EFFICACY AND KINETICS OF ADSORPTION OF SINGLE AND MULTIPLE HEAVY METAL CATIONS FROM AQUEOUS SOLUTIONS BY FRUIT WASTE PRODUCTS

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DECLARATION

This thesis is my original work and has not been presented for the award of a degree or any other award in any other University

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DEDICATION

I dedicate this work to my loving children Johnpeter and Joan for their support, encouragement and the sacrifice they gave me throughout my PhD Degree engagement.

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ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
MAS	Modified Avocado Seed
MBP	Modified Banana Peel
MLP	Modified Lemon Peel
MSYP	Modified Sweet Yellow Passion Peel
MWP	Modified Watermelon Peel
SEM	Scanning Electron Microscopy
UMAS	Unmodified Avocado Seed
UMBP	Unmodified Banana Peel
UMLP	Unmodified Lemon Peel
UMSYP	Unmodified Sweet Yellow Passion Peel
UMWP	Unmodified Watermelon Peel
WHO	World Health Organization
XRD	X-ray Diffraction

ABSTRACT

Removal of toxic heavy metals from water has been a major challenge, especially in rural areas. Various methods have been used for this purpose; among them is bio-sorption based technology. The technology has been recognized as an economical and eco-friendly method for removal of toxic anions and cations from wastewater. Moreover, the efficacy of biomass in adsorption of cations and anions can be improved by different modifications, including treatment with sulphuric acid. Numerous approaches have been developed for adsorption of single ions in solution. However, toxic metallic or non-metallic ions rarely occur singly in wastewater. The presence of multiple ions in solution may often have agonistic or antagonistic effect on the efficiency of an adsorbent, and there is insufficient information on the efficacy of different methods for removing multiple ions. This study assessed the efficacy and mechanism of acid treated (modified) and raw (unmodified) biosorbents (derived from lemon, sweet yellow passion, banana, watermelon peels, and avocado seeds) for removal of toxic cations (Cd, Pb and Cu) from water. Functional groups of adsorbents were identified by mid-infrared spectroscopy (MIR) and their surface morphology was probed by scanning electron microscopy (SEM). The efficacy of each adsorbent was evaluated by quantifying the kinetics and levels of cations adsorbed at different pH of the solution, initial concentrations, contact time and adsorbent dose. Desorption experiments were conducted to determine the possibility of recovering ions and reusing the sorbents for next cycle of deployment. Experimental data of each metal ion was described by either Freundlich isotherm or Langmuir isotherm. The acid treated fruit peels and avocado seeds recorded higher efficacy as compared to raw adsorbents. Generally, acid treated watermelon peels demonstrated the highest uptake of 130.23 mg/g of Pb (II), followed by 114.234 mg/g of Cu (II) and 97.14 mg/g of Cd (II) ions. Further adsorption trials with binary and ternary metal blends on showed significant reductions in metal uptake capacities of evaluated adsorbents as compared to single metal systems. On account of metal preference, the selectivity order for metal ions towards the all the studied biomass was Pb (II) > Cu (II) > Cd (II). Time-course measurements indicated involvement of pseudo-second-order kinetics in adsorptions. Desorption efficacies were high on acid-treated adsorbents: 99.97 % of Pb(II) ions from acid treated avocado seeds; and 99.79 % of Cu(II) and 99.23 % of Cd (II) from acid treated watermelon peels. The results show good performance of the fruit peels and avocado seeds in adsorbing single and multiple metal ions, and the potential of using such wastes for purifying drinking and cooking water at household level.

CHAPTER ONE

INTRODUCTION

1.1 Background information

Currently, water pollution by heavy metals is fast growing due to natural processes and increasing human activities which include mining, agriculture, and manufacturing industries. These heavy metals are non degradable and cannot be detoxified biologically (Kumar *et al.*, 2014). One of the ways to address heavy metal pollution is to treat the polluted water through removal of introduced contaminants. Industrial revolution on one hand has improved the living standards of life, and on the other hand it pollutes the environment due to untreated discharge of effluents (Mudhoo *et al*., 2011). Pollution of water resources due to disposal of heavy metals has been an increasing worldwide concern for the last few decades (Feng and Guo *et al*., 2012). Heavy metal contamination of water and industrial effluents is one of the key concerns environmental problems due to the toxic nature and accumulation of these metal ions in the food chain (Kumar *et al*., 2014).

The effluent from various processing industries such as electroplating industries is reported to contain large amounts of heavy metal ions such as nickel, iron, lead, zinc, chromium, cadmium and copper (Konstantinos *et al*., 2011). Other industrial processes like metal mining, mineral processing, pigment manufacture, painting, tanning in leather industry, dyeing in textile industry also contribute in the release of pollutants (Rasheed *et al.*, 2013).

Research into the contamination of water by metal species continue to attract special attention due to the high dilution capacity of water, the possible accumulation of heavy metals in plants, fish, and sediments (Minello *et al*., 2010). While many of the heavy metals are needed by biological systems at the micronutrient level, higher concentrations are known to produce a range of toxic effects (Fu and Wang, 2011).

Although several adverse health effects of these metals have been known for a long time, exposure to heavy metals continues and is still increasing in some parts of the world, especially in less developed countries (Moyo and Chikazaza, 2013). For example, mercury is still used in gold mining in many parts of Latin America, arsenic is still common in wood preservatives, and tetraethyl lead remains a common additive to petrol, although this use has decreased dramatically in the developed countries (Kumar *et al.,* 2014). Copper is used in electric equipment, water pipes, alloy, as chemical catalysts and in anti-fouling paints on ship hulls (Rasheed *et al*., 2013).

Heavy metals cannot be degraded and persist in the environment causing adverse effects on human and animals. Excessive ingestion of these metals by humans is reported to cause cancer, nervous system damage and ultimately death (Rasheed *et al.,* 2013). Therefore, metal concentration must be brought below permissible limits using efficient treatment technologies. Prolonged exposure to lead (Pb) causes encephalopathy, cognitive impairment, behavioral disturbances, kidney damage, anemia and toxicity to the reproductive system (Fu and Wang, 2011). Cadmium (Cd) has been established as a very toxic heavy metal. Due to its acute toxicity, Cd has recently joined lead and mercury in the most toxic ‘‘Big Three’’ category of heavy metals with the greatest

potential hazard to humans and the environment (Kumar *et al*., 2014). Symptoms of acute poisoning include headaches, nausea, vomiting, weakness, pulmonary edema and diarrhea. A disease known as *Itai–Itai* in Japan is specifically associated with cadmium poisoning, resulting in multiple fractures arising from osteomalacia (Farooq *et al.*, 2010, Kumar *et al*., 2014). High dose of copper concentrations can lead to weakness, lethargy, anorexia and damage to the gastrointestinal tract, Cu in the blood system may generate reactive free oxygen species and damage the protein, lipids and DNA. Excess copper compound in the body may also have effects on aging, schizophrenia, mental illness, Indian childhood cirrhosis, Wilson's and Alzheimer's diseases (Hossain *et al*., 2012).

A wide range of methods are used for removing heavy metal ions from aqueous solutions based on physical, chemical and biological mechanisms (Kumar *et al.,* 2014). Some of them involve coagulation, foam flotation, filtration, ion exchange, sedimentation, solvent extraction, adsorption, electrolysis, chemical oxidation, disinfection and chemical precipitation (Hossain *et al.*, 2012). Other technologies such as ultra filtration, nano-filtration, and reverse osmosis are associated with high capital and operational costs (Miretzky *et al*., 2006).

Among the various available technologies for water pollution control listed above, adsorption process is considered better compared to other methods because of its convenience, easy operation and simplicity of design (Amit and Minocha, 2006). Activated carbon has been the most popular and widely used adsorbent in wastewater treatment throughout the world, however, its use has been restricted by high cost and incomplete regeneration (Ahmed and Kumar, 2010). Attempts are being made to

develop low cost and effective anionic and cationic sorbents from natural materials, industrial wastes and agricultural wastes (Liang *et al.,* 2012).

Disposal of waste materials is increasingly becoming a major problem because these wastes represent unused resources and are also of health concerns (Amit and Minocha, 2006). A large number of solid wastes are produced in the agricultural sector in most of the countries, these include, yam peels, cassava peels, banana peels, orange peels, Irish potato peels, sweet potato peels, plantain peels, rice-husks, saw-dusts, maize cob, maize-husks, fluted pumpkin stem, okra stem derived cellulose, coca pods, coconut fibers, among others (Okoro *et al.,* 2007; Moyo and Chikazaza, 2013). Most of these wastes are normally disposed as waste or used as domestic fuels. However, these materials have relatively high fixed carbon content and porous structure, which can be explored as low cost alternative adsorbents (Amit and Minocha, 2006).

Many studies on biosorption have provided insights into the identification of several biomasses for single-metal-ion solutions (Shoaib *et al.,* 2011). However, single toxic metallic species rarely occur on their own in wastewaters. In fact, presence of multiple metal ions often causes an interactive effects and insufficient attention has been given to this problem (Sheng *et al*., 2007; Shoaib *et al*., 2011). The actual wastewater treatment systems have to deal with mixtures of heavy metals, however, most research work has focused on a single metal sorption, and to date, only a few studies have been reported on the adsorption of multiple ions in water (Khairia, 2012).

Adsorbents derived from fruit peels like orange and banana peels have been studied for removal of heavy metal ions from water (Husoon, 2013, Banerjee *et al.,* 2012, Ashraf *et al*., 2011). Avocado seeds have also not received serious consideration as a sorbent for binary and multiple metal ions in solution. Some of the advantages of using agricultural by-products for wastewater treatment include good adsorption capacity, particularly for selective adsorption of heavy metal ions, requiring minimal processing, low cost, free availability and easy regeneration (Shoaib *et al.,* 2011).

