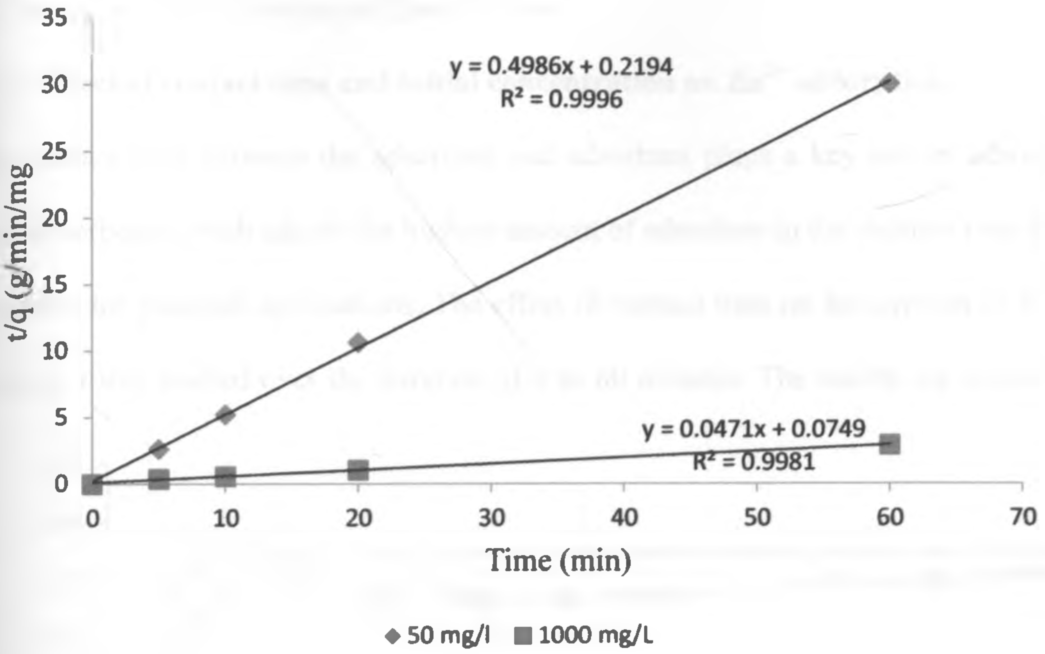

Figure 23. Pseudo-second-order plots for Cu^{2+} ions adsorption onto E. crassipes.

The results obtained suggested that the biosorption of copper onto *E. crassipes* biomass 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 0.9996 compared to a value of 0.998 based on a concentration of 50 mg L^{-1} as shown in table 6.

Table 6. Pseudo –second-order rate constants for adsorption of Cu (II) ions onto E. crassipes.

Concentration(mg L^{-1})	**Q_e(mg g^{-1})**	**Rate constant (g $mg^{-1}min^{-1}$)**	**R^2**
50	0.4986	0.2194	0.9996
1000	0.0471	0.0749	0.9981

4.2 Sorption characteristics of Zinc (II) ions

4.2.1 Effect of contact time and initial concentration on Zn^{2+} adsorption

The contact time between the adsorbate and adsorbent plays a key role in adsorption systems with adsorbents which adsorb the highest amount of adsorbate in the shortest time being the most desirable for practical applications. The effect of contact time on biosorption of Zn^{2+} ions on *E. crasippes* was studied over the duration of 0 to 60 minutes. The results are shown in figure 24.

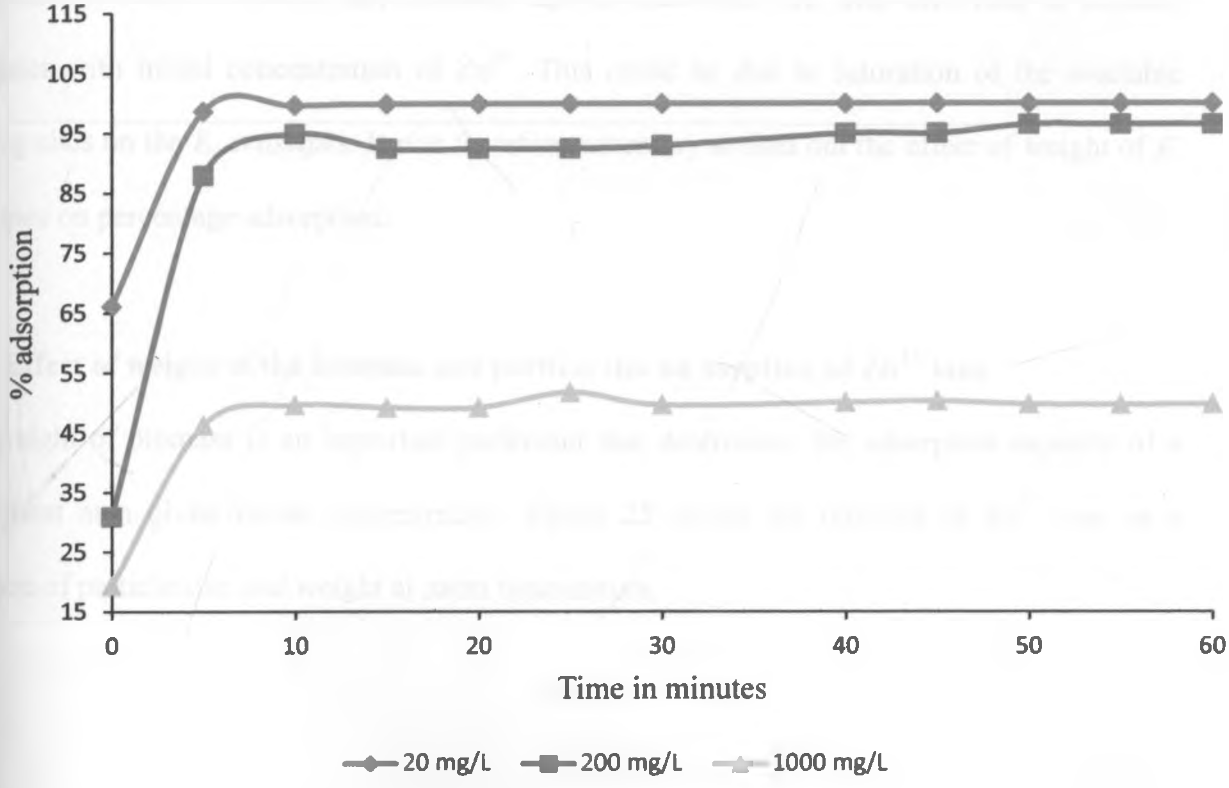

Figure 24: Effect of concentration and contact time on adsorption of Zn^{2+} ions by 0.5 g of E. crassipes

The percentage sorption of metal ions as a function of time indicate triphasic pattern with a rapid initial uptake in the first 5 minutes, which gradually reaches equilibrium after 20 minutes for all the concentrations investigated. The metal uptake increases to saturation, suggesting that the adsorption follows Langmuir model with monolayer coverage of the metal ions on surface of the adsorbent to be ascertained by Langmuir studies in sections ahead.

From the plots it can also be observed that for a low initial concentration of Zn^{2+}, percentage adsorption is higher at 66% immediately upon contact between the *E. crassipes* and the metal ion solutions and that 100% adsorption is achieved at 60 minutes equilibration time.

However, for higher initial concentration, the percentage adsorption recorded at near instantaneous contact between the adsorbate and the adsorbent (i.e. near zero time of contact) decreases with initial concentration of Zn^{2+}. This could be due to saturation of the available binding sites on the *E. crassipes.* It was therefore necessary to find out the effect of weight of *E. crassipes* on percentage adsorption.

4.2.2 Effect of weight of the biomass and particle size on sorption of Zn^{2+} ions

The weight of biomass is an important parameter that determines the adsorption capacity of a biosorbent at a given initial concentration. Figure 25 shows the removal of Zn^{2+} ions as a function of particle size and weight at room temperature.

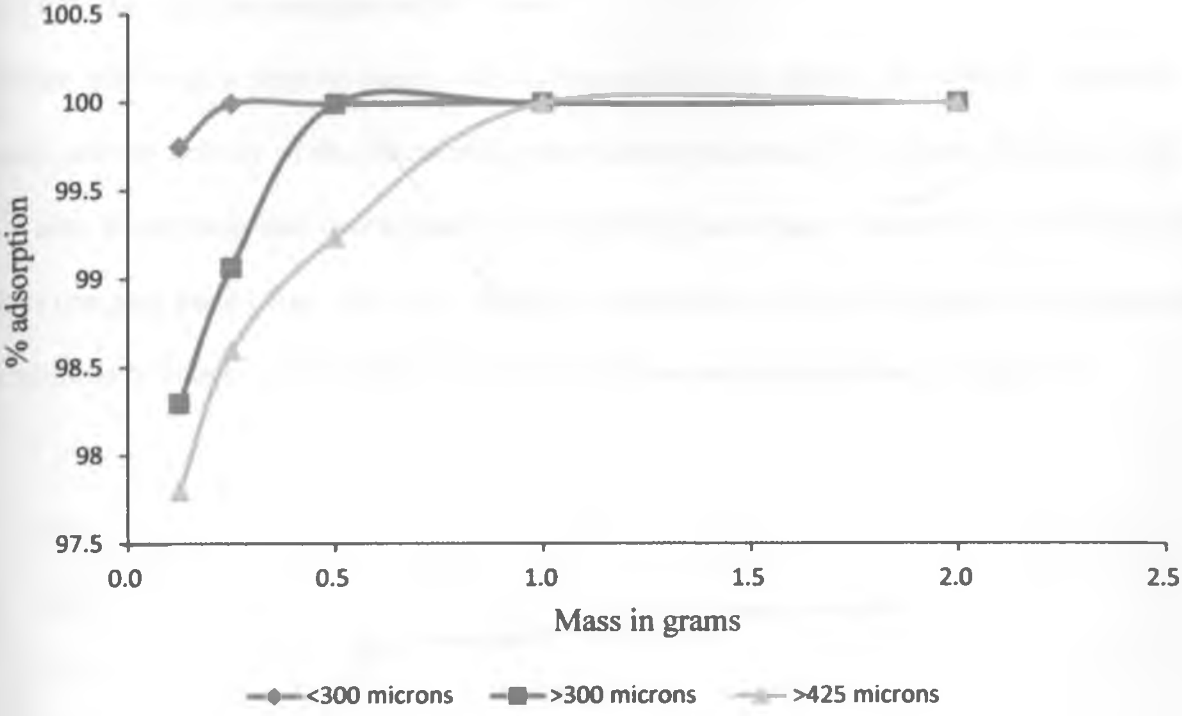

Figure 25 : Effect of weight and particle size on Zn $^{2+}$ (II) ions adsorption by E.Crassipes

It can be seen that there was 99.8% adsorption when 0.125g of *E. crasippes* was used to adsorb 10 mg L^{-1}. Decreasing the average particle size of the adsorbent increases the surface area, which in turn increases the percentage adsorption. The increase in adsorbent dosage also increases the percentage adsorption until the system plateaus beyond the 1.0 g of weight.

It can be noted that the sorption potential increases with increase in biomass dosage (0.125-2.0g). No significant increment in sorption tendency is observed on further raising the mass beyond 1.0g. Increase in mass of adsorbent increases the number of available binding sites for the metal ions in solution. Beyond the 1.0 g mark all the metal ions have been used up and therefore no more adsorbate available for adsorption.

4.2.3 Effects of pH on sorption of Zn^{2+} ions

Solution pH usually plays a major role in biosorption as it affects the solution chemistry of metals and the activity of the functional groups on the biomass. The impact of solution pH on Zn^{2+} ions biosorption was investigated by determining percentage adsorption at different pH values (ranging from 1.0 to 7.0) from a 20 mL metal solution. 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 26.

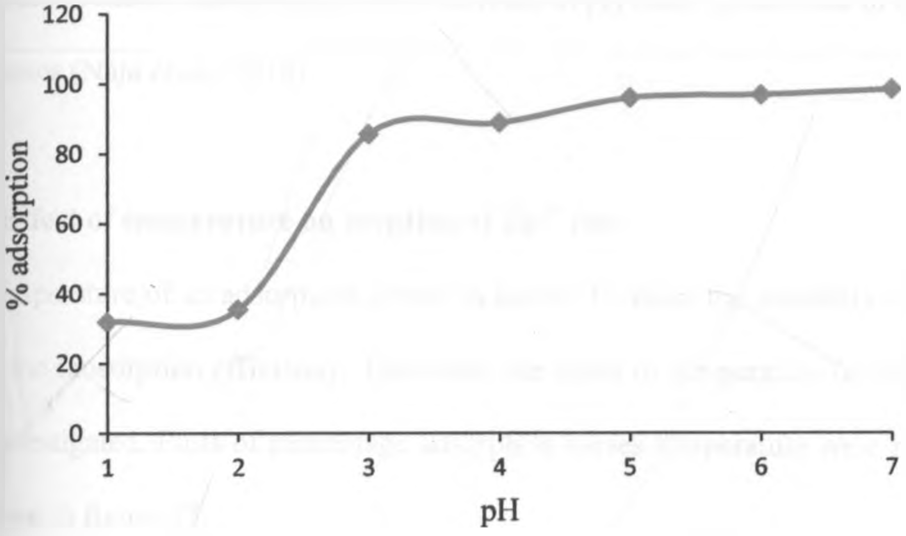

Figure 26: Effect of pH on percentage adsorption of Zn^{2+} ions by 0.5 g of E. crassipes

The percentage adsorption of Zn^{2+} ions increased from 32% at a pH of 2 to 92% at a pH of 7. At a pH values below 3.0, the adsorption of zinc was inhibited, possibly as a result of competition between H^+ ions and Zn^{2+} ions on the sorption sites, with an apparent preference for H^+ ions which restricts the approach of the metal cations as a consequence of repulsive forces between the metal cations and the protons both of which are positively charged.

As pH is increased the ligands such as hydroxyl and caboxylate groups in *E. crassipes* would be exposed; increasing the negative charge density on the biomass surface, thereby increasing the attraction of metallic ions with positive charge and allowing the biosorption on to the biosorbent surface. Maximum adsorption took place at pH 6.0. Similar results have been reported in the literature (Fan *et al.*, 2008).

However at pH above 7, insoluble zinc hydroxide starts precipitating from solution, so that Zn^{2+} ion removal by adsorption is decreased. The removal of zinc ions beyond this pH is by hydroxide precipitation rather than by adsorption. Increase in pH leads to decrease in the solubility of metal complexes (Naja *et al.*, 2010)

4.2.4 Effect of temperature on sorption of Zn^{2+} ions

The temperature of an adsorption system is known to affect the solubility of ions in solution and hence the biosorption efficiency. Therefore, the effect of temperature on adsorption of Zn^{2+} ions was investigated. Plots of percentage adsorption verses temperature were made for *E. crassipes* as shown in figure 27.

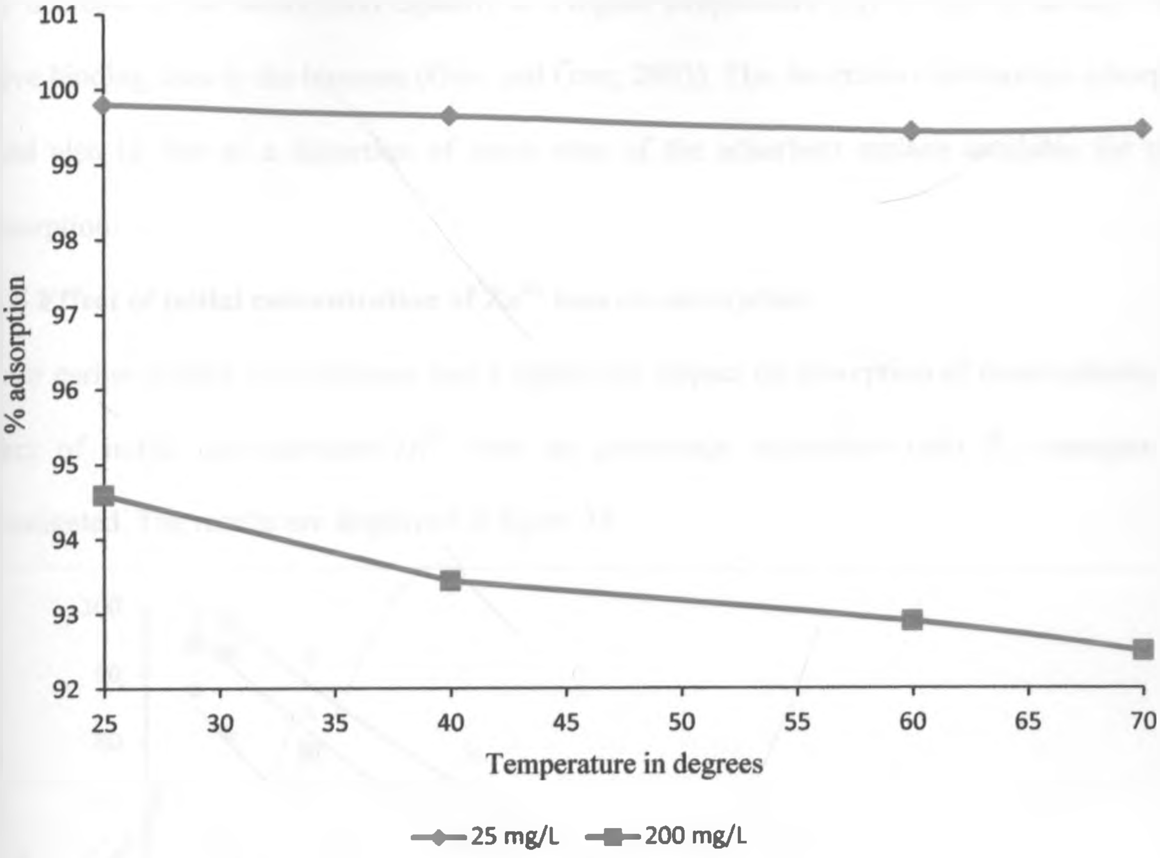

Figure 27: Effect of temperature on percentage adsorption of Zn^{2+} ions by 0.5 g of E. crassipes.