Pretreatment of plant wastes can remove soluble organic compounds and enhance chelating efficiency (Wan and Hanafiah, 2008). Use of different kinds of modifying agents such as basic solutions (sodium hydroxide, calcium hydroxide, sodium carbonate) mineral and organic acid solutions (hydrochloric acid, nitric acid, sulfuric acid, tartaric acid, citric acid, thioglycollic acid), organic compounds (ethylenediamine, formaldehyde, epichlorohydrin, methanol), oxidizing agent (hydrogen peroxide) and dye (Reactive orange 13) for the purpose of removing soluble organic compounds, eliminating colouration of the aqueous solutions and increasing efficiency of metal adsorption has been investigated by many researchers (Harman *et al*., 2007; Wankasi *et al.*, 2008)

Recovery and regeneration of spent adsorbents and metals is very important as it reduces the cost of remediation of heavy metals and other contaminants in water (Wankasi *et al*., 2008). Metals adsorbed on surface of biosorbents can be recovered by use of adequate eluents (Kumar *et al*., 2014). In this sense, desorption and reutilization of the biosorbents in adsorption–desorption cycles could help in reducing these residues

which can be carried out by proton exchange using acids, chelating agents (EDTA) or exchange with other ions (e.g. $CaCl_2$) (Mata *et al.,* 2010).

Biosorption isotherm models are widely employed to examine the relationship between the adsorbed and the aqueous concentrations at equilibrium (Ashraf *et al*., 2011). Adsorption equilibrium is established when the concentration of the adsorbate in a bulk solutions is in dynamic balance with that of the biosorbent interface (Banerjee *et al.,* 2012). An adsorption isotherm is characterized by certain constants, the values of which describe the surface properties and affinity of the biosorbent and can be used to compare adsorptive capacities of various biomasses (Herrero *et al*., 2005).

The degree of the adsorbent affinity to the adsorbate (metal ion) determines its distribution between the solid and liquid phases. The mathematical models are used for analysis of equilibrium data, which could be used for predicting metal ion biosorption, reflecting the mechanism of metal uptake and the influence of the variables such as pH, presence of competing metal ions among others (Feng and Guo, 2012).

Adsorption equilibrium studies are important to conclude the efficacy of adsorption. In spite of this, it is also necessary to identify the adsorption mechanism type in a given system. Kinetic models have been exploited to evaluate the mechanisms of biosorption of heavy metals and its potential rate controlling steps that include mass transport and chemical reaction processes (Kumar *et al.,* 2014). Information on the kinetics of metal uptake is required to select the optimum condition for full scale batch metal removal

processes (Febrianto *et al*, 2009). Various factors govern the adsorption capacity, i.e., initial heavy metals concentration, temperature, pH of solution, biosorbent dose and heavy metals nature.

A kinetic model is necessary to have an understanding of time dependence of concentration distribution of the solute in bulk solution and solid adsorbent (Koel *et al*., 2012). Several adsorption kinetic models have been established to understand the adsorption kinetics and rate limiting step. These include pseudo-first and -second-order rate model, Weber and Morris sorption kinetic model, Adam–Bohart–Thomas relation, first-order reversible reaction model, external mass transfer model, first-order equation of Bhattacharya and Venkobachar, Elovich's model and Ritchie's equation(Asku, 2001). The pseudo-first and second-order kinetic models are the most widely used (Kumar *et al.,* 2014).

1.2 Statement of the Problem and justification

Safe and sustainable water supply is paramount to human health and well being of any society. An estimated 1.2 billion people in the world drink unclean water which is a source of water borne diseases killing about 5-50 million people (Ahuja, 2009). In Kenya about 17 million people (43 %) do not have access to clean water (Samantha, 2011). Water shortage in Kenya has been a major issue caused by recurrent drought, poor management of water supply and contamination of available water due to high population growth. Only 42 % of rural population has access to water as opposed to urban population where 88 % of population has access to safe water (Mulei, 2012).

Pollution of water sources due to disposal of toxic heavy metals such as copper, zinc, nickel, cadmium and lead, among others, has been of great concern over the last few decades (Liang *et al.,* 2012). Unlike organic wastes, heavy metals are non-biodegradable and they can accumulate in living tissues, causing various diseases and disorders such as cancer. Therefore, they need to be removed before discharge (Liang *et al.,* 2009). Climate change and industrialization have made it difficult to provide sufficient clean water for domestic use. Currently there is a need to come up with simple and affordable methods of cleaning polluted water. This is especially important in developing countries where people depend on river water which is sometimes highly polluted.

While there are numerous conventional water treatment technologies available, for a huge population in rural areas, these systems are either inappropriate or too expensive. These rural communities have adopted some simple water treatment techniques such as filtration and water clarification which aim to remove visible impurities such as leaves, twigs or large suspended solids by from water collected from unprotected local sources (Virgneswaran and Sundaravadivel, 2015). It is estimated that approximately 50 % of households in Kenyan use dilute hypochlorite product sold in name of "Water Guard" which disinfects drinking water (Miguel, 2008). Of these methods heavy metal contamination is not addressed.

Decontamination of toxic pollutants from water poses a major challenge, and therefore numerous approaches have been explored for their removal (Jaramillo *et al.,* 2009).

Biosorption has shown promise in removal of toxic ions from water (Babel and Kurniawan, 2003). The adsorption properties of biological waste materials such as peat, wood, pine bark among others leaves have been mainly reported for carbonized samples (Pino *et al*., 2006). Activated carbon, which has been used in treating waste water, is not affordable, and therefore, there is need for alternative cheaper products (Babel and Kurniawan, 2003). Natural sorbents mainly obtained from plant wastes and fruit peels, banana, orange, are effective in removing copper from waste water without chemical modifications (Hossain *et al.,* 2012).

Treated sorbents derived from locally available materials such as fruits wastes have received increasing attention for removal and recovery of heavy metals from wastewater systems (Moyo and Moyo and Chikazaza, 2013). Fruits wastes are inexhaustible, non-edible and renewable polymeric materials which are in most cases discarded as wastes (Moyo and Chikazaza., 2013). Furthermore, fruit peels and seeds have not been tested for a wide range of metal ions. Actual wastewater treatment systems have to deal with a mixture of cations and anions, this is because single toxic ionic species rarely exist in waste waters (Shoaib *et al*., 2011). Presence of multiple ions often causes an interactive effect, and insufficient attention seems to have been given to the problem (Sheng *et al*., 2007).

Adsorption kinetics are one of the important characteristics in the defining the efficiency of an adsorption process and to understand the behavior of the adsorbent (Rasheed *et al.*, 2013). Kinetics experiments are initially necessary in order to

determine the time required to achieve the sorption equilibrium (Kumar *et al.,* 2014). The kinetic sorption may be controlled by several independent processes such as transport phenomenon (bulk, film or pore diffusion) and chemical reactions, which normally act in conjunction (Ho and Mckay, 1998).

There is also the need to establish the best adsorbent which can remove most of the ions in solution by performing competitive experiments with different types of ions. This study sought to assess the kinetics and efficiency of fruit wastes adsorbents derived from avocado seeds and peels (banana, watermelon, sweet yellow passion and lemon) in their natural and acid treated form for adsorption of Cu, Pb and Cd in single, binary and ternary systems. To shed light on the structural features of the adsorbents, their surface morphologies were assessed using scanning electron microscopy (SEM), in addition, candidate active sites were characterized using mid infrared spectroscopy (MIR).

1.3 Hypotheses

i. Adsorption process of metal ions onto biomass is affected by factors such as pH, concentration and residence time of the adsorbate and mass of adsorbent.
ii. Modification of adsorbents can improve sorption properties of toxic cations from water.
iii. A combination of different ions in solution can lead to antagonistic or agonistic effect on the efficiency of an adsorbent.

1.4 Objectives

1.4.1 General objective

To evaluate the kinetics and efficacy of fruit waste products in natural and acid treated form for removal of cations.

1.4.2 Specific objectives

i) To determine the rates and efficiency of adsorption of Cu (II), Pb (II), and Cd (II) ions on selected peels (lemon, banana, watermelon and sweet yellow passion) and avocado seeds in aqueous media.

ii) To determine the effect of chemical modifications involving treatment with sulphuric acid on the relative efficiency of the adsorbents.

iii) To determine efficiency of desorption of Cu (II), Pb (II), and Cd (II) ions on selected peels (lemon, sweet yellow passion, watermelon) and avocado seeds in aqueous media

iv) To determine the efficiency of the adsorbents in removal of Cu (II), Pb (II), and Cd (II) ions from real water samples

1.5 Significance of the study

The results from this study can be used to develop new and cheaper materials/adsorbents for removal of most of toxic ions from waste water. Water treatment using fruit wastes will provide a solution to the problems associated with

consumption of such water. Use of fruit waste will solve the environmental effects of dumping waste as well as provide jobs to those collecting waste.

1.6 Scope and limitations

In addition to heavy metals, there are other contaminants that get into water systems, such as bacteria and organic compounds. However, due to cost and limited time involved this study has focused only on three commonly occurring heavy metals (Pb, Cd and Cu) in local waste water. There are many agricultural wastes, however this study assessed on selected fruit wastes, without any considerations to species/variety, maturity, additives/treatment, season and geographical area, packaging and shelve life.

mount of heavy metals which cannot be removed using other methods (Vinh *etal*., 2015). This study investigated the efficiency of fruit waste in adsorbing heavy metal cations from water.

2.2 Adsorption process

Adsorption process is essentially a surface phenomenon (Ferreira *et al*., 2012). It results from electrostatic interactions and/or of the formation of complexes between metal ions and functional groups present on the surface of adsorbent (Feng and Guo, 2012). Various factors such as specific surface area, pore-size distribution, pore volume and presence of surface functional groups influence the adsorption capacity of adsorbents prior to their modification, so that they may be tailored to have the desired physical and chemical attributes to enhance their affinities towards metal ion uptake from aqueous solutions (Ferreira *et al.,* 2012). Adsorption capacity increases with increase in specific surface area due to the availability of the number of adsorption sites on surface of biomass (Ruthven, 1984; Kumar *et al*., 2014). The adsorptive properties also depend on the distribution of size pore and the nature of the solid surface (Rius *et al*., 2011).

Studies have been conducted to assess the potential for removing heavy metals from various biological materials (Ngah *et al.*, 2011), this includes a wide variety of bacteria and fungi (Watanabe *et al.*, 2003), agricultural residues (Suzuki *et al.,* 2007), among others. The adsorbents most commonly used on an industrial scale are the activated carbon, silica gel, activated alumina and molecular sieves (Ferreira *et al.*, 2012).

CHAPTER TWO

LITERATURE REVIEW

2.1 Water pollution

Existence of trace metals in water is widespread in surface water and ground water sources (Chakraborti, 2011). Heavy metals which are significantly toxic to human beings and ecological environments include mercury, copper, lead, cadmium, zinc, nickel among others (Liang *et al.,* 2009). Even when the levels of these metals are acceptable, there is a risk when ingested for a long period of time due to cumulative effect in the soft and hard tissues such as kidney and bones of our body (Mwangi *et al*., 2012). In addition to disinfection of water using chlorinated compounds, methods that remove heavy metals from water are required. More than 50% of rural population in Kenyan have no access to treated water and rely on traditional methods of water treatment such as filtration (World Bank, 2010).

Due to continued population growth it has been estimated that by 2025, Kenya's per capita water availability will be 235 m^3 per year, which is two thirds less than the current 650 m^3 per year (Samantha, 2011). Therefore, there is need to develop affordable methods of water treatment which are applicable at house hold levels. Several technologies are available for the treatment of heavy metals containing wastewaters. Among them, chemical precipitation, reverse osmosis oxidation-reduction, electro-dialysis, solvent extraction and adsorption (Jain *et al*., 2016). Adsorption is the most sort out technology for such kind of waters which contain trace

Charcoal is one of the most widely used solid, worldwide, as an adsorbent to remove pollutants in wastewater due to its high porosity, chemical structure and high surface area (Cm, 2015). In addition the chemical structure of this material allows surface modifications by chemical or physical treatments, allowing an increase in adsorption capacity of this material (Gönen and Serin, 2012).

2.3 Biosorption

Biosorption is the ability of certain inactive, dead microbial biomass to bind and concentrate heavy metals from aqueous solutions, the processes include ion exchange, coordination, complexation, chelation, adsorption and micro precipitation (Khan *et al.*, 2013). The biosorption process is based on the interaction of ions at an interface in a biomass/aqueous medium (Ferreira *et al*., 2012). The separation can be performed in packed columns, fluidized beds or in the form of discs to be used in the filtration process (Feng and Guo, 2012). This configuration allows for regeneration and reuse of the adsorbent and its proper disposal (Kumar *et al.*, 2014).

Dissolved metals exist as positively charged ions which can bind to negatively charged organic molecules (Molony and Bhamidipati, 2005). Research has shown that biomass can passively bind metals and other pollutants such as dyes or organic compounds on chemically active sites or functional groups (Mata *et al*., 2010). Waste from lignocellulosic biomass is one of the rich sources of low-cost adsorbents besides industrial by- product and natural materials (Srinivasa *et al.*, 2009). Due to its abundant

availability the waste such as peanut husk, rice husk, coconut shell, wheat bran and sawdust offer little economic value and, moreover, create serious disposal problems (Farooq *et al*., 2010). These products are renewable, biodegradable, cheap and readily available (Okoro and Okoro, 2011; Gönen and Serin, 2012). The waste has been used by researchers to remove and recover anions and cations from wastewater environments (Harman *et al.*, 2007; Okoro and Okoro, 2011).

Numerous materials have been studied for development of cheap and effective metal sorbents, they include, peat (Ma and Tobin, 2003; Husoon, 2013), Lemon peels (Husoon, 2013), sugarcane bagasse (Huu *et al.,* 2014), sawdust (Khan *et al.,* 2013), coconut husk (Benard and Jimoh, 2013), orange peels (Feng and Guo, 2012; Khalfaoui and Menai, 2012; Liang *et al*., 2012; Mandina *et al*., 2013), banana pith (Hossain *et al*., 2012) and pine bark (Benard and Jimoh, 2013) among other. Studies that have been conducted in Kenya include, use of lignocelluloses, clay non-composites (Bunhu and Tichagwa, 2009) and raw bouxite (Kayira *et al.*, 2009).

Many of these studies are based on adsorption of heavy metal ions from mono-metal solutions by various adsorbents (Li *et al*., 2003; Machida *et al.,* 2004; Sud and Mahajan, 2008; Reddy *et al*., 2010; Nguyen *et al*., 2013; Vinh *et al*., 2015;). Some of the experimental studies that have been conducted to determine equilibrium adsorption capacities for various ions on fruit peels are shown in table 2.1. Studies involving treatment of fruit waste with sulphuric acid have not been reported, therefore this study sort to investigate sorption of heavy metal cations in single, binary and ternary systems

on sulphuric acid treated avocado seed and fruit peels of banana, lemon, sweet yellow passion and watermelon.

Table 2.1: Adsorption capacity at equilibrium of selected agricultural byproducts

Adsorbent	Metal	Adsorption Capacity q_m(mg/g)	Reference
Pomelo peels	Cd (II)	21.83	(Saikaew *et al.*, 2009)
Watermelon peels (Raw)	Cu (II)	111.1	(Koel *et al.,* 2012)
Mango treated(HCl)	Cu (II)	42.6	(Reddy *et al.,* 1997)
Banana peels (Raw)	Pb(II	71.42	(Muhammad *et al.*, 2011)
	Cu (II)	1.439	(Hossain *et al.,* 2012)
Banana stem Treated (Fomaldehyde)	Pb (II)	91.74	(Neoline *et al.*, 2005)
	Cu (II)	13.46	
Orange peels	Pb (II)	113.5	(Liang *et al.*, 2012)
	Cu (II)	44.28	
Orange peels (modified)	Cu (II)	209.8	(Liang *et al.*, 2012)

Studies on multiple metals adsorption are important to assess the level of interference caused by other ions present in the water and the efficiency of adsorbent to remove those ions from water (Srivastva *et al.*, 2006). Recently, competitive adsorption of various heavy metals in multiple metal systems has been reported. These include; adsorption of Ni(II), Cd(II) and Cr (IV) from multi-metal aqueous solution using sunflower plant biomass (Jain *et al.*, 2015), adsorption of Cu(II), Pb(II) and Zn(II) from single, binary and ternary system using e-waste-based adsorbent (Hadi *et al,.* 2014), adsorption capacity of activated carbon for Cd(II) and Zn(II) in multi-metal system

(Mohan and Singh, 2002), adsorption capacity of Pb(II) and Cd(II) by dried *Carpobrothus edulis* in binery system (Chiban *et al*., 2011) among others. In multi-metal component system, metal ions interact with each other in synergistic, antagonistic or non-interactive manner and the results cannot be predicted on the basis of single metal studies (Ting and Teo, 1994; Jain *et al*., 2015). Therefore, it is worthwhile to study the simultaneous adsorption of two or more metals and also to quantify the interference of a metal with the adsorption of other.

2.4 Modification of adsorbent

In general, all types of biomaterials have shown good biosorption capacities towards all types of metal ions (Febrianto *et al*., 2009). However, studies have reported that uptakes of metals on raw lignocellulosic materials are usually low depending on metallic ion and operating conditions (Bilal *et al.*, 2013). Metal uptake on treated biomass is higher than that of untreated biomass depending on the chemical agent and operating conditions (Leyva-Ramos *et al*., 2012). Therefore, it is important to subject biomass to pre-treatment to obtain a better operating performance in pollutant removal using adsorption method (Naja *et al*., 2010).

Furthermore, it has been reported that during biosorption processes there is a problem of leaching of organic matter from the biosorbent which leads to change in color and taste of the final treated water a phenomenon known as secondary pollution (Chen and Yang, 2005). Metal ions contained in the biomass can also be leached in water when raw

biomaterial is used affecting the sorption process (Sheng *et al*., 2004). This limits the application of raw biomass for water treatment, particularly if intended for purposes of treatment of drinking water. In order to address the above challenge, chemical modification is required to offer possible solutions. Thus this study investigated effects of chemical modification of fruit waste in removal of copper, lead and cadmium from water.

Carbon surface can be treated to develop desirable physico-chemical properties by adequate choice of activation procedures. It is even possible to prepare carbons with designated proportions of pores (Srivastava *et al.,* 2009; Banerjee *et al.,* 2012; Kumar *et al.,* 2014). The techniques of modification of microbial cells in order to elucidate the mechanism of sorption can be categorized into three broad groups: chemical, physical and biological characteristics. The physical treatments include heating/boiling, freezing/thawing, drying and lyophilization (Kyzas *et al.,* 2014). Among these three methods, modification with chemical compounds has been more frequently employed to increase the adsorption and hence removal capacity of activated carbon or similar biosorbents (Kumar *et al*., 2014).