The difference in the data corresponding to both low (25mg L^{-1}) and high initial concentration of Zn^{2+} ions on the effect of temperature is almost negligible since over 99% adsorption was obtained at room temperature. Similar findings were reported for other types of biosorbent (Ucun *et al.*, 2009).

With higher initial concentration of Zn^{2+} ions, there is a slight reduction in the percentage adsorption from 94.6% at 25°C to 92.5% at 70°C. This confirms earlier reported results that indicated that adsorption reactions are exothermic, so biosorption capacity increases with decrease in temperature (Kapoor and Viraraghavan, 1997).

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

4.2.5 Effect of initial concentration of Zn^{2+} ions on adsorption

In our earlier studies concentration had a significant impact on adsorption of metal cations. The effect of initial concentration Zn^{2+} ions on percentage adsorption onto *E. crassipes* was investigated. The results are displayed in figure 28.

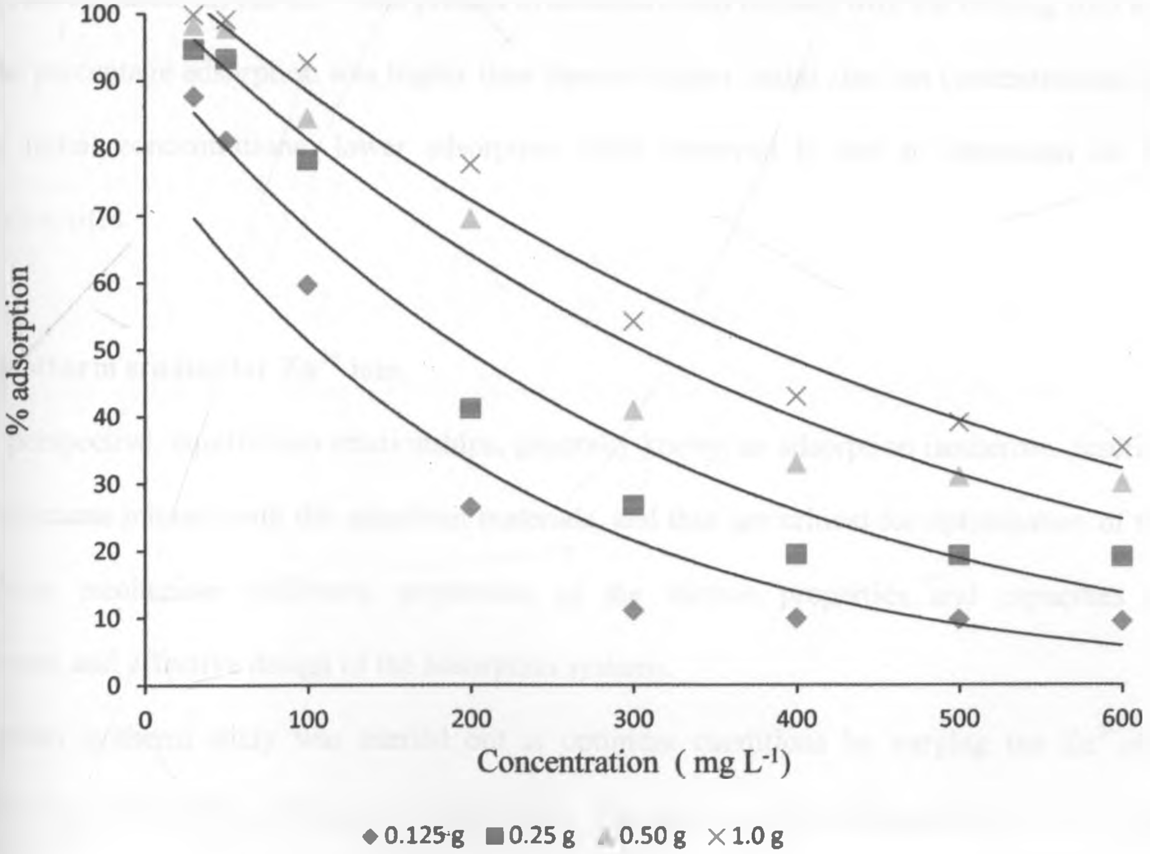

Figure 28: Effect of initial concentration of Zn^{2+} ions on adsorption by E. crassipes.

The plots show that the metal uptake increases with weight of biomass and percentage adsorption of Zn^{2+} ions decreases with increase in metal ions concentration.

The plots generally depict a decrease in percentage adsorption as the concentration is increased. The decrease in percentage adsorption may be attributed to lack of adsorption sites to accommodate much more metal available in solution. This was confirmed by increases the mass of the adsorbent which had an effect of increasing the percentage adsorption at a fixed initial concentration.

The percentage adsorption of higher initial concentration levels shows a decreasing trend. At a lower concentration, all the Zn^{2+} ions present in solution could interact with the binding sites and thus the percentage adsorption was higher than those at higher initial zinc ion concentrations. At higher initial concentrations, lower adsorption yield observed is due to saturation of the adsorption sites.

4.2.6 Isotherm studies for Zn^{2+} ions

in the perspective, equilibrium relationships, generally known as adsorption isotherms, describe how pollutants interact with the adsorbent materials, and thus are critical for optimization of the adsorption mechanism pathways, expression of the surface properties and capacities of adsorbents, and effective design of the adsorption systems.

Adsorption isotherm study was carried out at optimum conditions by varying the Zn^{2+}ions concentration from 20 to 100 mg L^{-1}. This study was done at room temperature (25°C). The results of the experiment are displayed in the figures 29 and 30.

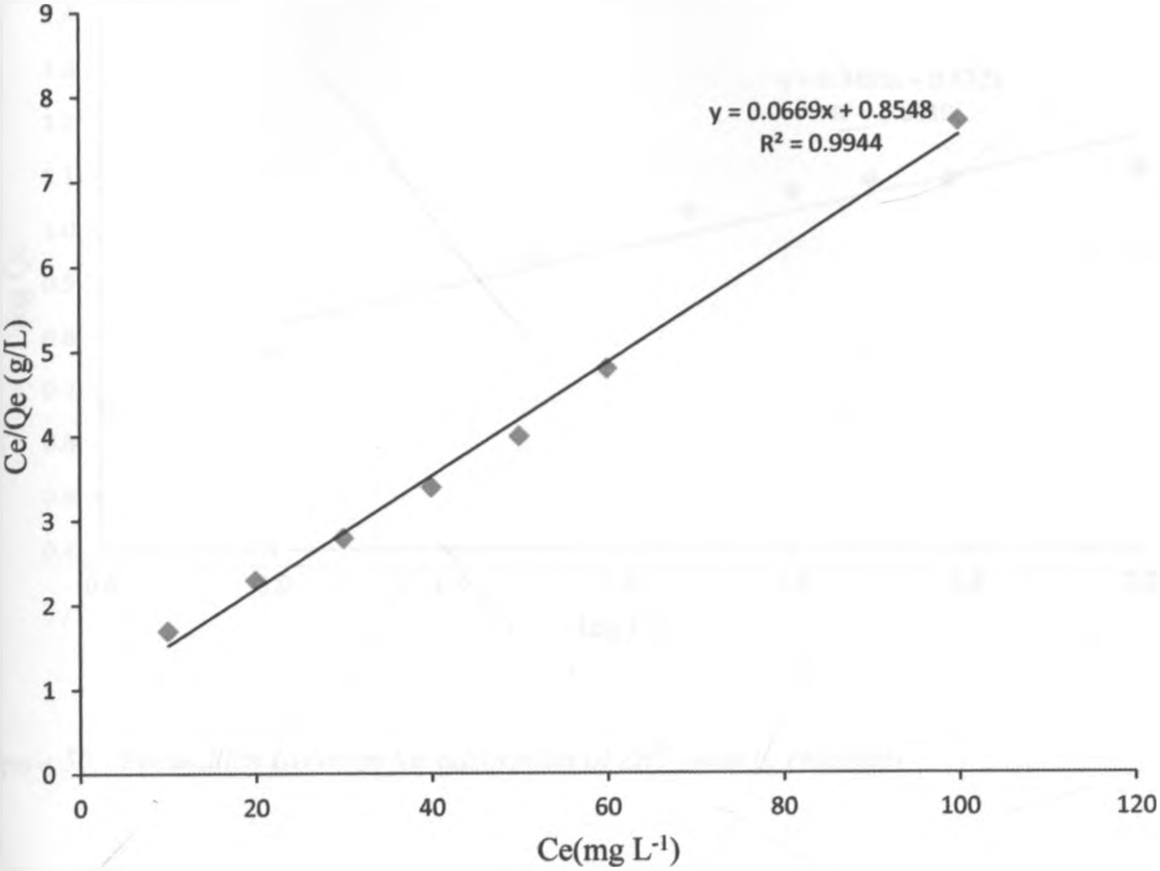

Figure 29: Linearized Langmuir isotherm for adsorption of Zn^{2+} *ions by E. crassipes.*

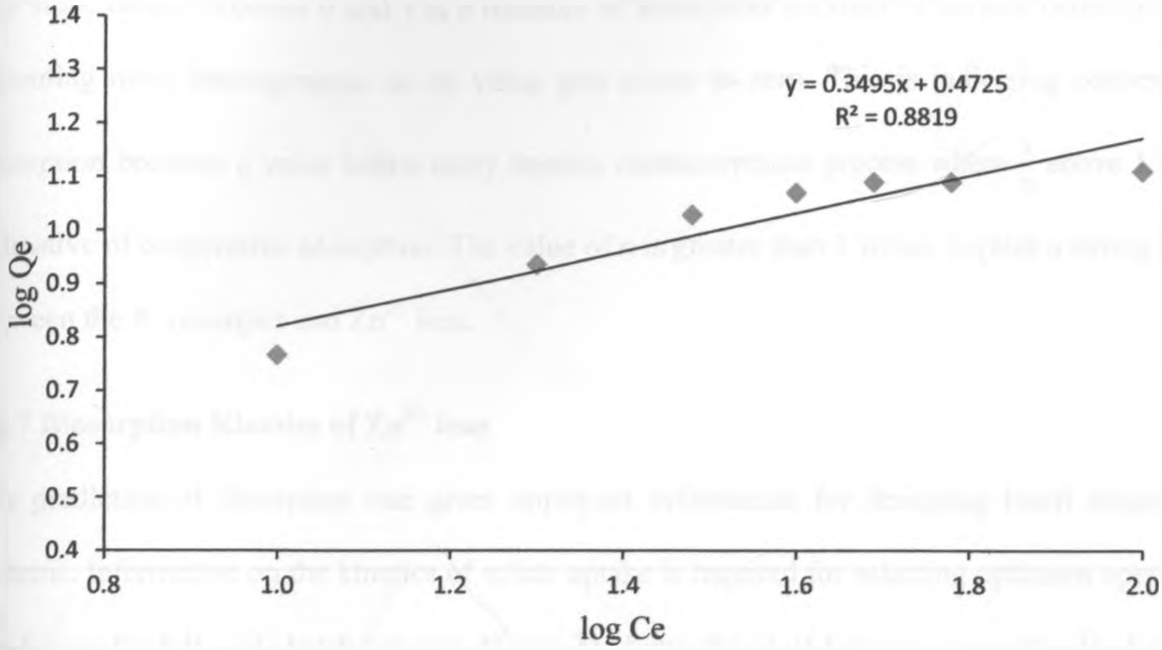

Figure 30: Freundlich isotherm for adsorption of Zn^{2+} *onto E. crassipes*

It is found that the adsorption of zinc on the *E. crassipes* correlated well with the Langmuir model as opposed to Freundlich model as exhibited in the correlation coefficients of the 2 models in figure 29 and 30. This implies that adsorption of zinc ions onto *E. crassipes* takes has a monolayer adsorption with the adsorption sites getting saturated .

The Langmuir and Freundlich Constants and correlation coefficients are given in table 7.

Table 7. Langmuir and Freundlich constants for Zn^{2+} *ions adsorption*

Langmuir			Freundlich		
Q_{max}(mg/g)	*b*(L/mg)	R^2	k_F	n	R^2
12.8205	0.1806	0.9994	1.7573	2.8653	0.8881

The slope ranges between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. This is indicating cooperative adsorption because, a value below unity implies chemisorptions process where $\frac{1}{n}$ above 1 is an indicative of cooperative adsorption. The value of n is greater than 1 which implies a strong bond between the *E. crassipes* and Zn^{2+} ions.

4.2.7 Biosorption Kinetics of Zn^{2+} ions

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of solute uptake is required for selecting optimum operating conditions for full-scale batch process. Figure 31 shows the plots between amounts adsorbed, *qe* (mg g^{-1}) versus time, *t* (min) for the given initial concentrations.

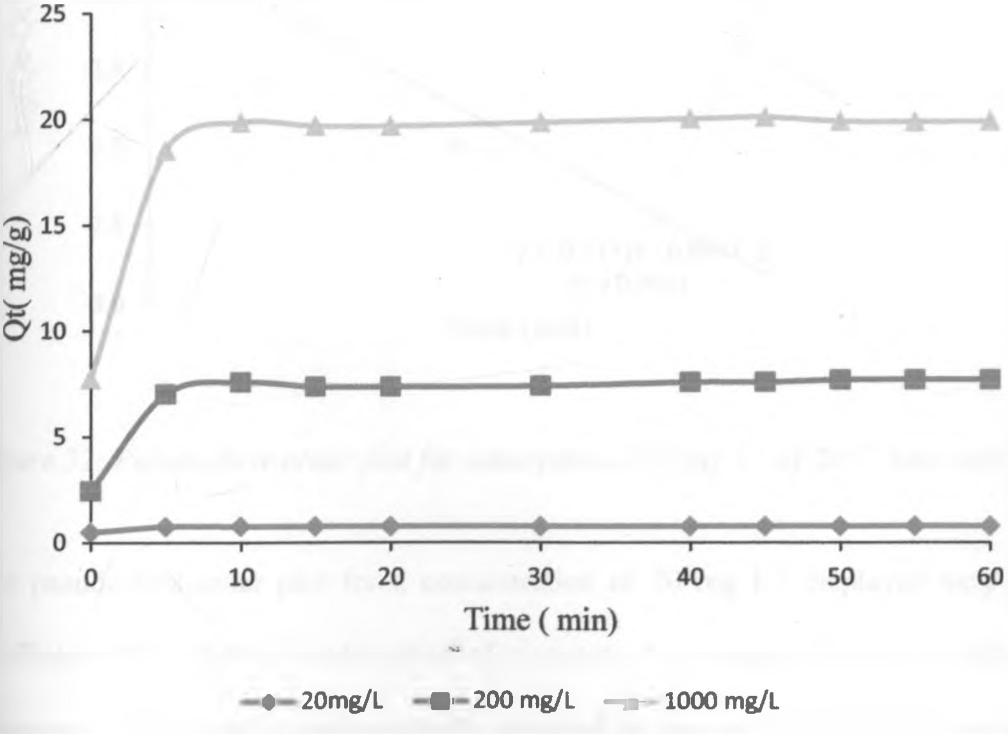

Figure 31: Effect of contact time on Zn^{2+} ions uptake by E. crassipes biomass.

The adsorption rate within the first 5 min was observed to be very high and thereafter the reaction proceeds at a slower rate till equilibrium and finally a steady state was obtained after equilibrium. The saturation time was found to be 10 min based on the initial metal concentration. The kinetics of the adsorption data was analyzed using two kinetic models, pseudo-first-order and pseudo-second-order kinetic model. These models correlate solute uptake, which are important in predicting the reactor volume. The results are presented in figure 32 and 33.