Pretreatments could modify the surface characteristics either by removing or masking the groups or by exposing more metal binding sites (Kumar *et al*., 2014). Physical methods include vacuum and freeze-drying, boiling or heating, autoclaving and mechanical disruption (Marandi, 2011; Kumar *et al*., 2014). Chemical methods include treatment with various organic and inorganic compounds, such as acid and caustic,

methanol, formaldehyde (Ashraf *et al*., 2011; Joseph *et al*., 2013). It appears that improvements on sorption properties of biomass are higher using acid treatment than those obtained with other chemical agents (Marshall *et al*., 1999; Leyva-Ramos *et al*., 2012; Bojic *et al.,* 2013). Treatment of biomass with strong and weak acids increases the total amount of acidic functional groups on the surface of biomass (Li *et al*., 2011). Of these acids, treatment with sulphuric acid has been reported to have the highest effect on efficiency of biomass on removal of heavy metal ions from water (Shah *et al.,* 2011; Díaz-muñoz *et al.*, 2016). Treatment of biomass with sulphuric acid has been associated with increase in porous structure of the biomass, during activation the acid reacts with the cellulosic, lignin and other functional groups and it also generates enormous amount of heat that helps to create active sites and poles which enhances the sorption capacity of metals (Anandkumar and Mandal, 2012). In this study treatment was carried out using sulphuric acid.

2.5 Heavy metal contamination

Heavy metals are natural constituents of the earth's crust. Human activities have drastically altered the biochemical, geochemical cycles and balance of some of the heavy metals (Shetty *et al*., 2006). Heavy metals are stable, persistent and accumulate in the environment, they cannot be degraded or destroyed (Longibrachiatum *et al*., 2012). Aquatic systems are particularly sensitive to pollution possibly due to the structure of their food chains and in many cases harmful substances enter the food chain and are concentrated in fish and other edible organisms (Longibrachiatum *et al*., 2012). As they

move from one ecological level to another, metallic species start damaging the ecosystem and also become difficult to track thereby accumulating in living tissues throughout the food chain (Longibrachiatum *et al.*, 2012). Due to biomagnifications, humans receive the maximum impact, since they are at the top of the food chain(Kumar *et al*., 2014).

Some metallic elements play an essential role in the functioning of living organisms, in some cases they constitute a nutritional requirement (Kumar *et al.*, 2014). However, overabundance of the essential trace elements may be toxic and can lead to death (Ashraf *et al.*, 2011). Metals such as Mn, Zn and Cr are toxic beyond a certain limit, whereas Pb, Ni and Cd are toxic even in trace amounts (Fernandes *et al*., 2008). These heavy metals: Pb, Ni, Mn, Zn and Cd have the following recommended limits: 0.01 mg/L, 0.07 mg/L, 0.4 mg/L, 3.0 mg/L, 0.003 mg/L respectively for drinking water (WHO/UNICEF, 2008). Studies conducted in Kenya indicate that Cu, Pb, Cd, Mn, Zn and Ni are the most common heavy metals in water (Ogoyi *et al*., 2011; Muiruri *et al*, 2013; Ndenda and Manohar, 2014; Otenyo, 2014). For the purposes of this study only lead, copper and cadmium were considered due to time and cost implications.

2.5.1 Copper

Copper ions are introduced to the aquatic streams by means of various industrial activities viz. mining, electroplating, refining ores, fertilizer industries, tanneries, batteries, paper industries, pesticides etc.(Pastircakova, 2004; Celik and Demirbas,

2005;Marandi, 2011; Koel *et al*., 2012). Copper is an essential trace element required for proper health in an appropriate limit *(Joseph et al.*, 2013). Its high uptake may be harmful for human health and causes a number of symptoms such as growth retardation, skin ailments, gastrointestinal disorders, a slow dysfunction of the liver and damage to the pancreas on the one hand, and the appearance of the Wilson disease (Joseph *et al.*, 2013). High dose of copper concentration can also lead to weaknesses and anorexia (Kumar *et al*., 2014).

Copper also causes itching and dermatizition, keratinization of the hands and also lung cancer after prolonged inhalation of copper spray (Koel *et al*., 2012). World health organization (WHO) in 2006 recommended 2.0 mg/L as maximum acceptable concentration of copper in drinking water (Muzenda *et al*., 2011). Several studies been done to show effect of fruit wastes in removal of copper from waste water, they include, banana peels watermelon peels, and orange peels (Ashraf *et al*., 2011; Marandi, 2011; Renata *et al*., 2011; Hossain *et al*., 2012; Koel *et al*., 2012;)

2.5.2 Lead

A high exposure to lead causes encephalopathy, cognitive impairment, behavioral disturbances, kidney damage, anemia and toxicity to the reproductive system (Fu and Wang, 2011). The highest allowed limit of lead in drinking water is 0.05 mg/L (Saif *et al*., 2012). Lead causes encephalopathy, heart disease, abnormalities in children, testicular atrophy, anemia and interstitial nephritis. It can also impair the nervous

system (Castro *et al*., 2011). The effectiveness of fruit waste products in removal of lead (II) ions has been demonstrated by various studies, some of which include, banana peel, apple peels and lemon peels (Ashraf *et al*., 2011; Ranata *et al*., 2011; Husoon *et al*., 2013; Rasheed *et al*., 2013).

2.5.3 Cadmium

Cadmium (Cd) has been established as a very toxic heavy metal (Ferreira *et al.*, 2012). Due to its acute toxicity, Cd has recently joined lead and mercury in the most toxic category of heavy metals with the greatest potential hazard to humans and the environment (Kumar *et al*., 2014). Symptoms of acute poisoning include headaches, nausea, vomiting, weakness, pulmonary edema and diarrhea. A disease known as Itai–Itai in Japan is specifically associated with cadmium poisoning, resulting in multiple fractures arising from osteomalacia (Farooq *et al.*, 2010). Biosorption of cadmium on aqueous solution has been studied using Mulberry wood dust treated with HCl acid (Shah *et al.,* 2011), banana peel (Farooq *et al*., 2010; Ashraf *et al*., 2011), apple peels (Rasheed *et al*., 2013), orange peels (Benard and Jimoh, 2013) among others.

2.6 Effects of experimental conditions on adsorption

Various conditions influence the adsorption capacity of adsorbents during adsorption process (Hossain *et al.,* 2012). The efficiency of adsorbents is strongly influenced by the temperature, pH of solution, shaking speed, agitation time, initial concentration and

adsorption dosage (Moyo and Chikazaza, 2013). These factors are briefly discussed in the following subsections.

2.6.1 Effect of contact time

Efficiency of any adsorbent is measured in relation with the contact time of adsorbate and adsorbent, and shorter time required for contact signifies the efficacy (Rasheed *et al.,* 2013). The rate of metal ion uptake is related to the efficiency of the sorbent binding sites to hold the metal as well as the activity of the metal, therefore controlling the residence time for metal ions on the solid-liquid interface (Demirbasa *et al.*, 2004; Mwangi *et al.*, 2012). The point at which the amount of ions adsorbing is equal to amount being desorbed the process is said to be in a state of dynamic equilibrium (Bello, 2010) as shown in Equation 2.1. The time required to attain this equilibrium is termed as the equilibrium time and the amount of adsorbate adsorbed at equilibrium time reflects the maximum adsorption capacity of the adsorbent under the specified conditions (Banerjee *et al.,* 2012);

$$Mn^{+} + {}_{n}(\text{-COOH}) \underset{}{\overset{\text{adorbent}}{\rightleftharpoons}} \text{-(COO)}_{n}M + nH^{+} \quad \text{..... Equation 2.1}$$

Studies done on adsorption of copper on watermelon peels reported a removal of 64 % in 5 minutes and maximum of 84 % in 120 minutes (Banerjee *et al*., 2012 and Cm, 2015). Orange peels activated carbon reported an optimum time of 60 minutes to attain 51.47 % adsorption of copper and 60 minutes a 100 % removal of lead (Benard and Jimoh, 2013). Equilibrium time for Cu (II) and Pb (II) on banana peels was achieved within 20 minutes with 94 % and 100 % removal respectively (Castro *et al*., 2011). Equilibrium time of 30 minutes was reported for HCl treated Malberry wood sawdust for cadmium (Shah *et al.,* 2011). It is thus important to establish the optimum time in adsorption studies.

2.6.2 Effect of pH

The pH is amongst the most important parameters for adsorption process as it controls the protonation of the functional groups on the biomass as well as the metal chemistry (Banerjee *et al*., 2012). Metal adsorption depends on the nature of the adsorbent surface and species solution, at lower pH, H^+ competes with metals for the exchange sites (Das *et al*., 2012), the biosorbent surface becomes more positively charged thus reducing attraction between the adsorbent and the metal ions (Saif *et al*., 2012). The heavy metals are completely released under circumstances of extreme acidic conditions. The amount of adsorption is a minimum at pH 2 and increases as pH increases until optimum pH is reached, further increment in pH decreases the adsorption (Das *et al*., 2012). The minimum adsorption at low pH (< 2) may be due to the higher concentration and high mobility of H^+ which are adsorbed instead of metal ions. Solution pH would affect both

aqueous chemistry and surface binding-sites of the banana peels. The amount of adsorption increases with increasing pH up to the point (> 8) where the metals precipitate (Weng *et al* , 2007).

The pH is a key controlling parameter in the bio-sorption process of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction (Khan *et al*., 2013). Studies done on copper have reported optimum pH for copper as pH 6–8 for banana peels (Koel *et al*., 2012), pH 8.0 for watermelon shell (Banerjee *et al*., 2012), at pH 6 on orange peel (42.64 %) (Benard and Jimoh, 2013), raw banana peels pH2-0.760 mg/g and 1.76 mg/g at pH6 (Hossain *et al.,* 2012). Maximum biosorption of cadmium on HCl treated Mulbrrry wood sawdust was achieved at pH 6 (Shah *et al*., 2011).

2.6.3 Effect of initial metal ion concentration

Initial metal ion concentration has a significant effect on the biomass (Najiah *et al*., 2014). Effect of initial metal ion concentration on its removal is normally carried out at optimized adsorbent dose, contact time, pH and temperature by varying the metal ion concentration (Mandina *et al.*, 2013). At lower concentrations, the ratio of the initial number of moles of metal ions to the available surface area is smaller and subsequently the fractional adsorption process becomes independent of the initial concentrations, however, at higher concentrations, the available sites of adsorption become fewer, and

hence the percentage removal of metal ions depends upon the initial concentration (Castro *et al.*, 2011). A study on adsorption of Cu on watermelon shell reported the following removal efficiencies, 90% in 6 µg/mL, 82 % in 10 µg/mL and 77 % in 20 µg/mL (Banerjee *et al.*, 2012).

2.6.4 Effect of adsorbent dose

Higher dosage of adsorbent increases the adsorption due to increase in surfaces and functional groups on the adsorbent (Mandina *et al.*, 2013). The partial aggregation among available active binding sites at higher doses and lack of binding sites at lower doses retards the metal ion adsorption (Anwar *et al.*, 2010). Copper adsorption was reported to be highest at 61.29 % (0.8 g) in orange peels activated carbon (Benard and Jimoh, 2013), 84 % (0.02g) in watermelon shell (Banerjee *et al.*, 2012), 88 % (10 mg/L) in banana peels (Hossain *et al.*, 2012), apple peels 99 % (0.25 g) (Rasheed *et al.*, 2013). While 100 % (0.2 g) removal of lead using orange peels (Benard and Jimoh, 2013).

2.7 Effect of binary and ternary metal systems

Multi-metal system follows three types of adsorption behavior: synergism, where the effect of the mixture is greater than that of each of the individual adsorbate in the mixture, antagonism, where the effect of the mixture is less than that of each of the individual adsorbates in the mixture, and non-interaction, where the mixture has no effect on the adsorption of each of the adsorbates in the mixture. To examine the

antagonistic adsorption interaction of the two or more metal ions, it is advisable to compare the adsorption capacity of the single and multiple component systems (Anandkumar and Mandal, 2012).

Antagonistic effects on sorption of Pb (II), Cu (II) and Cd (II) in multiple metal system has been reported using adsorbents such as; marine algae (Shoiab *et al*., 2011), acid treated eagle *marmelos correa* shell (Anandkumar and Mandal, 2012), fungi and natural sorbents (Shoaib *et al*., 2011), Marine Alga *Sargassum* sp. (Sheng *et al.,* 2007) and sawdust and treated peanut husk (Wang *et al*, 2006) among others.

Various studies have shown that composite mixtures of adsorbents can bring about synergistic effect of metal ions. These include; synergistic adsorption of Cd (II) in presence of Ni (II) ions by Supramolecular Polysaccharide Composite Materials from Cellulose, Chitosan and Crown Ether has been reported (Chieu, 2014), Cu (II), Zn (II) and Pb (II) by a composite mixture of sugarcane bagasse, watermelon rind and garden grass and Pb (II) in a mixture with Ni (II) by composite mixture of chitosasn and activated charcoal (Ngwu *et al*., 2015). Three types ions were considered in this study, copper (II), cadmium (II) and lead (II) ions.

2.8 Desorption studies

Regeneration and recovery of spent adsorbents and metals is very important as it reduces the cost of remediation of heavy metals and other contaminants in our

environment (Jnr and Harcourt, 2005). A number of studies have demonstrated the feasibility of using fruit waste products to remove heavy metal ions from aqueous solution (Liang *et al.*, 2012; Benard and Jimoh, 2013; Husoon, 2013; Mandina *et al.*, 2013, Khan *et al.*, 2013) among others. However, in the literature, information on desorption of adsorbed metals from biomass is scanty (Jnr and Harcourt, 2005).

Desorption can be carried out by proton exchange using acids, chelating agents (EDTA) or exchange with other ions, e.g. $CaCl_2$. Different eluents have been used in the past to carryout desorption studies including, tap water, milli-Q water, distilled water, H_2SO_4, HCl, HNO_3, NaOH and CH_3COOH (Hossain *et al.*, 2012a). An efficient eluant is one that desorbs the metal completely without deteriorating the biomass, a metal concentrated solution is obtained from eluent after which metals can be recovered using electrochemical or other conventional techniques (Mata *et al.*, 2010).

In desorption system, H^+ released from acids replace metal ions on the surface of the adsorbent (Hossain *et al.*, 2012a). Previous studies on cadmium, lead and copper desorption from sugar-beet pectin xerogels, have shown that HNO_3 is more effective than other inorganic acids (HCl or H_2SO_4) (Mata *et al.*, 2009) and also $CaCl_2$ (Mata *et al.*, 2010). Studies on desorption of copper from banana peels, the highest (94 %) recovery was found with the use of 0.1N H_2SO_4 while HCl and HNO_3 showed lower efficacy of 54 and 72 % respectively (Hossain *et al.*, 2012a). A study on banana peels

desorption showed that HCl recorded the highest desorption capacities of Cu^{2+} (2.14 mg/g) in banana and 1.85 mg/g in Pb^{2+} (4.00 mg/g in banana and 3.20 mg/g in orange (Annadurai *et al*., 1994).

2.9 Adsorption isotherms

Adsorption as well as desorption process can be quantified by adsorption isotherm equation. The parameters used to derive the mathematical equation in the isotherm are related to the surface properties of the adsorbent (Hossain *et al.,* 2012). The isotherms indicate how the adsorbed molecules distribute between the liquid phase and the solid phase when the adsorption process reaches equilibrium state (Hossain *et al*., 2012). Equilibrium is established when the concentration of the sorbate in the bulk solution is in dynamic balance with that at the sorbent interface, the most used isotherm models include Langmuir, Freundlich and Temkin models (Koel *et al*., 2012).

Freundlich isotherm model deals with adsorption at multilayer heterogeneous (Heidari *et al*., 2013). According to this model during adsorption process stronger binding sites will occupy first (Tan *et al.*, 2009). As more sites are occupied by metal ion, the binding strength becomes weaker (Etim *et al*., 2012). The Freundlich isotherm (Moyo and Chikazaza, 2013) is given by equation 2.2;

$$q_e = K_f C_e^{\frac{1}{n}} \quad \text{.....Equation2.2}$$

where q_e is the maximum amount of adsorption (mg/g), K_f the constant representing the

adsorption capacity, and n is the constant depicting the adsorption intensity. If n = 1 then the partition between the two phases are independent of the concentration. If value of 1/n is below one it indicates a normal adsorption. On the other hand, 1/n being above one indicates cooperative adsorption (Dada *et al.*, 2012). However, K_f and n are parameters characteristic of the sorbent-sorbate system, which must be determined by data fitting and linear regression is generally used to determine the parameters of kinetic and isotherm models (Dada *et al.*, 2012). The parameters can be linearized by taking logarithms to determine the parameters K_f and n;

$$Inq_e = InK_f + \frac{1}{n} InC_e \quad \text{..... Equation 2.3}$$

A plot of $In\ q_e$ versus $In\ C_e$ gives a straight line, and K_f and n can be calculated from the intercept and slope, respectively. The Langmuir model assumes all sites on the adsorbent have equal energy (Kwon *et al.,* 2010; Liang *et al.*, 2011). During adsorption process, metal ions forms a monolayer on the adsorbent surface and when all sites are occupied there will be no more binding to take place (Sureshkumar *et al.*, 2010; Etim *et al.*, 2012). The linearized Langmuir equation is:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{(bq_{max})(C_e)} \quad \text{.....Equation 2.4}$$

where, qe is the amount of metal adsorbed at equilibrium (mg/g), b is the Langmuir constant related to affinity of binding sites and a measure of energy of absorption. The higher b is, the higher is the affinity of the biosorbent for the metal ions. The q_{max} is the monolayer sorption capacity (mg/g) which can also be interpreted as the total number of binding sites that are available for biosorption and C_e is the metal ions at the

concentration at equilibrium (Hossain *et al*., 2012). A plot of $1/q_e$ versus $1/C_e$ gives a straight line with $1/q_{max}$ as the intercept and $1/bq_{max}$ as the slope, and hence q_{max} and b can be calculated.

Table 2.2: Overview summary of Freundlich isotherm parameters on selected studies on Cu (II), Pb (II) sorption by biosorbents

Adsorbent	Metal	Kf	1/n	R2	Reference
Acid treated maize tassel	Pb	0.077	0.482	0.9515	Moyo and Chikazaza, 2013
Acid treated *Aegle Marlos* correa shell	Pb	77.956	0.09206	0.9846	Anndkumar *et al.*, 2012
Acid treated banana peels	Pb	2.87	1.77	0.9994	Anndurai, 1994
	Cu	0.98	1.22	0.9989	
Acid treated orange peels	Pb	1.79	1.42	0.98758	
	Cu	0.59	1.10	0.9908	

Adsorption isotherms are very useful for analyzing the nature of adsorbate-adsorbent interaction. So, in order to optimize the design of a successful adsorption unit to remove trace metal ions from waste water, it is significant to establish the best correlation for the equilibrium isotherms

2.10 Kinetic studies

To evaluate the performance of unit processes utilizing adsorption, it is necessary to have an understanding of the time dependence of the concentration distribution of the solute in both the bulk solution and solid adsorbent phases and to identify the rate-determining step (Koel *et al*., 2004). In order to evaluate the kinetic parameters, pseudo-

first order and pseudo-second-order models were tested to analyze the adsorption kinetics. The Pseudo-first-order equation is expressed as:

$$\log\left(q_e - q_t\right) = \log q_e - \left(K_1 t / 2.303\right) \quad \text{.....Equation 2.5}$$

The pseudo-second order model has been widely used for adsorption for the following reasons: it does not have the problem of assigning an effective adsorption capacity, the adsorption constant capacity, rate constant and initial adsorption rate can all be determined from the equation without knowing any parameter beforehand (Moyo and Chikazaza, 2015). The Pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \text{.....Equation 2.6}$$

Where, q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is the mass of metal at time t (min), K_1 the first-order reaction rate constant of adsorption (min^{-1}) and K_2 the pseudo-second-order rate constant of adsorption (mg/ g).The values of K_1 and qe calculated from the slope and intercept of the plot of log (qe–qt) versus t while the values of K_2 and qe were evaluated from the intercept and slope of a plot of t/qt versus t, respectively (Mekonnen *et al.*, 2015).