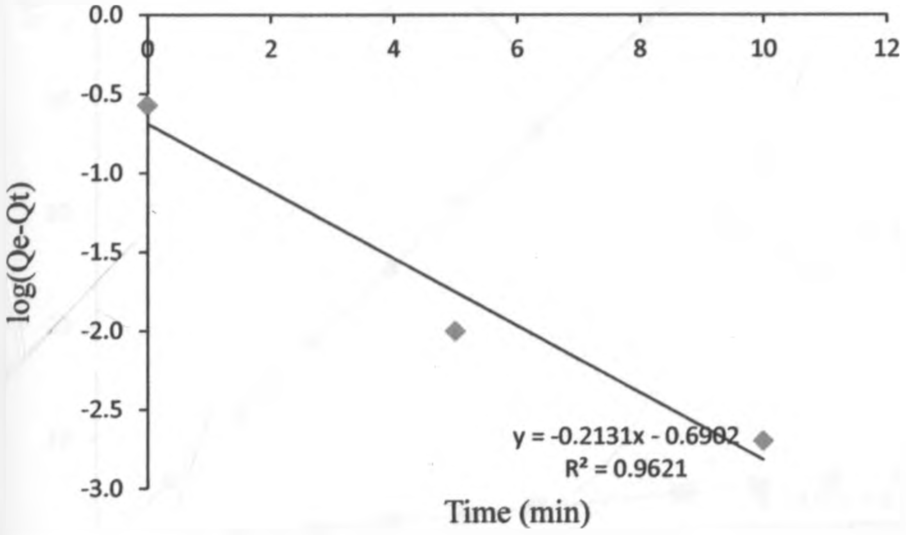

Figure 32: Pseudo-first-order plot for adsorption of 20 mg L^{-1} of Zn^{2+} ions onto E. crassipes

The pseudo-first-order plot for a concentration of 20 mg L^{-1} displayed very high correlation coefficient ($R^2 = 0.96$) on adsorption of zinc onto *E. crassipes* biomass as shown in figure 32. However, the reaction is predominantly assumed to proceed via pseudo-second-order evidenced by higher correlation coefficient (R^2) of between 0.999) for a similar concentration as shown in figure 33.

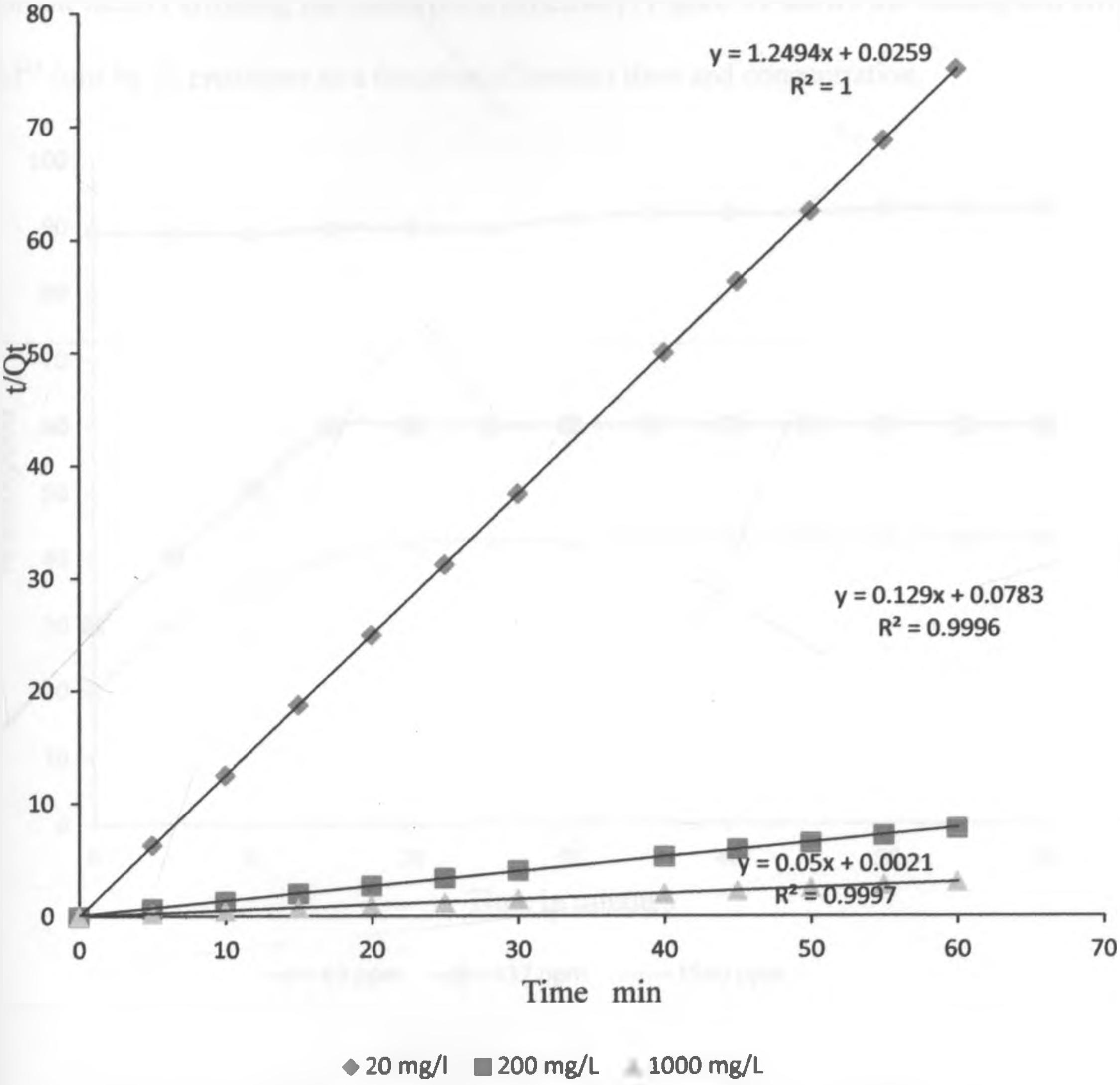

Figure 33: Pseudo-second- order plots for Zn^{2+} ions adsorption by E. crassipes.

4.3. Sorption characteristics of Cd^{2+} ions

4.3.1 Effect of contact time and initial concentration on sorption of Cd^{2+} ions

The contact time between the adsorbent and the Cd^{2+} ions was evaluated as one of the most important factors affecting the biosorption efficiency. Figure 34 shows the biosorption efficiency of Cd^{2+} ions by *E. crassipes* as a function of contact time and concentration.

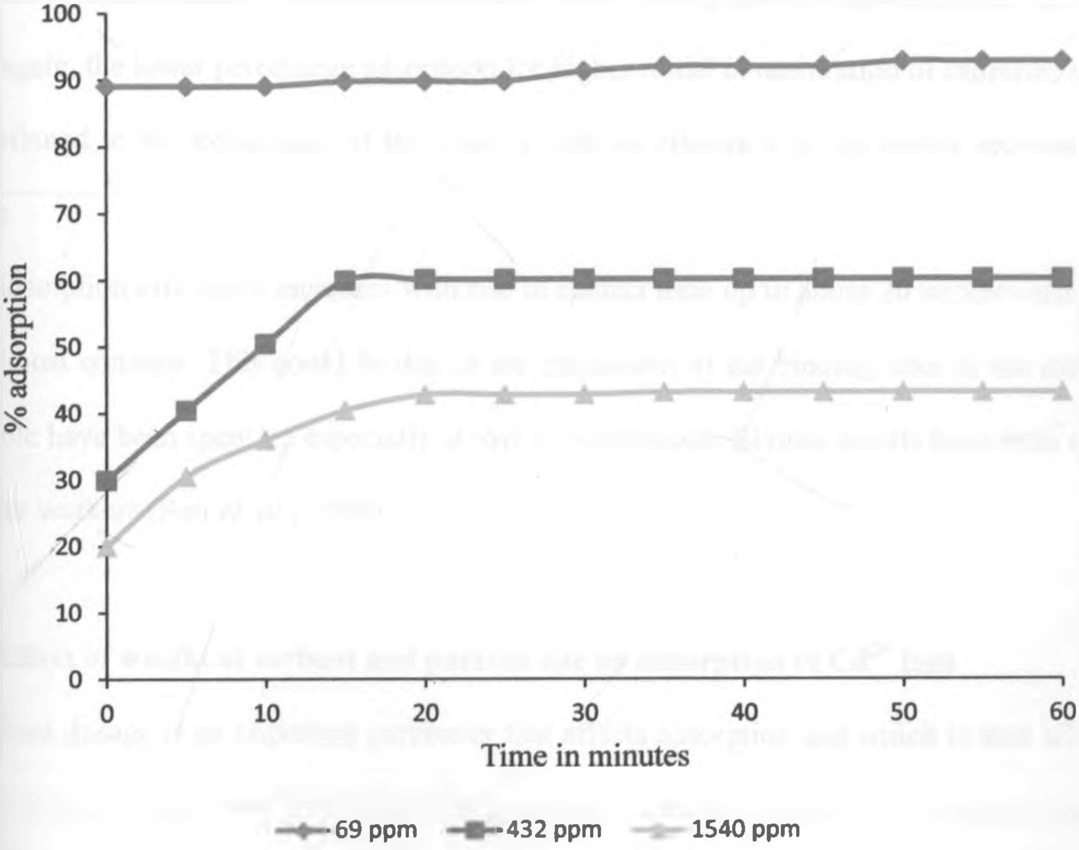

Figure 34: Effect of contact time on adsorption of Cd^{2+} ions by E. crassipes

The figure 34 comprises of three independent initial concentrations' of aqueous cadmium (69, 432 and 1540 mg L^{-1}).

From the results it can be seen that at a lower initial concentration of 69 mg L^{-1}, a higher percentage adsorption of 89.13% can be attained instantaneously upon the contact of the *E. crassipes* biomass with the metal ion solution. However, at a higher initial concentration of 1540 mg L^{-1}, a reduced adsorption percentage of about 43 % was achieved within 20 minutes of contact time, and about 45 % within 60 minutes.

It can be concluded that 20 minutes of contact time is adequate for near maximum adsorption. Once again, the lower percentage adsorption for higher initial concentration of cadmium ions can be attributed to the exhaustion of the binding sites as discussed in the earlier sections of this Thesis.

The biosorption efficiency increases with rise in contact time up to about 20 minutes after which it is almost constant. This could be due to the exhaustion of the binding sites or the metal ions available have been spent up especially at low concentrations. Similar results have been reported by other workers (Sari *et. al.*, 2008).

4.3.2 Effect of weight of sorbent and particle size on adsorption of Cd^{2+} ions

Adsorbent dosage is an important parameter that affects adsorption and which in turn affects the cost of using the adsorbent for commercial purposes. Therefore the effect of biomass dosage on biosorption of Cd^{2+} ions was studied using adsorbent dosages in the range of 0.125 to 2.0 g. The results obtained are presented in figure 35.

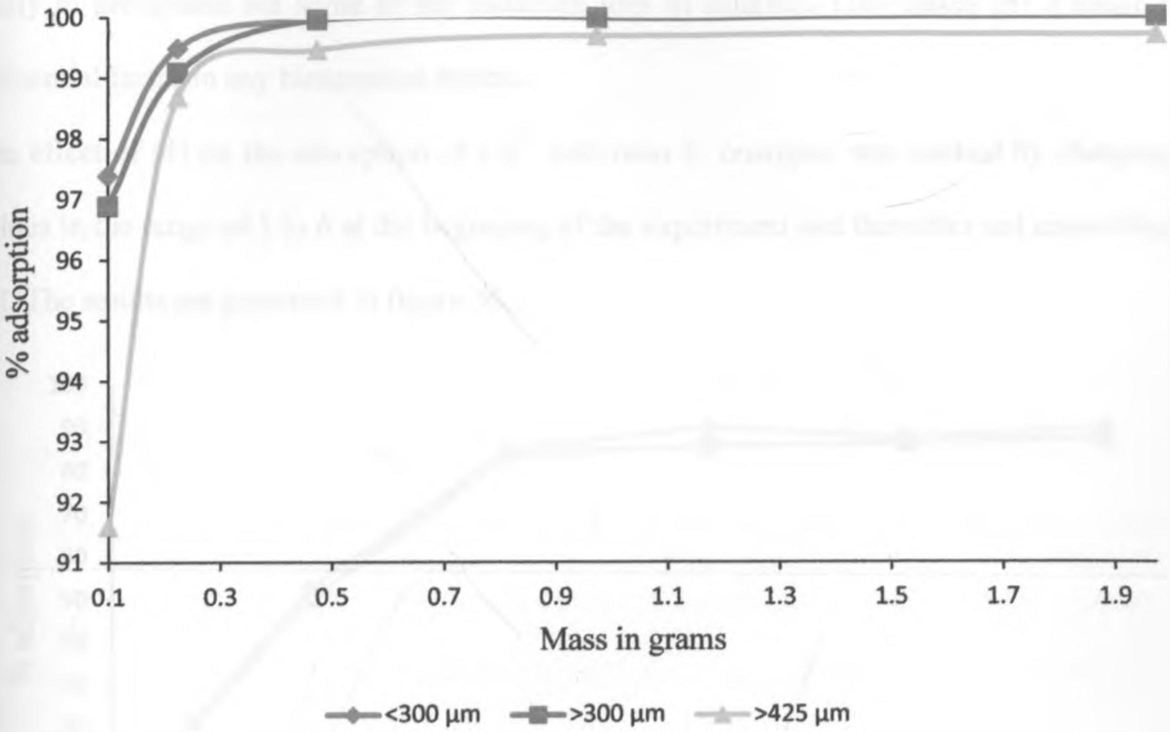

Figure 35: Effect of weight and particle size on Cd^{2+} ions adsorption by E. crassipes.

As shown in the figure, the biosorption efficacy is highly dependent on the mass of biomass that is available for adsorption. Also percentage adsorption increases with decrease in particle size and increase in the biomass dosage. Decrease in particle size leads 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. Increase in mass on the other hand yields more adsorption sites.

4.3.3 Effect of pH on adsorption of Cd^{2+} ions

Plant biomasses contain a high content of carboxyl groups, which suggests that the biosorption process could be affected by changes in the pH of the solution. An increase in the pH is also likely to precipitate out some of the cadmium ions in solution. This makes pH a single most influential factor in any biosorption system.

The effect of pH on the adsorption of Cd^{2+} ions onto *E. crassipes* was studied by changing pH values in the range of 1 to 6 at the beginning of the experiment and thereafter not controlling the pH. The results are presented in figure 36.

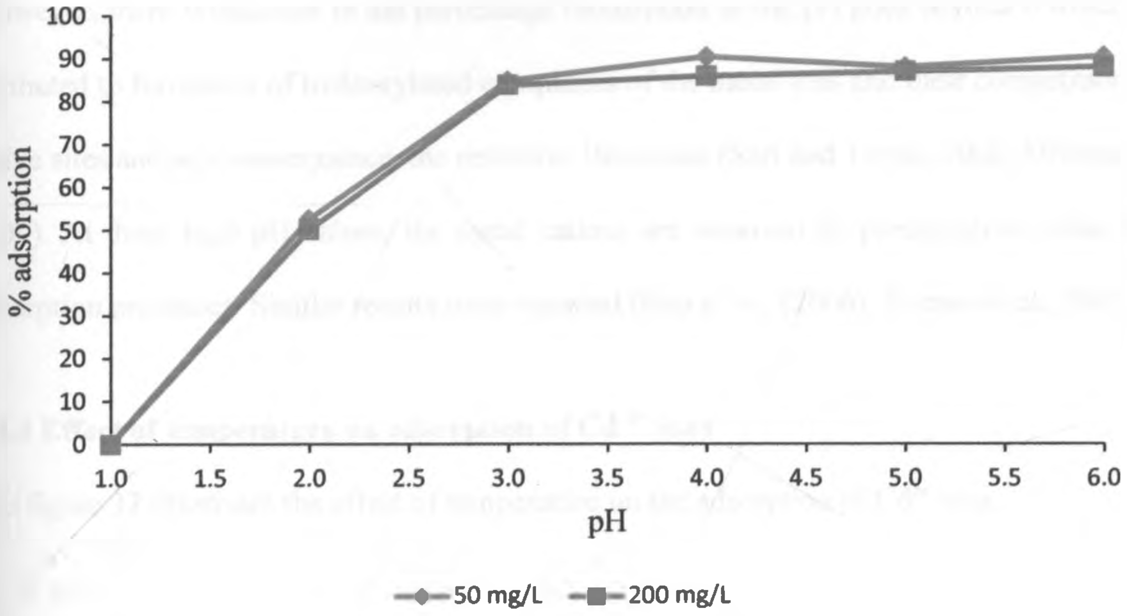

Figure 36: Effect of pH on percentage adsorption of Cd^{2+} ions by 0.5 g of E. crassipes

The high biosorption efficiency was obtained at 85 %, 90.5 % and 90.5 % at pH of 3.5, 4.0 and 6.0 respectively, for a concentration of 50 mg L^{-1}. At a higher concentration of 200 mg L^{-1}, the highest percentage adsorption recorded was 88.0% at pH of 6.0. This suggests that the optimum pH range for adsorption of Cd^{2+} ions is between 4 and 6. At a lower pH, the percentage biosorption yield for cadmium was dramatically reduced. This is 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^+ ions compete with the metal ions for the adsorption sites on the adsorbent, so adsorption of the metal ions increases with increase in pH from 2 to 6 (Taty- Coscodes *et al.,* 2003).

In contrast, when the pH is increased, the biomass surface is expected to be more negatively charged and the adsorption of the cations which are positively charged is facilitated reaching a maximum of 90.5 %.

However, there is decrease in the percentage biosorption as the pH goes beyond 6 which can be attributed to formation of hydroxylated complexes of the metal ions and their competition for the active sites and as a consequence, the retention decreases (Sari and Tuzen, 2008; Modenes *et al.*, 2009). At these high pH values, the metal cations are removed by precipitation rather than by adsorption processes. Similar results were reported (Rao *et al.*, (2006); Kumar *et al.*, 2006).

4.3.4 Effect of temperature on adsorption of Cd $^{2+}$ ions

The figure 37 illustrates the effect of temperature on the adsorption of Cd^{2+} ions.

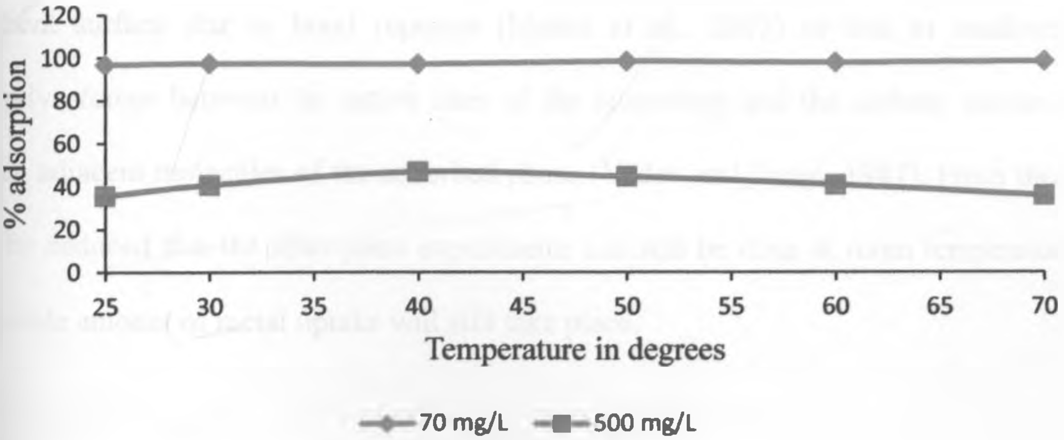

Figure 37: Effect of temperature on percentage adsorption of Cd^{2+} ions by E. crassipes.

The percentage adsorption at a lower concentration remains relatively constant 97-99%. This implies that increase in temperature has a negligible effect on the adsorption process. However, when the concentration is high (500 mg L^{-1}), the adsorption increase from 36 to 45% at 40 °C, after which it drops very slightly with any further increase in the temperature to 70°C. This trend was also reported by Ramadhan *et al.*, (2010).

The results indicate an exothermic nature of Cd^{2+} ions adsorption onto the biomass. A decrease in the biosorption of Cd(II) ions with temperature increase may be due to either damage of the binding sites (Özer and Özer, 2003) or increasing tendency to desorb metal ions from the interface back to the solution (Sari and Tuzen, 2008).

The above results indicate the exothermic nature of Cd^{2+} ions biosorption onto *E. crassipes*. The decreasing biosorption efficiency may be attributed to many parameters. These include the relative increase in the escaping tendency of Cd^{2+} ions from the solid phase to the bulk of the solution; deactivating of the biosorbent surface or destruction of some active sites on the biosorbent surface due to bond ruptures (Meena *et al.*, 2005) or due to weakness of the biosorptive forces between the active sites of the biosorbent and the sorbate species and also between adjacent molecules of the adsorbed phase (Yadav and Tyagi, 1987). From these results it can be deduced that the adsorption experiments can still be done at room temperature and an appreciable amount of metal uptake will still take place.

4.3.5 Effect of initial concentration of Cd^{2+} ions on adsorption

The biosorption capacity of metal ions was reported to be related to the ratio of initial concentration of metal ions to the concentration of the biomass (Vasudevan *et al.*, 2003;

Vijayarangharam and Yun, 2008). 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 E. *crassipes* biomass. Figure 38 shows the results obtained.

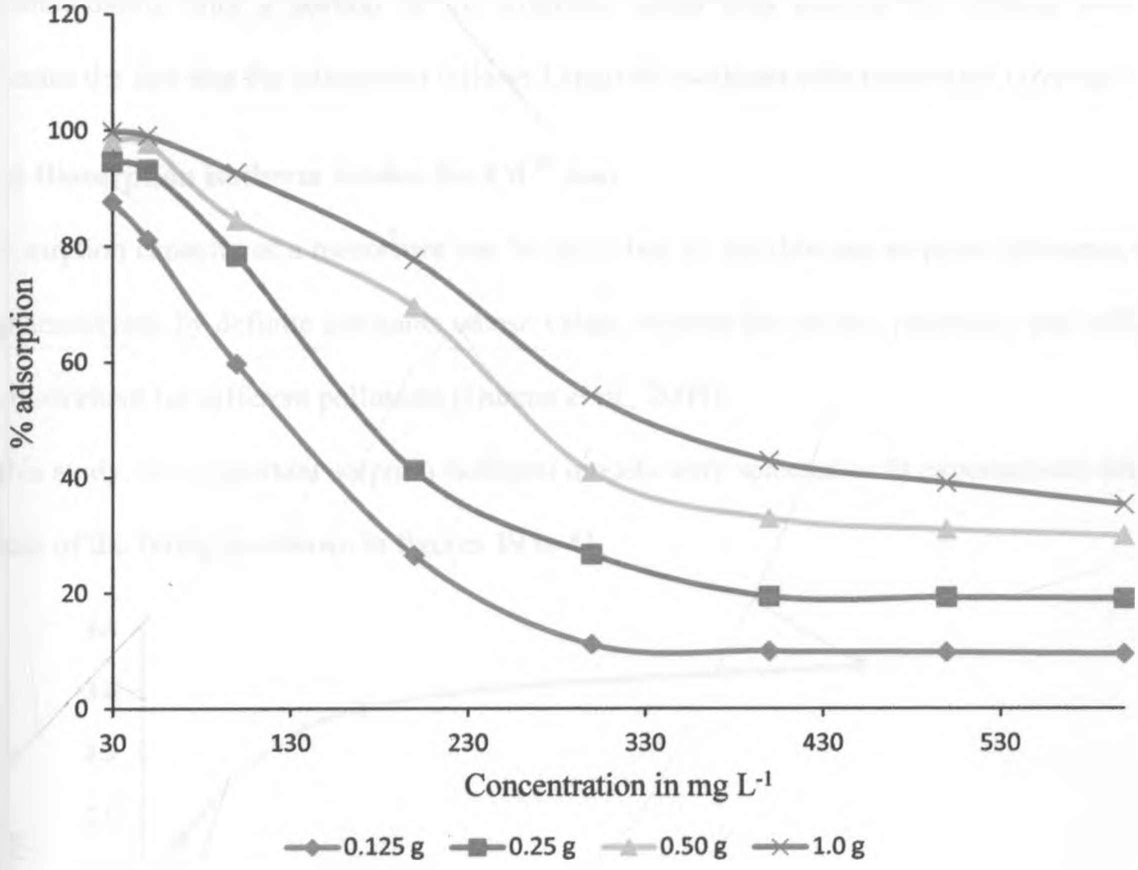

Figure 38: Effect of initial concentration of Cd^{2+} ions on adsorption by E. crassipes.

It can be seen from the results that at lower concentrations, we have higher adsorption (99.98%) of the metal ions onto the *E. crassipes* biomass. At lower initial solute concentrations, the ratio of the initial moles of solute to the surface area is low; subsequently fractional sorption becomes independent of concentration. The higher percentage adsorption observed for low concentration could also be attributed to the availability of many adsorption sites on the *E.crassipes,* thus less competition among the metal ions for the binding sites. However, at higher initial concentration the adsorption decreases to about 35% using 1.0 g of the biomass.

Nevertheless, as the concentration increases, binding sites become nearly saturated, accommodating only a portion of the available metal ions looking for binding sites. This indicates the fact that the adsorption follows Langmuir isotherm with monolayer coverage.

4.3.6 Biosorption isotherm studies for Cd $^{2+}$ ions

The sorption capacity of a biosorbent can be described by equilibrium sorption isotherms, which is characterized by definite constants whose values express the surface properties and affinity of the biosorbent for different pollutants (Dursun *et al.*, 2005).

In this study, two important sorption isotherm models were selected to fit experimental data. The results of the fitting are shown in figures 39 to 41.

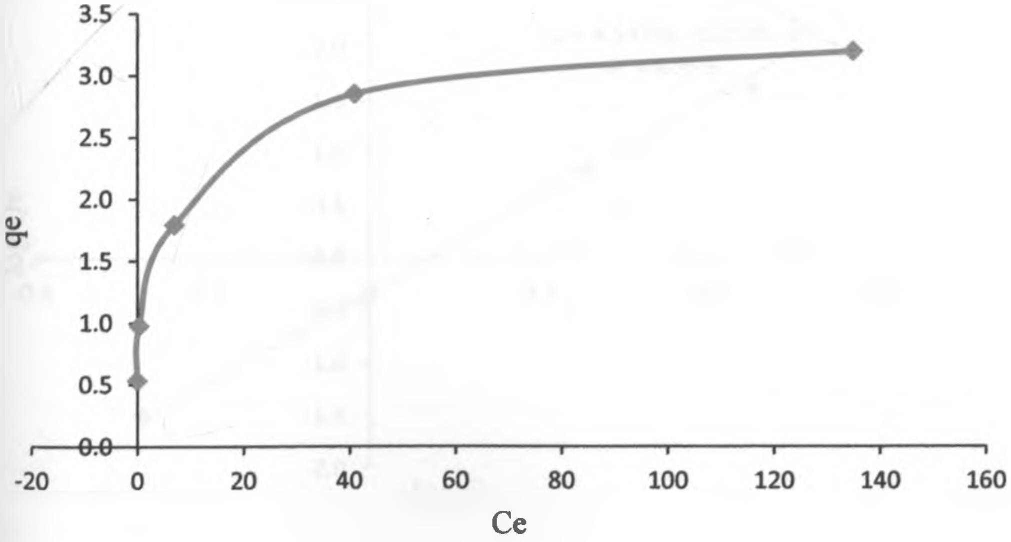

Figure 39: Langmuir isotherm for Cd $^{2+}$ ions using E. crassipes at room temperature.

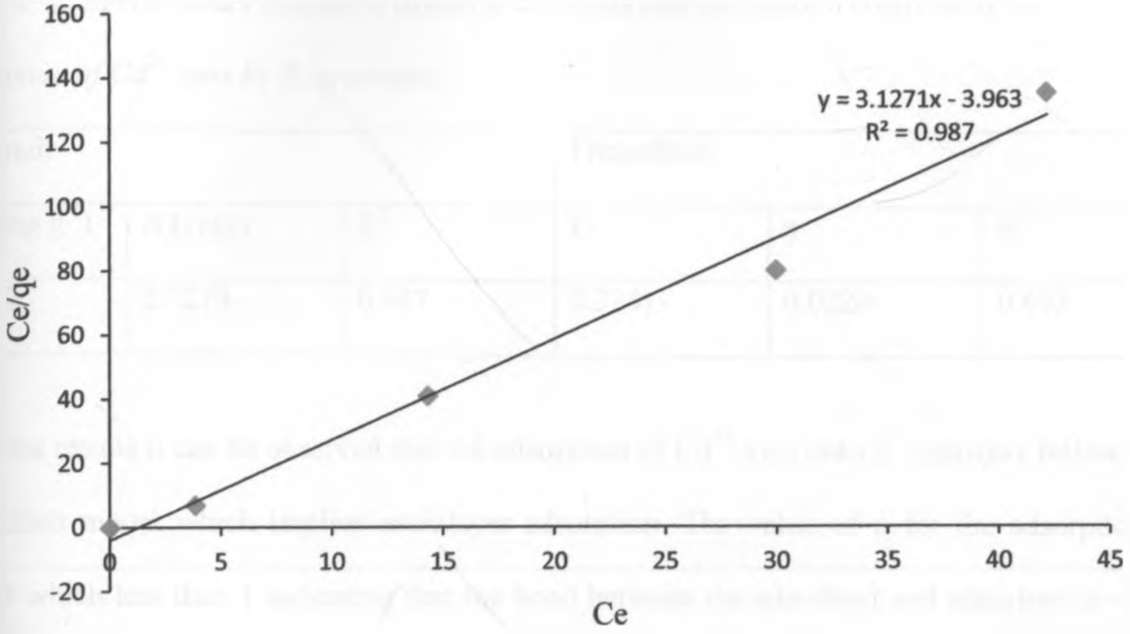

Figure 40: Linearized Langmuir isotherm plot for adsorption of Cd^{2+} by E. crassipes.

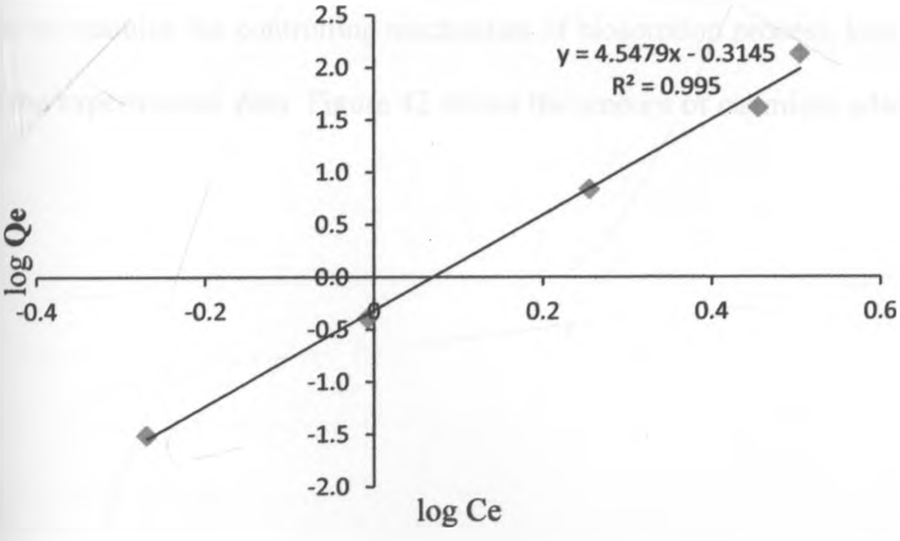

Figure 41: Freundlich isotherm plot for adsorption of Cd^{2+} ions by E. crassipes

Table 8. Langmuir and Freundlich isotherm constants and correlation coefficients for adsorption of Cd^{2+} ions by E. crassipes.

Langmuir			Freundlich		
Q_{max}(mg g^{-1})	*b*(L/mg)	R^2	k_F	n	R^2
3.2379	2.7279	0.987	0.3241	0.0224	0.995

From the results it can be observed that the adsorption of Cd^{2+} ions onto *E. crassipes* follows the Freundlich model which implies multilayer adsorption. The value of n for the adsorption is 0.0224 which less than 1 indicating that the bond between the adsorbent and adsorbate is weak suggesting physisorption.

4.3.7 Biosorption Kinetics for Cd^{2+} ions

In order to examine the controlling mechanism of biosorption process, kinetic models were used to test the experimental data. Figure 42 shows the amount of cadmium adsorbed as a function of time.

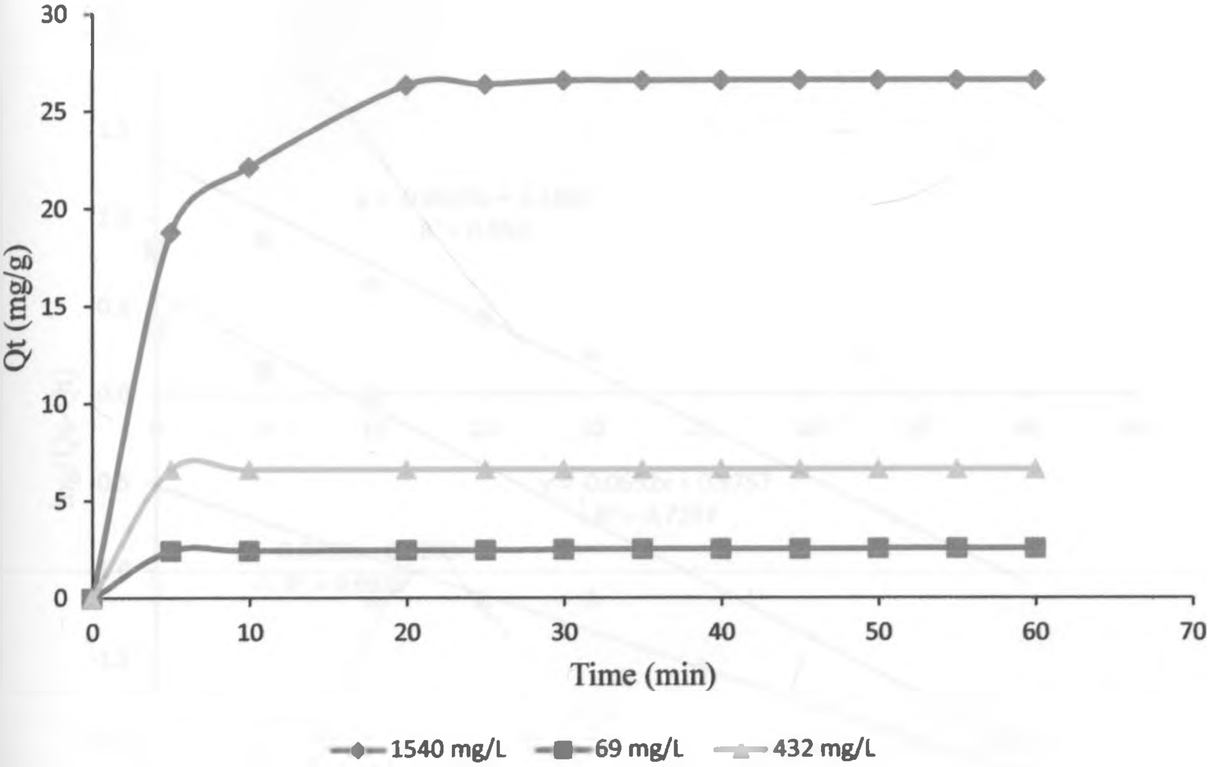

Figure 42: Effect of contact time on Cd^{2+} *ions uptake by E .crassipes biomass.*

Pseudo-first-order model assumes the rate determining step is physisorption, while pseudo-second-order model is based on the assumption that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites. The adsorption data was analyzed using pseudo-first-order and pseudo-second- order models. The results are displayed in the figures 43 to 44 and table 9.