2.11 Interactive behavior of metal ions

The selectivity of the adsorbents for metal ions in both binary and tertiary mixture in solution is determined in terms of relative metal *i* adsorption that is *Ri* (%) (Chang and

Cheng, 1998). The percentage *Ri* (Equation 2.7) will determine whether the combination in binary system is antagonistic or synergistic in nature;

$$Ri = \frac{metal\ i\ adsorption\ capacity\ with\ coexistence\ of\ metal\ i\ and/or\ k}{metal\ i\ adsorption\ capacity\ without\ coexistence\ of\ metal\ i\ and/or\ k} X100$$

.....Equation 2.7

If R_i > 100 %, it indicates that the interactive effect of the mixture of metals is synergistic, R_i < 100 % indicates antagonistic behavior and R_i = 100 % indicates non interactive heavier (Jain *et al.*, 2016).

2.12 Mid Infrared spectroscopy

2.12.1 Working principle

Mid infrared spectroscopy (MIR) is a high rapid and high throughput method for characterizing the chemical composition of materials. Infrared spectroscopy (IR) is a technique based on the vibrations of the atoms of a molecule. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy (Ferreira *et al.,* 2012). The goal of the basic infrared experiment is to determine changes in the intensity of a beam of infrared radiation as a function of wavelength or frequency. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule (Liang *et al.*, 2009). The wavelength at which absorption

takes place helps in determination of functional groups present in the material, that may be responsible for the reactions of the material (Ferreira *et al.,* 2012).

The MIR spectrum can be divided into four regions. The X-H, (O-H, C-H, and N-H) stretching region (4,000-2,500 cm^{-1}). Triple bond C=C and C=N region (2,500-2000 cm^{-1}). The double bond (C=C, C=O and C=N) region (2000-1500 cm^{-1}) and the finger print region (1500-600 cm^{-1}). Vibrations can involve either a change in bond length (stretching) or bond angle (bending). The infrared spectroscopy is used to analyze the effect of the chemical treatment on the surface structure of biomass (Barreto *et al.,* 2011). An important consideration is the broadening of the hydroxyl band, characteristic of the axial vibration of hydroxyls from cellulose (carbons 2, 3 and 6 of the glucose) (Ferreira *et al*., 2012) as a function of the chemical treatment with sodium hydroxide and due to changes of the inter- and intra-molecular hydrogen bonding in polysaccharides (Esmeraldo *et al*., 2010).

Acid treatment has been reported to remove or decrease some modes in vibration of lignin: absorptions due to C–Hn (alkyl and aromatic) stretching vibrations, absorptions characteristic of the C=O stretching modes, and a signal typical of an aromatic skeleton. It was noted that the intensities of almost all bands were lower after acid treatment (Ferreira *et al*., 2012). Thus, IR spectroscopy is an important tool to evaluate the changes modification of the biomass structure before and after to the chemical treatment. Studies have shown that banana peels contain nitrogen, sulfur, and carboxylic acids groups that are responsible for the peels' ability to bind the toxic metals and

remove them from the water and powdered avocado seeds constituents are reported to be mainly phenolic and proanthocyanin compounds (Maria *et al.*, 2007). The avocado seeds contain acidic groups, mainly phenolic moieties in natural and treated forms (Maria *et al.*, 2007).

2.12.2 Instrumentation

A common FTIR spectrometer consists of a source, interferometer, sample compartment, detector, amplifier, A/D convertor, and a computer. The source generates radiation which passes the sample through the interferometer and reaches the detector. Then the signal is amplified and converted to digital signal by the amplifier and analog to digital converter, respectively. Eventually, the signal is transferred to a computer in which Fourier transform is carried out.

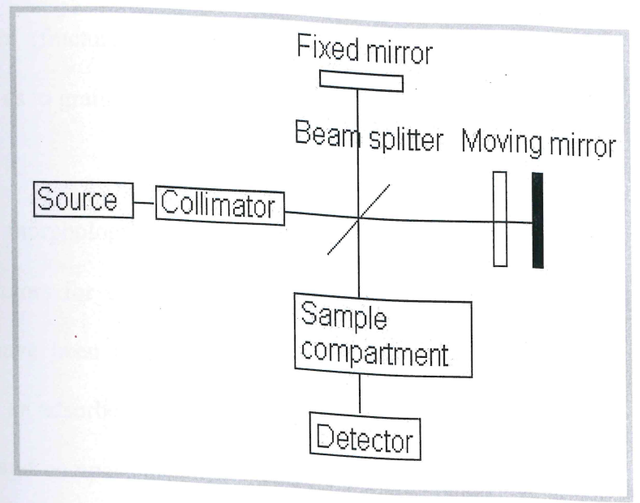


Figure 2.1: Block diagram for FTIR spectrometer

2.13 Scanning electron microscopy (SEM)

2.13.1 Working principle

The SEM provides the investigator with a highly magnified image of the surface of a material that is very similar to what one would expect if one could actually "see" the surface visually (Hossain *et al*., 2012). The SEM images of the sample surface are obtained by scanning it with electron beams in a raster scan pattern. The electrons interact with the sample atoms producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity (Liu *et al*., 2010).

Not only is topographical information produced in the SEM, but information concerning the composition near surface regions of the material is provided as well. Additionally, the SEM can also be used to provide crystallographic information. Surfaces that exhibit grain structure (fracture surfaces, etched, or decorated surfaces) can obviously be characterized as to grain size and shape (Anandkumar and Mendal, 2012).

The surface morphology and porosity of natural fiber have been recognized as significant factors for composite interfaces, and their effects on the performance of composites have been investigated (Han and Choi, 2010). This information is also important for an adsorbent. It is possible to observe the grain or fiber size, porosity and morphology and compare it before and after some chemical treatment employed. The increase or decrease in adsorption capacity can be explained by changes observed on

the surface of adsorbent. Thus, surface morphology and microstructure of the adsorbents can be studied by SEM. For biomass, it is necessary to coat the sample with a conductor material, as gold, platinum or with a layer of carbon. This happens due to slow electron conductivity of the kind of the material and this affects the images quality (Kumar *et al*., 2014).

2.13.2 Instrumentation

The main SEM components include: Source of electrons, Column down which electrons travel with electromagnetic lenses, Electron detector, Sample chamber and Computer to display and view the images (Figure 2.2).

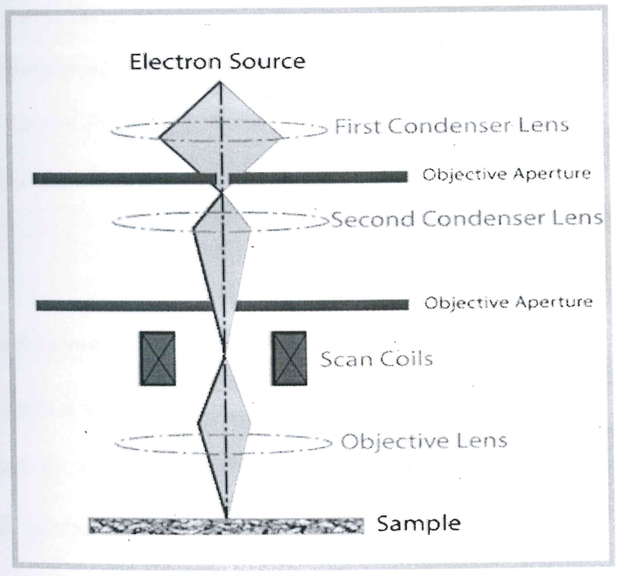


Figure 2.2: Schematic diagram for scanning electron microscope (NI, 2016).

2.14 Atomic absorption spectroscopy (AAS)

2.14.1 Working principle

In AAS a substance is vaporized and decomposed into gaseous atoms in flame or electrothermal atomizer. The concentration of an element is measured by the absorption of radiation with characteristic frequency by free atoms of an element. Light of certain wavelength produced by monochromatic or hollow cathode lamp emits spectral lines corresponding to energy required for excitation of an element of interest. The analytical signal is obtained from the difference between the intensity of the source in the absence of the element of interest and the decreased intensity obtained when the element of interest is present in the optical path. Absorption of light is associated with transition process from one steady state to another. The technique makes use of absorption spectrometry to assess the concentration of an analyte in a sample. It relies heavily on Beer – Lambert law. The electrons of the atoms in the atomizer can be promoted to higher orbitals for a short amount of time by absorbing a set quantity of energy. This amount of energy is specific to a particular electron transition in a particular element and this ensures elemental selectivity.

2.14.2 Instrumentation

In order to analyze a sample for its constituents, it has to be atomized. The sample is then illuminated by light. The light transmitted is finally measured by a detector. Spectrometer is placed between the atomizer and the detector to reduce the effect of emission from the atomizer.