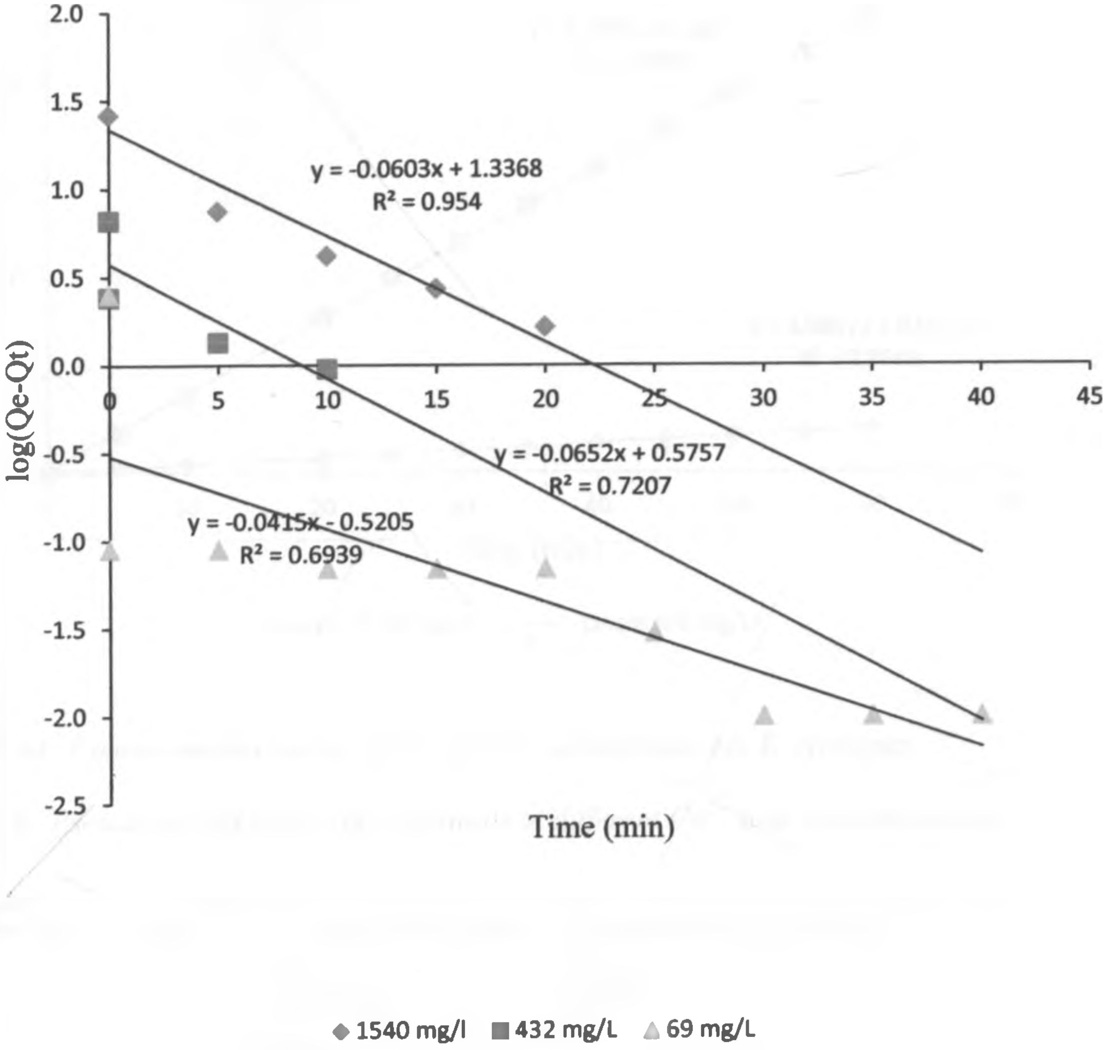

Figure 43: Pseudo-first-order plots of Cd^{2+} ions adsorption onto E. crassipes

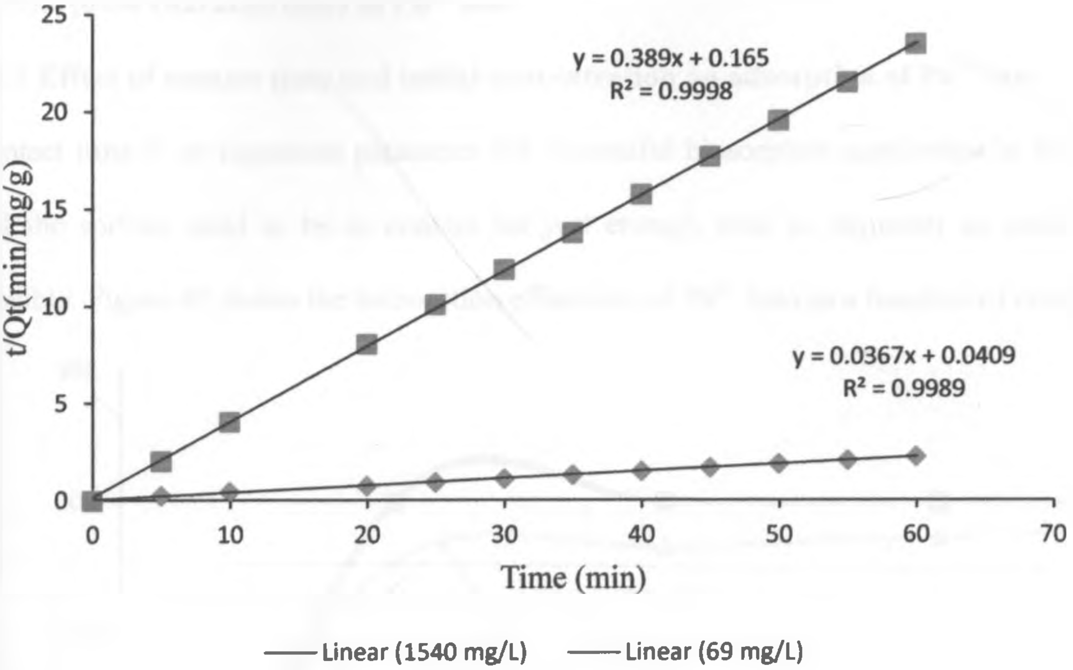

Figure 44: Pseudo-second -order- plots of Cd^{2+} *adsorption onto E. crassipes.*

Table 9. Pseudo second order rate constants at different Cd^{2+} *ions concentrations*

Concentration (mg L^{-1})	Rate constant(k_2)	Correlation coefficient (R^2)
69	0.036	0.999
1540	0.389	0.998

From the above results the pseudo-second -order plots have a higher correlation coefficient R^2 = 0.999 and 0.998. This indicates that the rate limiting step is chemisorption. Therefore adsorption of Cd^{2+} fits pseudo-second-order mechanism with rate constants of 0.036 g mg^{-1} min^{-1} for a concentration of 69 mg L^{-1} and 0.389 g mg^{-1} min^{-1}. Similar conclusions were reported in the literature (Jayaram et al., 2009), it was also observed that most sorption systems follow the pseudo-second-order model.

4.4. Sorption characteristics of Pb^{2+} ions

4.4.1 Effect of contact time and initial concentration on adsorption of Pb^{2+} ions

Contact time is an important parameter for successful biosorption application as the biosorbent and the sorbate need to be in contact for just enough time to sequester as much cations as possible. Figure 45 shows the biosorption efficiency of Pb^{2+} ions as a function of contact time.

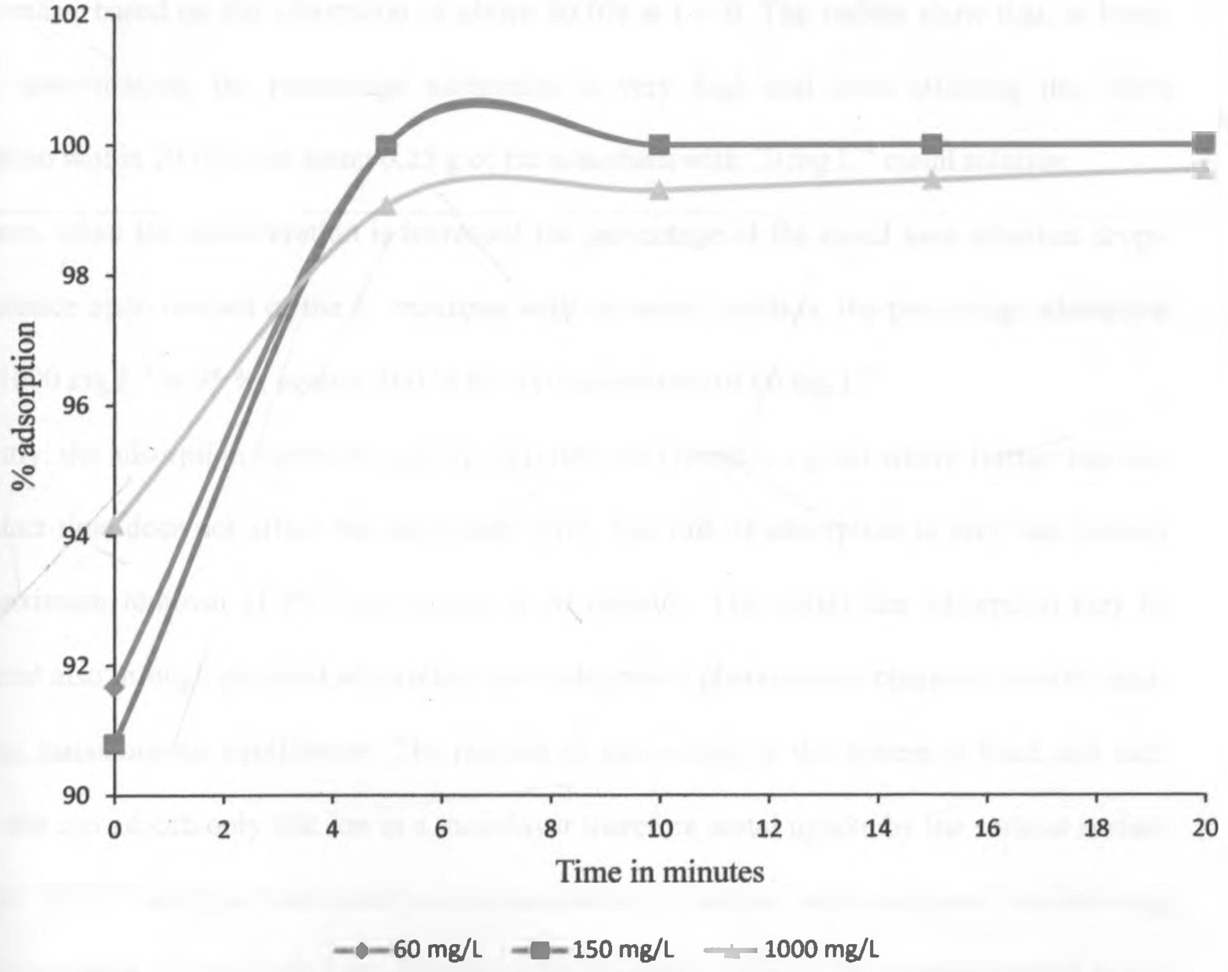

Figure 45: Effect of contact time and initial metal ion concentration on percentage adsorption of Pb^{2+} ions by E. crassipes.

The figure comprises of 3 independent concentrations of Pb^{2+} ions (60, 150 and 1000 mg L^{-1}).

As shown, at lower initial Pb^{2+} ion concentration, the percentage adsorption is very high even attaining the 100% mark after just 5 min upon contact. At high concentration of 1000 mg L^{-1}, a reduced adsorption is observed within 20 minutes of contact time, and even after 60 minutes (99.8 %). It was also noted that the adsorption of Pb^{2+} is highest compared to the other metals studied. Upon contact of the biomass with the metal ions, the metal ions are rapidly taken up by the biomass, based on the adsorption of above 90.0% at t = 0. The results show that, at lower initial concentration, the percentage adsorption is very high and even attaining the 100% adsorption within 20 minutes using 0.25 g of the adsorbent with 10 mg L^{-1} metal solution.

However, when the concentration is increased the percentage of the metal ions adsorbed drops. For instance upon contact of the *E. crassipes* with the metal solution, the percentage adsorption using 1000 mg L^{-1} is 95 %, against 100 % for a concentration of 60 mg L^{-1}.

Evidently, the adsorption increases rapidly with time and reaches a point where further increase in contact time does not affect the adsorption level. The rate of adsorption is very fast initially and maximum removal of Pb^{2+}ions occurs at 20 minutes. The initial fast adsorption may be explained also through physical adsorption since adsorption phenomenon characteristically tends to attain instantaneous equilibrium. The number of active sites in the system is fixed and each active site can adsorb only one ion in a monolayer therefore metal uptake by the sorbent surface is rapid initially and then decreases as the availability of active sites decreases thus slowing down the transfer of metal ion from solution to the adsorbent surface. The adsorption sites at this point have been saturated; therefore it can not adsorb any more of the metal ions.

4.4.2 Effect of weight and particle size on adsorption of Pb^{2+} ions

The effect of biomass dosage on adsorption of Pb^{2+} was studied using different biomass dosage in the range of 6.25 g L^{-1} to 100 g L^{-1} and a concentration of 10 mg L^{-1} and the results are displayed in Figure 46.

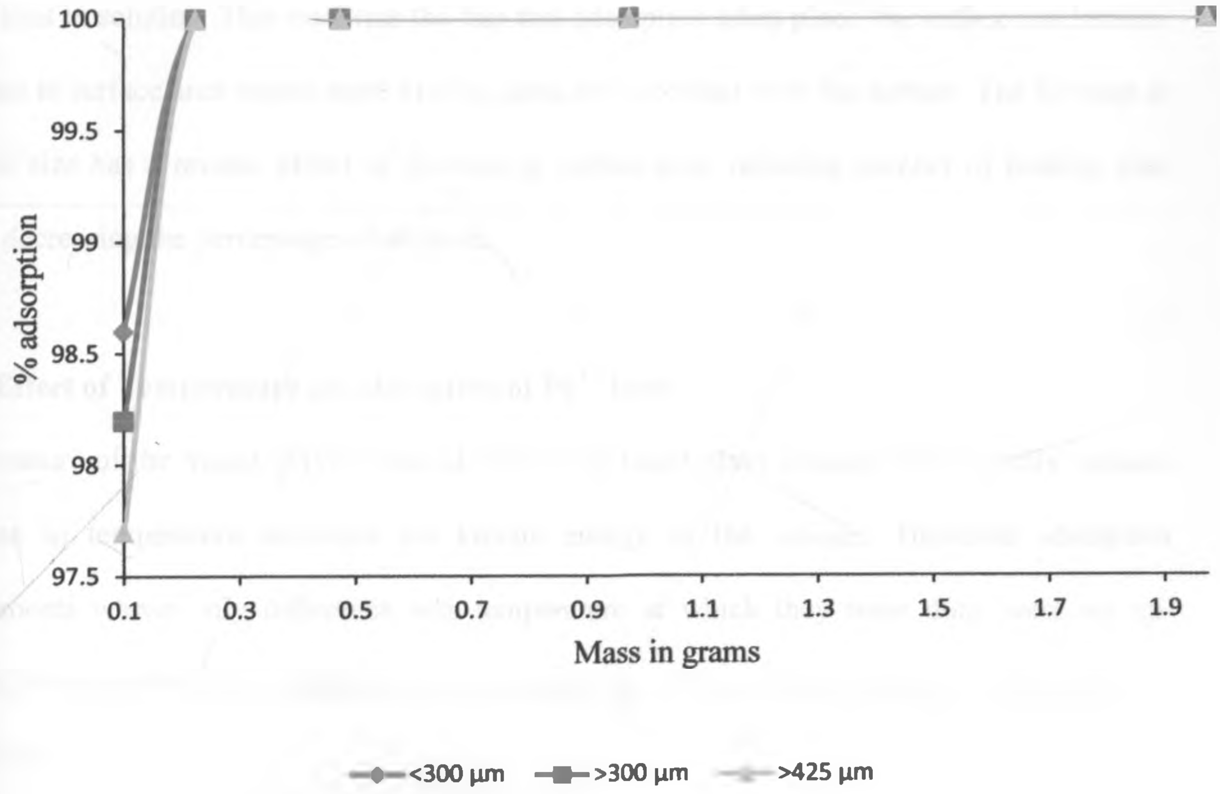

Figure 46: Effect of weight and particle size of E. crassipes on adsorption of 10 mg L^{-1} Pb^{2+} ions.

The figure shows an increase in the percentage adsorption from 98 to 100 % with a mass of 0.25 g using a particle size of <300 µm of *E. crassipes*. The above results indicate that as the mass of the adsorbent increases, the percentage adsorption increases along. The increase in the adsorption is due to the availability of more binding sites for metal ions.

The decrease in particle size also has an influence of increasing the percentage adsorption as the particle size decreases. The smallest particle size used of 300 μm gave the highest percentage 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 means more binding sites are in contact with the sorbate. The increase in particle size has a reverse effect of decreasing surface area, reducing number of binding sites hence decreasing the percentage adsorption.

4.4.3 Effect of Temperature on adsorption of Pb^{2+} ions

Temperature of the media plays a crucial role in the biosorption process; this is partly because increase in temperature increases the kinetic energy of the cations. Therefore adsorption experiments whose only difference was temperature at which they were done were set up. Several experiments were conducted to investigate the effect of temperature on adsorption of Pb^{2+} ions.

A percentage of 100 % adsorption was achieved at all the temperatures tested for all the concentrations under investigation (Refer to appendix III). This means that increase in temperature has no effect on the adsorption of Pb^{2+} ions. This implies that the process of adsorption of Pb^{2+} ions can still be conducted at room temperature with the same level of efficacy of removal. Since high temperature means more operating costs, adsorption process can be done at room temperature, thus leading to energy savings hence costs cutting.

4.4.4 Effect of pH on adsorption of Pb^{2+} 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^{2+} ions adsorption onto *E. crassipes,* the pH of solution was varied from 2.0 to 7.0.The results are displayed in figure 47.

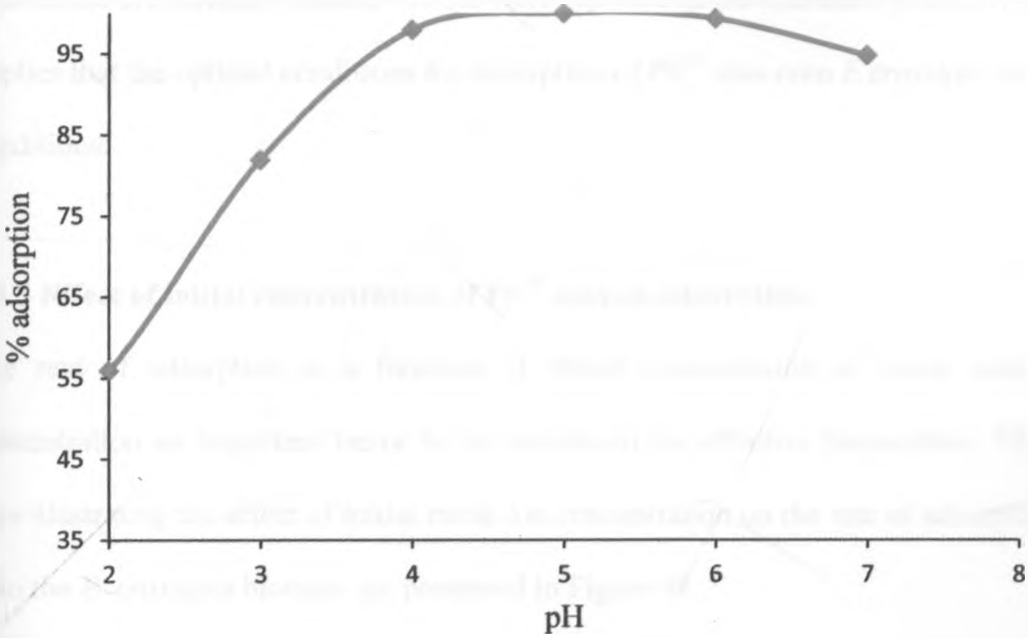

Figure 47: Effect of pH on percentage adsorption of Pb^{2+} ions onto E. crassipes.

As shown in figure 47 there is an increase in Pb^{2+} ions uptake as the pH value increases from 1.0 to 7.0. The biosorption is minimum at pH 1.0 with 40.0% adsorption. This is because the H^+ ions compete with the metal ions for the exchangeable sites on the sorbent then the H^+ are preferentially adsorbed rather than the metal ions. At higher pH values, the numbers of H^+ ions are fewer hence the surface becomes negatively charged. Consequently, the attraction of the cations would be enhanced. However, when the pH is increased above 7.0, the Pb^{2+} ions get precipitated due to the hydroxyl ion forming insoluble lead hydroxide precipitate (Feng *et al.*, 2010).

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 (Barka *et al.*, 2010). This implies that the optimal conditions for adsorption of Pb^{2+} ions onto *E.crassipes* are weakly acidic conditions.

4.4.5 Effect of initial concentration of Pb^{2+} 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 biosorption. The experimental data illustrating the effect of initial metal ion concentration on the rate of adsorption of Pb^{2+} ions onto the *E. crassipes* biomass are presented in Figure 48 .

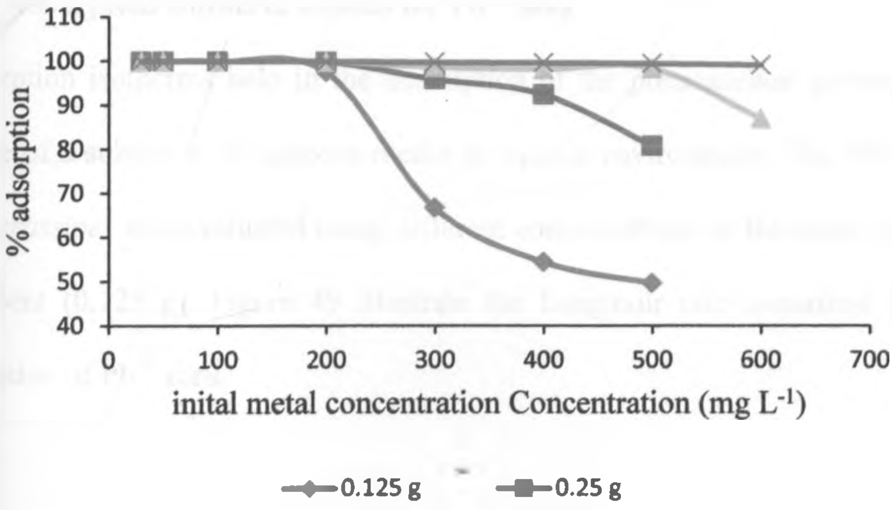

Figure 48: Effect of initial concentration of Pb^{2+} ions on adsorption by E. crassipes.

When the initial metal ion concentration is increased from 30 to 400 mg L^{-1}, the percentage adsorption is almost the same (100 %). However, as the concentration changes from 400 to 1000 mg L^{-1}, the adsorption decreases from 98 % to a low of 70 %. As the initial concentration is increased, the percentage adsorption of the Pb^{2+} ions decreases. This may be attributed to saturation of the active adsorption sites on the *E. crassipes*. At higher concentrations: here metal ions need to diffuse to the biomass surface by intra-particle diffusion and greatly hydrolyzed ions are diffused at a much slower rate (Lawal *et al.,* 2010). This accounts for the reduction in the percentage adsorption. From the above results it can be concluded that the *E. crassipes* is a very effective adsorbent in the removal of Pb^{2+} ions from water and waste waters at low concentrations of lead. Further, an increase in the amount of the *E. crassipes* biomass used, increases the percentage adsorption, probably due to the increased ratio of mass of adsorbent to concentration of the adsorbate.

4.4.6 Adsorption isotherm studies for Pb^{2+} ions

Adsorption isotherms help in the description of the phenomenon governing the retention and release of a substance in aqueous media or aquatic environment. The Pb^{2+} ions uptake capacity of *E. crassipes* was evaluated using different concentrations of the metal ions on a fixed mass of adsorbent (0.125 g). Figure 49 illustrate the Langmuir non linearized isotherm obtained for adsorption of Pb^{2+} ions.

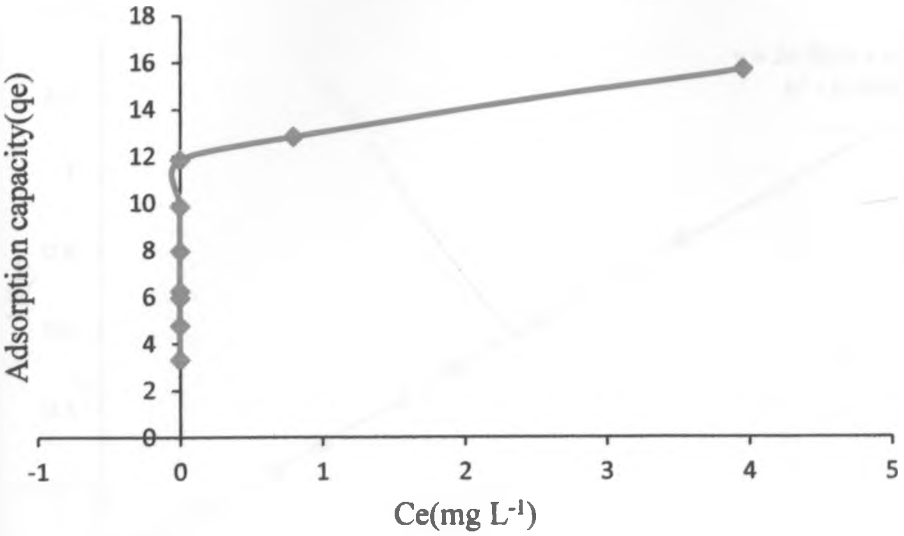

Figure 49: Langmuir non linearized isotherm for adsorption of Pb^{2+} *ions.*

The sorption capacity of the adsorbent was found to be 16.35 mg g^{-1}. The data fits well with Langmuir isotherm, implying that the adsorption takes place via monolayer coverage with saturation being reached. The data was further evaluated using the Linearized Langmuir isotherm model and the results are displayed in figure 50.

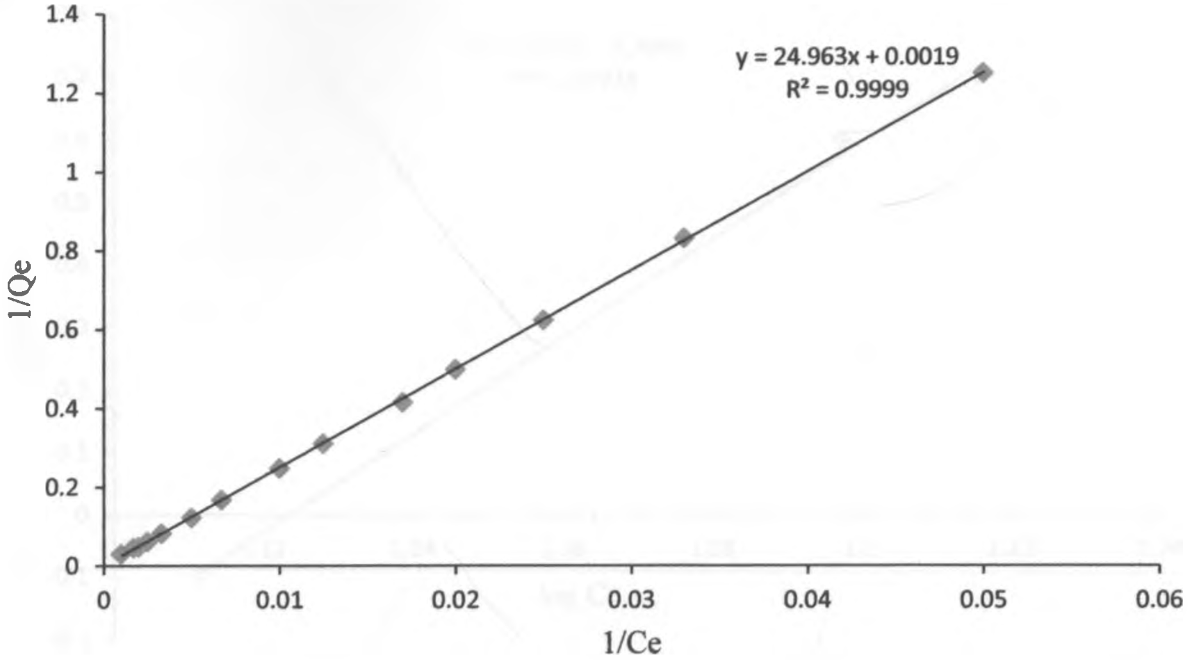

Figure 50: Linearized Langmuir isotherm for adsorption of Pb^{2+} *ions.*

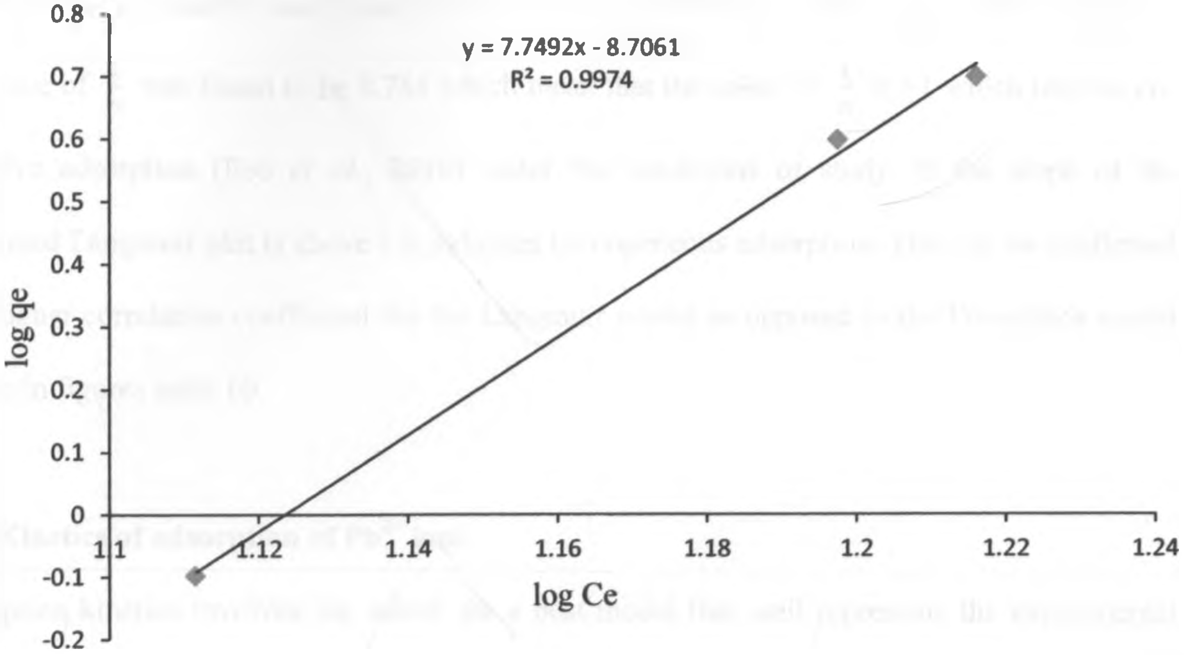

Figure 51: Linearized Freundlich isotherm plot for the adsorption of Pb^{2+} onto E. crassipes.

The correlation coefficient (R^2) was found to be 0.9984 for Pb^{2+} biosorption using Langmuir model (See Table 10). The high value indicated that the equilibrium data fitted well to the Langmuir model, which means that sorption of the metal ions onto the *E. crassipes* took place at the functional groups / binding sites on the surface of the biomass by monolayer biosorption.

Table 10. Langmuir and Freundlich isotherm constants and their correlation coefficients for Pb^{2+} ions adsorption.

Langmuir			Freundlich		
Qmax(mg L^{-1})	b(L mg^{-1})	R^2	k_F(mg/g)	n	R^2
16.166	0.0197	0.9984	-8.7061	7.749	0.9974

The biosorption capacity was found to be 16.166 mg of Pb^{2+} per gram of the sorbent material. The value of $\frac{1}{n}$ was found to be 8.761 which mean that the value of $\frac{1}{n}$ is >1 which implies co-operative adsorption (Foo *et al.*, 2010) under the conditions of study. If the slope of the Linearized Langmuir plot is above 1 it indicates homogeneous adsorption. This can be confirmed by a higher correlation coefficient for the Langmuir model as opposed to the Freundlich model as seen in figures table 10.

4.4.7 Kinetics of adsorption of Pb^{2+} ions

Adsorption kinetics involves the search for a best model that well represents the experimental data. Biosorption experiments were conducted in order to understand the behavior of *E.crassipes* and also to determine the rate controlling mechanism of the biosorption of Pb^{2+} ions onto *E. crassipes* biomass. First experiments were conducted to investigate the effect of contact time on the adsorption capacity of *E. crassipes* and the results of this study are shown in figure 52 which shows the plot between amounts adsorbed, Q_t (mg g^{-1}) versus time, t (min) for different initial concentrations.