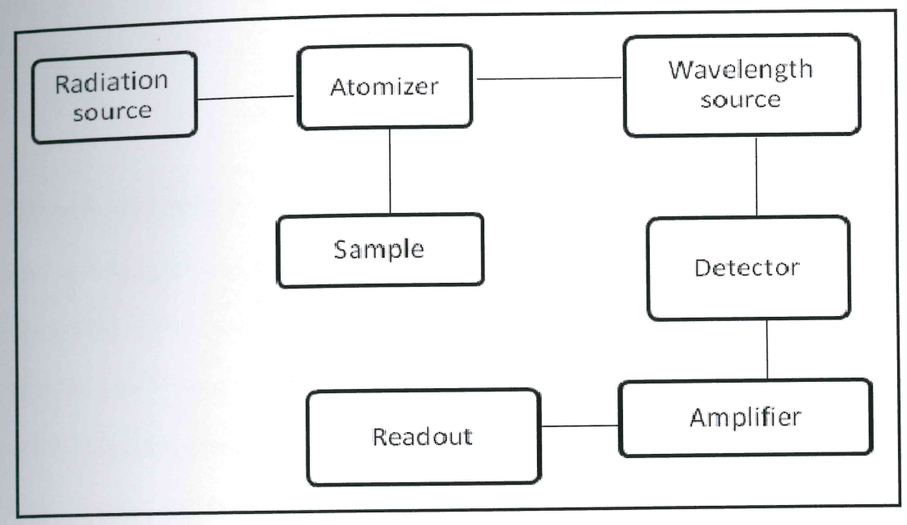


Figure 2.3: AAS instrumentation

The intense resonance line (frequency), which corresponds to the transition ground state atoms of the analyte to an excited state, originates from the Hollow-cathode lamp. This resonance line (λ) is absorbed by atoms in the flame and is characteristic of the elements under investigation making AAS highly selective with a high degree of specificity. The amount of radiant energy absorbed by the Photo Multiplier Tube (PMT) detector is directly proportional to the concentration of the absorbing atoms in the flame. AAS technique has some advantages that include less spectral interference, versatile and has high sensitivity (can detect up to 0.1 mg /l). In the analysis of lead (II) and cadmium (II) ions the signal is subject to interference from the other transition metals, phosphates and formation of variable refractory oxides in air acetylene flame. Better sensitivity is achieved by use of reducing condition of nitrous oxide- acetylene flame.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Research approach

Biomass consisting of fruit peels of banana, watermelon, lemon, sweet yellow passion and avocado seed were collected locally. The biomass was washed, dried and ground. The powder was divided into two portions; one was treated with sulphuric acid. The raw and acid treated materials were characterized using scanning electron microscope and FTIR. Batch experiments were performed to determine the most efficient biomass in removing copper, lead and cadmium metal ions. The most efficient adsorbents were used for binary and ternary metal systems and desorption studies as shown in figure 3.1.

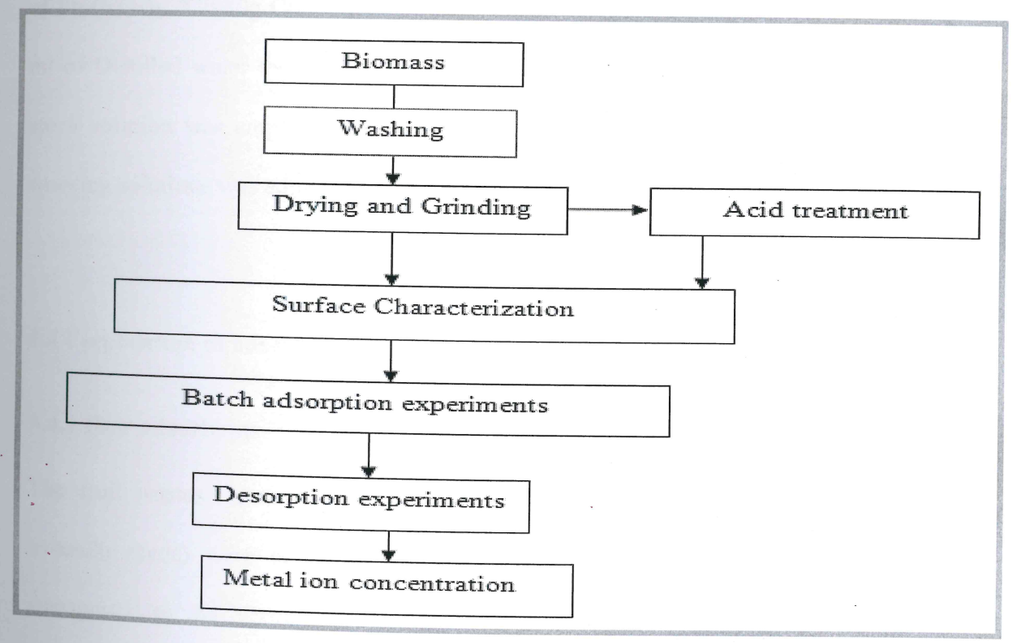


Figure 3.1: Research design

3.2 Reagents, chemicals and solvents

All solutions were prepared in double distilled water. Metal solutions were prepared in 0.1M sodium acetate to maintain constant ionic strength. All the chemicals and reagents were of analytical grade (Purity of > 98.9%). Chemicals used included soluble salts of metals (Pb^{2+}, Cu^{2+}, Cd^{2+}) and KNO_3, NaOH, HCl, H_2SO_4, sodium acetate, sodium bicarbonate which were obtained from Associated Chemical Supplies Ltd, Fluka Analytical Buchs, Switzerland.

3.3 Preparation of stock solutions

Stock solutions of 1000 mg/L of Pb^{2+}, Cu^{2+}, Cd^{2+} were prepared by dissolving 1.598 g of Pb $(NO_3)_2$, 3.7980g $Cu(NO_3)_2.3H_2O$ and 2.74g Cd $(NO_3)_2.4H_2O$ respectively in 250 ml of Distilled water then topped to a litre. The progressive dilution procedure of the stock solution was employed in the preparation of working solutions. The pH of the working solutions was adjusted to the required value with 0.1 M NaOH or 0.1 M HNO_3.

3.4 Preparation of adsorbents

3.4.1 Raw adsorbents

The fruit wastes (lemon, banana, watermelon and sweet yellow passion peels and avocado seeds) were collected locally (markets in Nairobi and Mwea) and were transported to the laboratories, washed thoroughly with deionized water to remove impurities, then cut into small pieces and dried in an oven at 105 °C to eliminate

The pellet was then analyzed by an FTIR spectrophotometer. The spectra of adsorbents were measured within the range of 600–4000 cm^{-1}. The spectra were plotted using the same scale on the absorbance axis before and after acid modification. The surface morphologies of the fruit wastes (natural and acid treated forms) were determined using Scanning Electron Microscope (Carl Zeiss ultra plus field emission electron microscopy (FEGSEM), Carl Zeiss, Cambridge, UK). Powdered samples were pressed on double sided carbon tape mounted on aluminum stubs, then placed within the microscope and analyzed at an accelerating voltage of 10 kV.

3.6 Optimization of adsorption parameters

Effect of parameters such as contact time, initial metal ion concentration, adsorbent dosage and pH on adsorption of the heavy metal ions (Pb (II), Cd (II) and Cu (II)) on removal efficiency of the raw and treated adsorbents were optimized by keeping other parameters constant while varying the one under consideration as described by Bernard and Jimoh (2010). The process parameters were varied as follows; initial metal ion concentration (10 - 500 mg/L), contact time (5 - 180 min), solution pH (2 - 14) and adsorption dose (0.01 - 0.5 g) in 50 mL aqueous solutions and temperature (25° ± 1°C).

3.7 Effects of experimental conditions

The effects of pH, equilibrium time, initial metal ion concentration and doses of anions (adsorption) onto fruit waste (raw materials), were investigated as described by (Koel *et al.*, 2012).

moisture. The dried adsorbents were ground to fine powder and sieved. The resulting powders were labeled as MAS (acid treated avocado seed), UMAS (raw avocado seed), UMWP (watermelon peel), MWP (acid treated watermelon peel), MLP (acid modified lemon peel), UMLP (lemon peel), MSYP (acid treated sweet yellow passion peel) UMSYP (sweet yellow passion peel), MBP (acid treated banana peel), UMBP (banana peel) were kept in desiccators ready to use

3.4.2 Chemical modification of the adsorbents

Each of the raw powdered adsorbent was mixed with 1N sulphuric acid solution at a ratio of 1:2 (Weight:Volume), and heated at a temperature of 150 °C for 24 hours. Each product was then cooled and washed with distilled water to remove the excess acid, filtered and kept in sodium bicarbonate solution $NaHCO_3$ (1 %) overnight to eliminate the acid residue (Khalfaoui and menai, 2012; Moyo and Chikazaza, 2013). Finally, each treated adsorbent was dried at 105 °C to a constant weight.

3.5 Surface characterization

Functional groups present in the banana peels, watermelon peels, sweet yellow passion peels, lemon peels and powdered avocado seeds products were characterized by FT-IR spectra (SHIMADZU FTIR 8400S (Kyoto, Japan) spectrometer). The FTIR analysis samples were obtained by mixing 1 mg of the dried sample of material with 50 mg KBr (1:50), grinding the mixture to fine powder and then pressed under vacuum to a pellet.