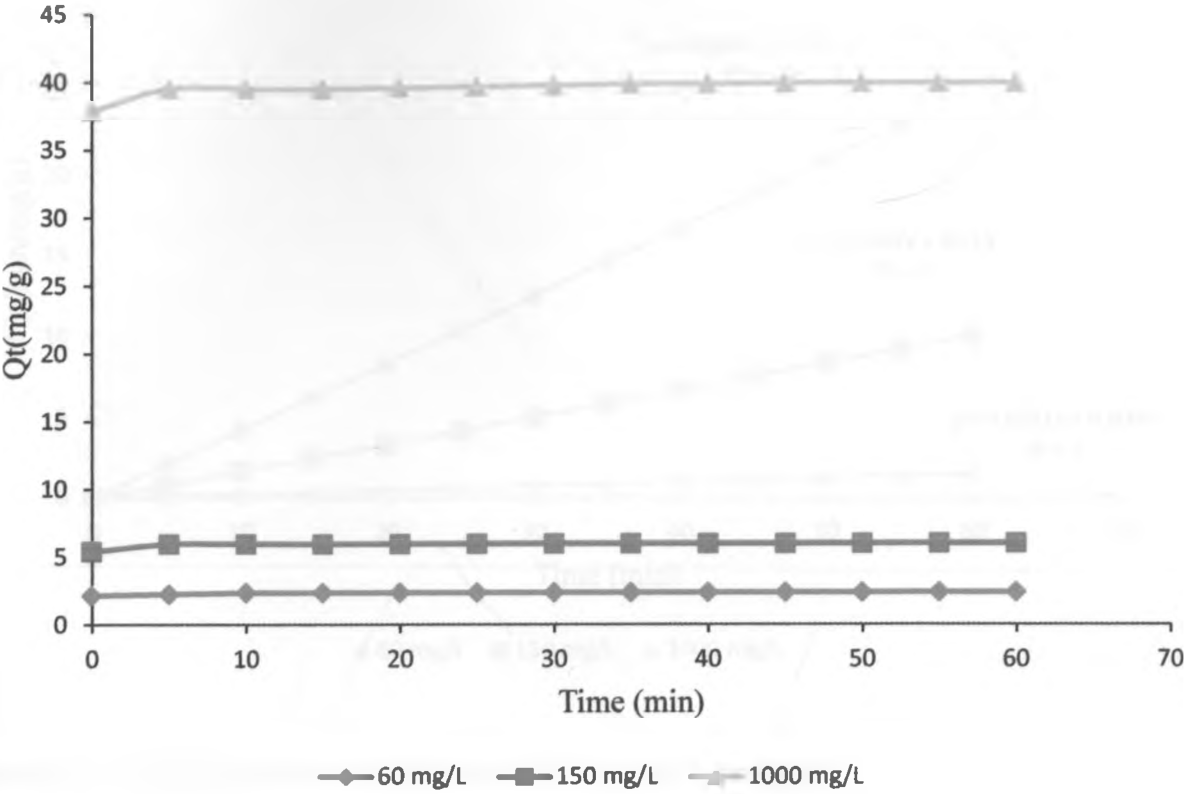

Figure 52: Effect of contact time on uptake of Pb^{2+} ions uptake by E. crassipes.

From figure 52 it can be observed that Q_t increases with increase in initial lead concentration. The adsorption rate within the first 5 minutes was observed to be very high and thereafter the reaction proceeds at a slower rate till equilibrium and finally at a steady rate after equilibrium. The adsorption equilibrium data were then analyzed using pseudo-first-order and pseudo-second-order models. The prediction of adsorption rate law gives important information for designing batch adsorption systems. The figures 53 and 54 show the evaluation.

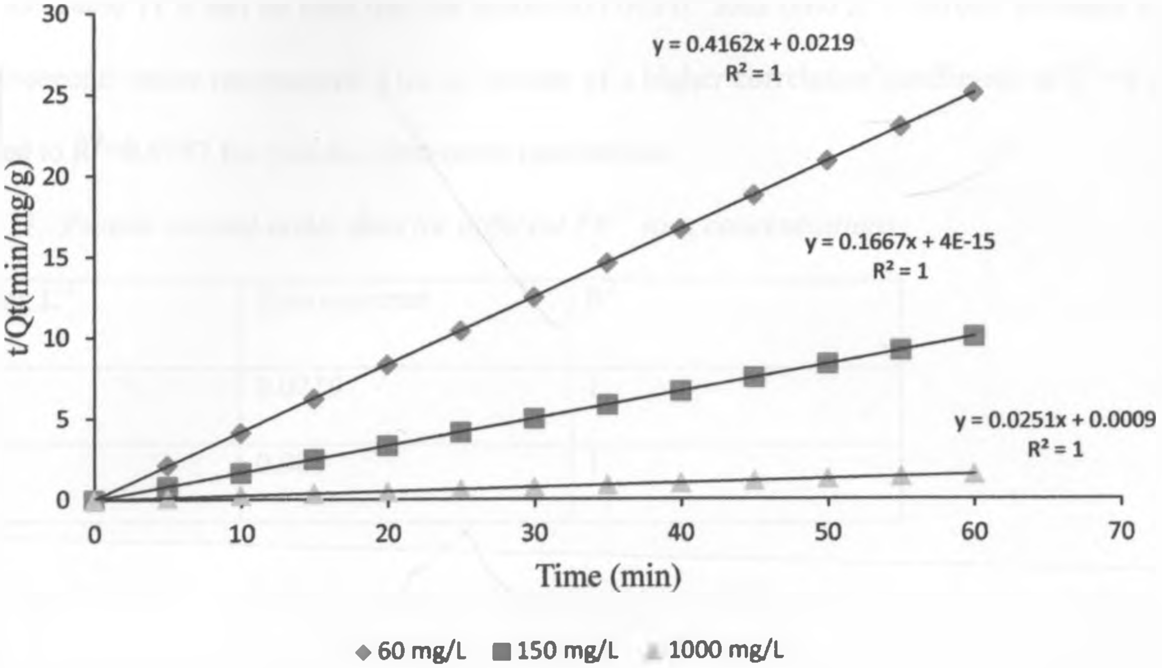

Figure 53: Pseudo-second-order plots for Pb^{2+} ions by E.crassipes.

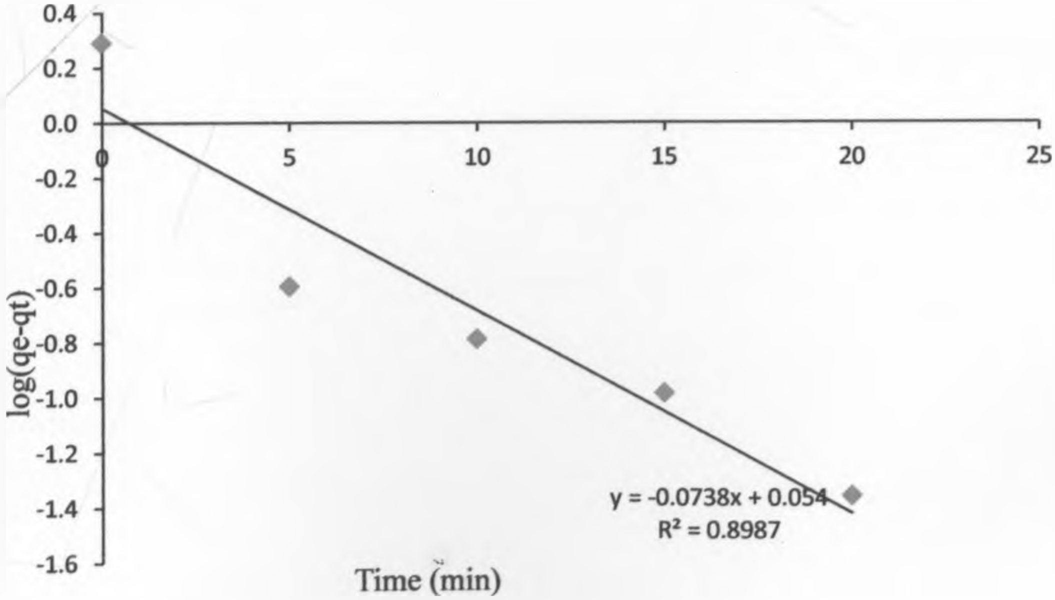

Figure 54: Pseudo-first-order plot of Pb^{2+} adsorption onto E. crassipes.

From the Table 11 it can be seen that the adsorption of Pb^{2+} ions onto *E. crassipes* proceeds via pseudo-second -order mechanism. This is because of a higher correlation coefficient of R^2 =1 as opposed to R^2=0.8987 for pseudo –first-order mechanism.

Table 11. Pseudo-second-order data for different Pb^{2+} ions concentrations

[Cd] mg L^{-1}	Rate constant	R^2
60	0.0219	1
1000	0.009	1

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

Results obtained in this study have demonstrated that *E. crassipes* is an effective, low-cost adsorbent that can be used to remove heavy metals from aqueous solutions. Therefore this material can be effectively used to remove heavy metals from water and waste water which will help in the conservation of the environment .This will go a long way in helping Kenya to meet the MDG number 7 which advocates for sustainability in environmental conservation. The use of *E. crassipes* will also help maintain the biodiversity in Lake Victoria thus helping the lake to meet the needs of the riparian population hence helping alleviate poverty in the region. Because the material is of biological origin there is no production of sludge during treatment and the raw material is also renewable. In the economic perspective the country will be able to save foreign exchange used to buy chemicals used in water treatment. Given that the species is abundantly available the plant biomass can therefore be used as an alternative adsorbent in water treatment since it is as its cheap readily available and requires little or no treatment for use as a solution to water pollution problems.

5.1 Conclusions

After this study the following conclusions were made

1. That water hyacinth biomass can be used as a natural sorbent for the removal of heavy metals from aqueous solutions.

2. That the removal of metal ions is affected by pH, biomass dosage, contact time, initial concentration of metal ions. The maximum removal of metal was at a pH range of between 4 and 6
3. The equilibrium metal ion removal was attained in 20 minutes.
4. That temperature has negligible effect on adsorption at a lower concentration between 25 and 40°C and that beyond that temperature increase in temperature leads to a decrease in the adsorption hence the adsorption process is exothermic. However the adsorption of Pb^{2+} is independent of the temperatures for the concentrations studied.
5. The experimental data fitted well with the Langmuir isotherm which means that adsorption took place via monolayer coverage. However there is a possibility of heterogeneous adsorption taking place.
6. The adsorption data fitted well for pseudo-second-order mode for all the metals under study.
7. That adsorption takes place by mainly ion exchange and complexation, evidence from the FT-IR indicates that the adsorption takes place at the functional groups on the biosorbent.
8. The whole *E. crassipes* plant (roots, stems and leaves) can be utilized for adsorption of heavy metals in aqueous systems as it is an effective adsorbent.
9. That adsorption can be best conducted at room temperature and the solutions must be diluted to enhance the efficacy.
10. That the whole *E. crassipes* plant can be utilized as an effective adsorbent for heavy metals removal from aqueous solutions.
11. That the maximum adsorption capacities range from 3.2 to 17.82 mg g^{-1} then the material is best suited for removal of Cu^{2+} ions.

5.2 Recommendations

The following recommendations are therefore made

1. More studies to be conducted on the mechanisms of adsorption by use of Scanning Electron Microscopy (SEM) and Energy dispersive Spectroscopy (EDS) in order to understand how the adsorption takes place.
2. Modification of the plant biomass using the various modifying agents to be done to study their influence on adsorption capacity of the plant material and possibly improve the adsorption efficacy of the biosorbent.
3. A multi component study to be done using binary and ternary systems to establish the effect of metal ions on adsorption of other metal ions.
4. Activated carbon to be developed from the plant biomass material and its adsorption characteristics to be compared with the native, modified and activated carbon in removal of heavy metals.
5. Column studies to be conducted to determine the breakthrough point and to consider the possibility of regeneration of the column material once spent.
6. Regeneration studies need to be done in detail with pollutants-laden adsorbents to recover the adsorbate as well as the adsorbents. This will enhance the economic feasibility of the process. This will involve iterative methods involving adsorption and the metals are recovered from the spent biomass by electrolysis and other electrochemical methods. The metals can then be recovered for reuse while the biosorbent can be recycled.
7. The potential of the low-cost adsorbent under multi-component systems needs to be assessed. This would make a significant impact on the potential, commercial application of the low cost adsorbents for industrial systems. This application will help the country to

attain its Vision 2030 goals on the conservation of the environment to safeguard the future generations.

8. Experiments involving real industrial effluents from a point source to be done to evaluate the efficacy of the biomaterial in alleviating the problem of dangerous pollutants affecting the environmental and human health.

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APPENDICES

APPENDIX (I) Effect of contact time on adsorption

Metal	**Initial concentration**	**% adsorption after time (t) min**												
		0	5	10	15	20	25	30	35	40	45	50	55	60
Cd	80	89.13	89.13	89.13	89.13	89.85	91.30	92.02	92.02	92.02	92.02	92.75	92.75	92.75
	400	30.00	40.50	50.50	60.18	60.18	60.18	60.18	60.18	60.18	60.18	60.18	60.18	60.18
	1000	20.00	30.52	36.04	40.50	42.85	42.85	42.85	43.18	43.18	43.18	43.18	43.18	43.18
Cu	50	100	100	100	100	100	100	100	100	100	100	100	100	100
	300	31.25	100	100	100	100	100	100	100	100	100	100	100	100
	1000	10.70	46.2	58.92	66.07	69.64	69.64	69.64	69.64	69.64	69.64	69.64	69.64	69.64
Pb	60	96.33	96.17	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00
	150	96.36	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00	96.00
	1000	96.20	96.04	96.03	96.03	96.02	96.02	96.01	96.01	96.01	96.01	96.01	96.01	96.01
Zn	20	66.20	98.75	99.75	100	100	100	100	100	100	100	100	100	100
	200	31.00	88.00	95.00	92.50	92.50	92.50	93.00	95.00	95.00	96.50	96.50	96.50	96.50
	1000	19.40	46.40	49.70	50.10	50.30	49.80	51.8	49.7	50.1	50.3	49.8	49.7	49.8

APPENDIX (II) Effect of pH on adsorption

Concentration Mg L^{-1}	Metal	% adsorption at given pH							
		1	2	3	4	5	6	7	8
50	**Cd**	0.05	52.75	85.00	90.50	88.00	90.5		
	Cu	84.48	89.22	98.96	99.12	99.02	99.26		
	Pb	40.00	56.00	82.00	98.00	100	99.38		
	Zn	32.00	35.6	85.8	89.00	96.06	96.94		
200	**Cd**	0.03	50.25	84.01	86.00	87.00	88.00		
	Cu	N/A	N/A	N/A	N/A	N/A	N/A		
	Pb	N/A	N/A	N/A	N/A	N/A	N/A		
	Pb	N/A	N/A	N/A	N/A	N/A	N/A		

APPENDIX (III) Effect of Temperature on adsorption

Temperature(°C)	Cadmium		Copper		Lead		Zinc	
mg L^{-1}	70	500	50	400	70	500	25	200
	% adsorption							
25	97.09	35.89	98.82	95.9	100	100	99.808	94.6
30	97.65	41.02	98.72	96.75	100	100	99.556	92.3
40	97.53	47.22	98.58	96.63	100	100	99.648	93.45
50	98.54	44.87	98.62	96.5	100	100	99.808	94.45
60	97.97	41.02	98.56	95.38	100	100	99.428	92.9
70	98.6	36.1	98.1	88.55	100	100	99.456	92.5

APPENDIX (IV) Effect of concentration on adsorption

(a) Cadmium

Concentration (mg L^{-1})	**Mass of sorbent**			
	0.125 g	0.25 g	0.50 g	1.0 g
30	87.8	94.74	98.33	99.89
50	81.21	93.3	97.86	99.17
100	59.79	78.35	84.54	92.78
200	26.63	41.3	69.57	77.72
300	11.19	26.78	41.02	54.24
400	10	19.5	33	43
500	9.8	19.3	31.04	39.1
600	9.5	19.1	30.03	35.4

(b) Copper

Concentration	**Mass of sorbent**		
mg/L	0.125 g	0.25 g	0.50 g
30	94.03	97.5	98.2
50	85.4	95.76	98.02
100	80	94.43	95.87
200	64	90.45	95.87
300	62.3	73.2	89.1
400	54.5	67.5	81.85
500	51	66	80.4
600	36	50.67	69.33

(c) Lead (II)

Concentration	**Mass of sorbent**			
mg/L	0.125 g	0.25 g	0.50 g	1.0 g
30	100	100	100	100
50	100	100	100	100
100	100	100	100	100
200	97.64	99.93	100	100
300	66.85	96.01	98.69	99.81
400	54.51	92.49	98.17	99.68
500	49.76	80.81	98.34	99.46
600			86.99	99.08

(d) Zinc (II)

	Mass and % adsorption			
Concentration	0.125 g	0.25 g	0.50 g	1.0 g
30	89.3	96.21	98.57	99
50	67.25	94.7	96.02	96.74
100	55	77.35	89.8	96
200	40	71.45	77	95.32
300	31	65	76.86	88.85
400	28.6	58	63.1	78.8
500	27	40.2	58.78	71.05
600	26.79	29	38.375	69.78

APPENDIX (V) Adsorption isotherms data

(a) Cadmium

Co	Ce	Qe	1/qe	1/ce	Log Qe	Log Ce
14.75	1.2	2.168	0.461	0.8	-0.7176	-0.7176
28	3.9	3.856	0.259	0.257	-0.39019	-0.39019
41	7.75	5.32	0.188	0.129	-0.28133	-0.28133
78	35.5	6.8	0.147	0.013	-0.17718	-0.17718
468	300	6.72	0.148	0.002	-0.06824	-0.06824

(b) Copper

Co	Ce	V	M	Qe	1/Qe	1/Ce	logQe	log Ce
10.28	0.7	20	0.125	1.5328	0.652401	1.428571	-0.7176	-0.7176
21.3	0.94	20	0.125	3.2576	0.306974	1.06383	-0.39019	-0.39019
28.8	2.64	20	0.125	4.1856	0.238914	0.378788	-0.28133	-0.28133
30	0.75	20	0.25	2.34	0.42735	1.333333	-0.17718	-0.17718
38.2	4.95	20	0.125	5.32	0.18797	0.20202	-0.06824	-0.06824
50	2.12	20	0.25	3.8304	0.261069	0.471698		
51.8	9.07	20	0.125	6.8368	0.146267	0.110254		
100	5.57	20	0.25	7.5544	0.132373	0.179533		
200	19.1	20	0.25	14.472	0.069099	0.052356		
300	80.4	20	0.25	17.568	0.056922	0.012438		
400	130	20	0.25	21.6	0.046296	0.007692		
500	170	20	0.25	26.4	0.037879	0.005882		
600	184	20	0.25	33.28	0.030048	0.005435		
1000	565	20	0.25	34.8	0.028736	0.00177		

(c) Lead Langmuir data

Co	**Ce**	**qe**	**1/Ce**	**1/qe**
20	0	0.8	0.05	1.25
30	0	1.2	0.033	0.833
40	0	1.6	0.025	0.625
50	0	2	0.02	0.5
60	0	2.4	0.017	0.417
80	0	3.2	0.0125	0.3125
100	0	4	0.01	0.25
150	0	6	0.0067	0.17
200	0	8	0.005	0.125
300	3.91	11.8436	0.0033	0.085
400	7.3	15.708	0.0025	0.064
500	8.27	19.6652	0.002	0.051
600	78.04	20.8784	0.0017	0.0478
1000	228	30.88	0.001	0.0324

2. Freundlich data

ce	**qe**	**logCe**	**logqe**
0	3.344		
0	4.8		
0	5.984		

0	6		
0	6.288		
0	8		
0	9.888		
0	11.89		
0.8	12.928	-0.09691	1.111531
3.96	15.7592	0.597695	1.197534
4.99	16.448	0.698101	1.216113

(d) Zinc

Co	**Ce**	**V**	**M**	**Qe**	**Ce/qe**	**Ce**	**Qe**	**log Qe**	**logCe**
15.4	0.196	20	0.125	2.43264	0.080571	0.196	2.43264		
37.8	6.4	20	0.125	5.024	1.273885	6.4	5.024	0.386078	-0.70774
57.9	7.5	20	0.125	8.064	0.93006	7.5	8.064	0.906551	0.875061
76.4	14.2	20	0.125	9.952	1.426849	14.2	9.952	0.99791	1.152288
97.5	16.93	20	0.125	12.8912	1.313299	16.93	12.8912	1.110293	1.228657

Zinc adssorption isotherms data

Ce	**Qe**	**Ce/Qe**	**Ce**	**Ce/Qe**	**log Ce**	**log Qe**
10	5.88	1.7	10	1.7	1	0.769
20	8.696	2.3	20	2.3	1.3	0.94
30	10.71	2.8	30	2.8	1.48	1.03
40	11.76	3.4	40	3.4	1.6	1.07
50	12.5	4	50	4	1.69	1.09
60	12.5	4.8	60	4.8	1.78	1.09
100	12.96	7.71	100	7.71	2	1.11

Appendix (VI) Kinetics data

(a) Cadmium

(i) Kinetics data for cadmium adsorption (69 mg L^{-1})

Time(t min)	**Co**	**Ce**	**V**	**M**	**Qt**	**Qe**	**Qe-Qt**	**log(Qe-Qt)**
0	69	69	20	0.5	0	2.55	2.55	0.40654
5	69	7.5	20	0.5	2.46	2.55	0.09	-1.04576
10	69	7.5	20	0.5	2.46	2.55	0.09	-1.04576
15	69	7	20	0.5	2.48	2.55	0.07	-1.1549
20	69	7	20	0.5	2.48	2.55	0.07	-1.1549
25	69	7	20	0.5	2.48	2.55	0.07	-1.1549
30	69	6	20	0.5	2.52	2.55	0.03	-1.52288
35	69	5.5	20	0.5	2.54	2.55	0.01	-2
40	69	5.5	20	0.5	2.54	2.55	0.01	-2
45	69	5.5	20	0.5	2.54	2.55	0.01	-2
50	69	5	20	0.5	2.56	2.55	-0.01	
55	69	5	20	0.5	2.56	2.55	-0.01	
60	69	5	20	0.5	2.56	2.55	-0.01	

(ii) 432 mg L^{-1}

Time(t mins)	Co	Ce	V	M	Qt	qe	qe-qt	
0	432	432	20	0.5	0	6.64	6.64	0.822168
5	432	327	20	0.5	4.2	6.64	2.44	0.38739
15	432	300	20	0.5	5.28	6.64	1.36	0.133539
20	432	290	20	0.5	5.68	6.64	0.96	-0.01773
25	432	266	20	0.5	6.64	6.64	0	
30	432	239	20	0.5	7.72	6.64	-1.08	
35	432	235	20	0.5	7.88	6.64	-1.24	
40	432	210	20	0.5	8.88	6.64	-2.24	
45	432	216	20	0.5	8.64	6.64	-2	
50	432	173	20	0.5	10.36	6.64	-3.72	
55	432	172	20	0.5	10.4	6.64	-3.76	
60	432	172	20	0.5	10.4	6.64	-3.76	
65	432	152	20	0.5	11.2	6.64	-4.56	

(iii) Change in adsorption capacity with time

t	Time in minutes/ adsorption capacity at time t(Qt)											
Concentration	0	5	10	20	25	30	35	40	45	50	55	60	
69 mg L^{-1}	0	2.03	4.06	8.06	10.08	11.90	13.78	15.75	17.72	19.53	21.48	23.44	
1540 mg L^{-1}	0	0.27	0.45	0.76	0.95	1.13	1.32	1.50	1.69	1.88	2.07	2.26	

(b) Kinetics for copper adsorption

(i) 50 mg L^{-1}

50 ppm	ce	co	v	M	Qt	Qe	Qe-Qt	log(Qe-Qt)	t/Qt
0	4.81	50	20	0.5	1.808	2	0.193	-0.71579	0
5	2.41	50	20	0.5	1.904	2	0.096	-1.01592	2.626602
10	2.15	50	20	0.5	1.914	2	0.086	-1.06550	5.22466
20	2.90	50	20	0.5	1.884	2	0.116	-0.93554	10.61571
60	0	50	20	0.5	2	2	0		30.00000

(ii) 1000 mg L^{-1}

1000ppm	Ce	Co	V	M	Qt	Qe	Qe-Qt	log Qe-Qt	t/Qt
0	811	1000	20	0.5	7.56	19.52	11.96	1.077731	0
5	662.5	1000	20	0.5	13.5	19.52	6.02	0.779596	0.37037
10	556.5	1000	20	0.5	17.74	19.52	1.78	0.25042	0.563698
20	512	1000	20	0.5	19.52	19.52	0		1.02459
60	481	1000	20	0.5	20.76	19.52	-1.24		2.890173

(c) Kinetics data for lead adsorption

(i) 60 mg L^{-1}

60 mg/L	Ce	Co	V	M	Qt	Qe	Qe-Qt	log(qe-Qt)	t/Qt
0	4.972	60	20	0.5	2.20112	2.4	0.19888	-0.7014	0
5	0	60	20	0.5	2.3	2.4	0		2.173913
10	0	60	20	0.5	2.4	2.4	0		4.166667
15	0	60	20	0.5	2.4	2.4	0		6.25
20	0	60	20	0.5	2.4	2.4	0		8.333333
25	0	60	20	0.5	2.4	2.4	0		10.41667
30	0	60	20	0.5	2.4	2.4	0		12.5
35	0	60	20	0.5	2.4	2.4	0		14.58333
40	0	60	20	0.5	2.4	2.4	0		16.66667
45	0	60	20	0.5	2.4	2.4	0		18.75
50	0	60	20	0.5	2.4	2.4	0		20.83333
55	0	60	20	0.5	2.4	2.4	0		22.91667
60	0	60	20	0.5	2.4	2.4	0		25

(ii) 150 mg L^{-1}

150 mg/L	**Ce**	**Co**	**V**	**M**	**Qt**	**Qe**	**Qe-Qt**	**log(Qe-Qt)**	**t/Qt**
0	13.8	150	20	0.5	5.448	6	0.552	-0.25806	0
5	0	150	20	0.5	6	6	0		0.833333
10	0	150	20	0.5	6	6	0		1.666667
15	0	150	20	0.5	6	6	0		2.5
20	0	150	20	0.5	6	6	0		3.333333
25	0	150	20	0.5	6	6	0		4.166667
30	0	150	20	0.5	6	6	0		5
35	0	150	20	0.5	6	6	0		5.833333
40	0	150	20	0.5	6	6	0		6.666667
45	0	150	20	0.5	6	6	0		7.5
50	0	150	20	0.5	6	6	0		8.333333
55	0	150	20	0.5	6	6	0		9.166667

(iii) 1000 mg L^{-1}

1000 mg/L	**Ce**	**Co**	**V**	**M**	**Qt**	**Qe**	**Qe-Qt**	**log(Qt-Qe)**	**t/Qt**
0	52	1000	20	0.5	37.92	39.888	1.968	0.294025	0
5	9.2	1000	20	0.5	39.632	39.888	0.256	-0.59176	0.126161
10	6.9	1000	20	0.5	39.724	39.888	0.164	-0.78516	0.251737
15	5.4	1000	20	0.5	39.784	39.888	0.104	-0.98297	0.377036

20	3.9	1000	20	0.5	39.844	39.888	0.044	-1.35655	0.501958
25	4.12	1000	20	0.5	39.8352	39.888	0.0528	-1.27737	0.627586
30	4.68	1000	20	0.5	39.8128	39.888	0.0752	-1.12378	0.753527
35	2.56	1000	20	0.5	39.8976	39.888	-0.0096		0.877246
40	3.42	1000	20	0.5	39.8632	39.888	0.0248	-1.60555	1.003432
45	2.76	1000	20	0.5	39.8896	39.888	-0.0016		1.128114
50	2.8	1000	20	0.5	39.888	39.888	0		1.25351
55	2.8	1000	20	0.5	39.888	39.888	0		1.378861
60	2.8	1000	20	0.5	39.888	39.888	0		1.504212

(d) Kinetics data for zinc adsorption

(i) (20 mg L^{-1})

t	**Ce**	**Co**	**v**	**M**	**Qt**	**Qe**	**Qe-Qt**	**log(Qe-qt)**	**t/Qt**
0	6.76	20	20	0.5	0.5296	0.8	0.2704	-0.568	0
5	0.25	20	20	0.5	0.79	0.8	0.01	-2	6.329114
10	0.05	20	20	0.5	0.798	0.8	0.002	-2.699	12.53133
15	0	20	20	0.5	0.8	0.8	0		18.75
20	0	20	20	0.5	0.8	0.8	0		25
25	0	20	20	0.5	0.8	0.8	0		31.25
30	0	20	20	0.5	0.8	0.8	0		37.5
40	0	20	20	0.5	0.8	0.8	0		50
45	0	20	20	0.5	0.8	0.8	0		56.25
50	0	20	20	0.5	0.8	0.8	0		62.5
55	0	20	20	0.5	0.8	0.8	0		68.75
60	0	20	20	0.5	0.8	0.8	0		75

(ii) 200 mg L^{-1}

t	Ce	Co	V	M	Qt	Qe	Qe-Qt	log(Qe-Qt	t/Qt
0	138	200	20	0.5	2.48	7.4	4.92	0.691	0
5	24	200	20	0.5	7.04	7.4	0.36	-0.444	0.710227
10	10	200	20	0.5	7.6	7.4	-0.2		1.315789
15	15	200	20	0.5	7.4	7.4	0		2.027027
20	15	200	20	0.5	7.4	7.4	0		2.702703
25	15	200	20	0.5	7.4	7.4	0		3.378378
30	14	200	20	0.5	7.44	7.4	-0.04		4.032258
40	10	200	20	0.5	7.6	7.4	-0.2		5.263158
45	10	200	20	0.5	7.6	7.4	-0.2		5.921053
50	7	200	20	0.5	7.72	7.4	-0.32		6.476684
55	7	200	20	0.5	7.72	7.4	-0.32		7.124352
60	7	200	20	0.5	7.72	7.4	-0.32		7.772021

(iii) 1000 mg L^{-1}

t	Ce	Co	V	M	Qt	Qe	Qe-Qt	log(Qe-Qt
0	806	1000	20	0.5	7.76	19.72	11.96	1.077731
5	536	1000	20	0.5	18.56	19.72	1.16	0.064458
10	503	1000	20	0.5	19.88	19.72	-0.16	
15	507	1000	20	0.5	19.72	19.72	0	
20	507	1000	20	0.5	19.72	19.72	0	
25	482	1000	20	0.5	20.72	19.72	-1	
30	503	1000	20	0.5	19.88	19.72	-0.16	
40	499	1000	20	0.5	20.04	19.72	-0.32	
45	497	1000	20	0.5	20.12	19.72	-0.4	
50	502	1000	20	0.5	19.92	19.72	-0.2	
55	503	1000	20	0.5	19.88	19.72	-0.16	
60	502	1000	20	0.5	19.92	19.72	-0.2	

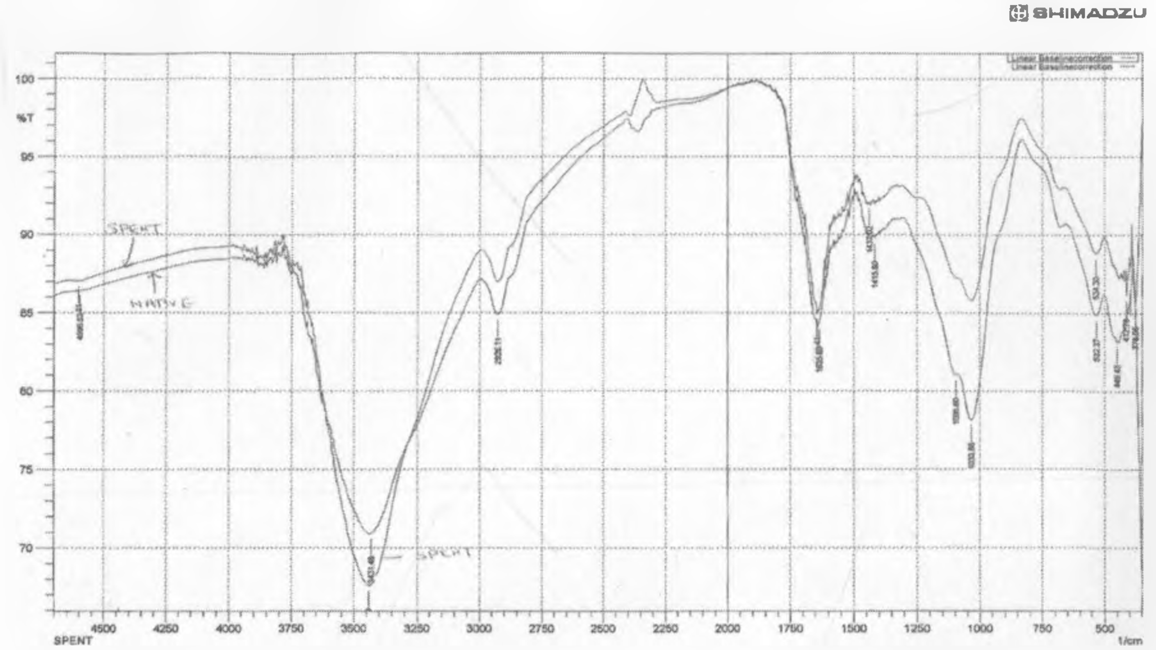
(iv) Relationship between adsorption capacity and time for adsorption of zinc onto *E.crasippes*

Time(t) in min	**0**	**5**	**10**	**15**	**20**	**25**	**30**	**40**	**45**	**50**	**55**	**60**
20 mg L^{-1}	0	6.34	12.54	18.75	25.00	31.25	37.50	50.00	56.25	62.50	68.75	75
200 mg L^{-1}	0	0.72	1.32	2.02	2.70	3.38	4.03	5.27	5.92	6.48	7.12	7.77
1000 mg L^{-1}	0	0.26	0.50	0.76	1.01	1.21	1.51	1.99	2.24	2.51	2.77	3.01

APPENDIX (VII) Point of zero charge determination

pHo	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
ΔpH	4	5	4.25	3.6	3	1.8	0	-2

APPENDIX (VIII) FTIR SPECTRA



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SPENT Resolution; 14/06/2010 Administrator

NATURE Administrator