3.7.1 Effect of adsorbent dosage

The effect of adsorption of Cu (II), Pb (II) and Cd (II) ions on banana, watermelon, sweet yellow passion peels, lemon peels and powdered avocado seeds both natural and acid treated was studied by varying the quantity of each adsorbent (10-500 mg) in the test solution and keeping the initial concentration, pH, temperature and constant. Metal ion solutions were adjusted to their respective optimum pH using nitric acid and sodium hydroxide solutions. The experiments were conducted in triplicates and stirred for 2- 3 hours in plastic bottles on the water bath shaker. At the end of the contact time, the samples were centrifuged, decanted and filtered. The concentrations of Cu^{2+}, Pb^{2+} and Cd^{2+} ion were determined using flame atomic adsorption spectrometry.

3.7.2 Effect of contact time

The rate of metal ion (Cu (II), Pb (II) and Cd (II)) sorption by both acid-treated and raw banana, watermelon, sweet yellow passion peels, lemon peels and powdered avocado seeds was studied by mixing 0.05 g of each sorbent material with 50 ml of metal ion solution of (10 – 50) µg/mL. 0.01M sodium acetate was added to maintain a constant pH (5.9 and 4.2 for lead, 4 and 5.8 for cadmium and 4.2 and 5.9 for copper with treated and raw sorbent respectively). The pH's of the sample solutions were adjusted using 0.1M nitric acid and 0.1M sodium hydroxide solutions The mixtures were equilibrated for predetermined time of 5- 360 minutes in bottles on a shaker at 120 rpm. The solutions were then centrifuged and the filtrates subjected to atomic absorption

spectroscopy to record the absorbance of Cu (II), Pb (II) and Cd (II) ions.3.7.3 Effect of initial metal ions concentration

3.7.3 Effect of initial metal ion concentration

The extent of metal ions (Cu (II), Pb (II) and Cd (II)) taken up as a function of initial metal concentration was investigated by mixing 0.05 g of each natural and acid activated banana, watermelon, sweet yellow passion peels, lemon peels and powdered avocado seeds with 50 ml of the metal solutions (5- 200) µg/mL buffered at optimum pH of each metal. The contact time was kept at 2 h, filtered and the concentrations of Cu (II), Pb (II) and Cd (II) determined using flame atomic adsorption spectroscopy (FAAS). All runs were conducted in triplicates.

3.7.4 Effect of pH

The effect of pH on removal of metal ions (Cu (II), Pb (II) and Cd (II)) was investigated at various pH levels. Approximately 0.05 g of each of the natural and acid treated adsorbents was mixed with 50 mL of aqueous metal solutions containing (10 – 50) µg/mL of test solutions, buffered with 0.1 M sodium acetate. The pH of the solutions was varied from pH 2 to pH 10 using 0.03 molar nitric acid and 0.1 molar sodium hydroxide solutions. The samples were stirred at a speed of 120 rpm for 2 h in triplicates. At the end of the contact time, samples were filtered and concentrations of Pb^{2+} and Cd^{2+} determined using flame atomic adsorption spectrometry.

3.8 Batch adsorption studies

3.8.1 Single metal component

Batch mode adsorption studies for of Pb (II), Cd (II) and Cu (II) by the fruit waste adsorbents were performed to determine their adsorption capacities in single metal system using optimized conditions as described by Jain *et al.*, (2016). Fifty milliliters of metal ion solution of concentration of 50 mg/L with adsorbent dosage of 50 g (raw adsorbents), 20 g (acid treated adsorbents for Pb (II) and Cu (II)) and 10 g (acid treated adsorbents for Cd (II)) was agitated temperature (25°C ± 1°C) using a mechanical shaker for 2 - 3 hrs at 160 rpm. All experiments were carried out at optimum pH of 4.2-5.9 based on optimized conditions above. The solutions were then filtered through Whatman 42 filter paper and the residual concentration of metal ion was determined by AAS method.

3.8.2 Batch experiments for binary and multiple metal systems

The best three adsorbents obtained through biosorption screening trials were further subjected to batch examinations in binary and multiple metal mixtures. The three binary mixtures comprised of Pb^{2+}/Cu^{2+}, $Cu^{2+}/Cd^{2+}$and Pb^{2+}/Cd^{2+} and a ternary mixture of $Cu^{2+}/Cd^{2+}/Pb^{2+}$, $Cd^{2+}/Cu^{2+}/Pb^{2+}$ and $Pb^{2+}/Cd^{2+}/Cu^{2+}$ ions. For binary metal systems and tertiary metal systems adsorption metal and co-cation concentration were maintained at a ratio of 1:1 and 1:1:1 respectively. Adsorption studies were carried out by keeping the

concentration of the first metal constant and varying the concentration of other metal (s) ions at optimum pH of the former metal ion obtained in case of single metal system.

The process parameters optimized for single metal ion were applied for binary and tertiary metal systems, viz. volume = 50 mL, pH 4.2 and 5.9 for Cu^{2+} in raw and acid treated adsorbents, pH 5.8 and 5.9 in raw and acid treated adsorbents for Cd^{2+} and pH 5.9 for Pb^{2+}. Co-cation concentration was varied between 10-200 mg/L binary system and between 10:10 – 200:200 mg/L in tertiary system. Adsorbent dosage was 50 g (raw adsorbents), 20 g (acid treated adsorbents for Pb (II) and Cu (II)) and 10 g of acid treated adsorbents for Cd (II), contact time was 3 hours for raw adsorbents and 2 hours for acid treated adsorbents and agitation speed was 160 rpm.

3.9 Desorption Studies

Desorption and reuse experiments were done to determine desorption ratio and reusability of raw materials. These experiments were carried out as described by Liang *et al*., (2012) and (Hossain *et al*., 2012). Desorption studies for Pb (II), Cd (II) and Cu (II) ions were conducted on MSYP, MAS, MLP and MWP using the following eluents; 0.1 mol/l NaOH, 0.1 mol/L HCL, 0.1 mol/L H_2SO_4, 1 mol/L HNO_3, 0.1 mol/L CH_3COOH, Tap water and distilled water.

The 2 g of MSYP were placed in 100 mL of (10-100 µg/mL) of each of Pb (II), Cd (II) and Cu (II) ions and the mixtures were shaken in rotator for 2- 3 hours. The solutions were filtered and the amount of each metal adsorbed was determined. The metal loaded

adsorbent was dried and 50 mL of eluent (0.1 mol/L NaOH) was added and shaken for (10-180) minutes, then the metal ion concentration in solution was determined. Same process was repeated using 0.1 mol/L HCl, 0.1mol/L H_2SO_4, 0.1 mol/L HNO_3, 0.1 mol/L CH_3COOH, tap water and distilled water for MAS, MLP and MWP. Using the best eluent the regenerated material was washed three times in distilled water and the metal ion added again for another adsorption-desorption cycle. This procedure was repeated nine times.

3.10 Calibration of flame atomic spectrometry

In this study, the instrument was calibrated by analyzing calibration solution (0-10 mg/mL) for each element: Pb (II), Cd (II) and Cu (II) ions. Regression analysis was done where the slope (m), and intercept (b) of linear equation (Y= mx + c) that best fitted data from calibrations were determined, i.e. where x and y have a strong positive correlation, r is close to 1 (Gareth, 2011). New calibration standards were prepared where error in preparation was observed.

3.11 Determination of the metal ions concentration

Determination of Cu^{2+}, $Cd^{2+}$and Pb^{2+} was done in replicates using computerized Varian Atomic Absorption spectrometer model AA-10. The samples were analyzed in triplicates under the same conditions as standards and blanks. For precision, standards were measured before and after the sample solution. The calibration of the instrument

using standards and blank was frequently done between samples to ensure stability of the base line.

3.12 Data analyses

Metal uptakes from natural and acid treated banana, watermelon, sweet yellow passion peels, lemon peels and powdered avocado seeds were calculated from sorption results using $q_e = \frac{(C_i - C_e)V}{M}$

Equation 3.1

where, q_e is the metal uptake (mg metal adsorbed per *g* adsorbent), *Ci* and *Ce* are the initial and equilibrium metal concentration, V is the volume of the reaction mixture and M is the mass of dried adsorbent used (Moyo and Chikazaza, 2013). The percentage of removed Pb (II), Cd (II) and Cu (II) ions (R %) in solution was calculated using

$$R\% = \frac{(C_i - C_o)100}{C_i} \quad \text{.....Equation 3.2}$$

Where, *Ci* and *Co* are the initial and equilibrium metal concentrations. The correlation between the experimental data and the model-predicted values were examined by R^2, the normalized standards deviation (NSD) and average relative error (ARE).

3.13 Kinetic studies

Applications of the rate equations (equations 2.5 and 2.6) for describing the kinetics studies were investigated for Pb (II), Cd (II) and Cu (II). For this, flasks of 50 mL at 25±0.5 °C, pH 4.2 and 5.9 for Cu^{2+} in raw and acid treated adsorbents, pH 5.8 and 5.9 in raw and acid treated adsorbents for Cd^{2+} and pH 5.9 for Pb^{2+} were put in mechanical shaker and agitated for 5 minutes to 4 hours. After a predetermined time, volumes of the solution were removed, filtrated and analyzed. The amount of adsorption was calculated at equilibrium achieved in 4-5 hours by equation 3.1.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Introduction

This Chapter reports all the findings obtained for all the experimental work carried out in this study. This includes results from characterization of the adsorbents, batch adsorption and desorption experiments results. Parameters such as, effect of contact time, pH, sorbent dosage and initial metal ion concentration were optimized. The following subsections give the discussions of the results obtained.

4.2. Characterization

4.2.1 Scanning electron microscope (SEM)

The SEM images of powdered (avocado seeds, lemon peels, watermelon peels, sweet yellow passion and banana peels) before and after H_2SO_4 activation are shown in figure 4.1- 4.5 (a) and (b) respectively.

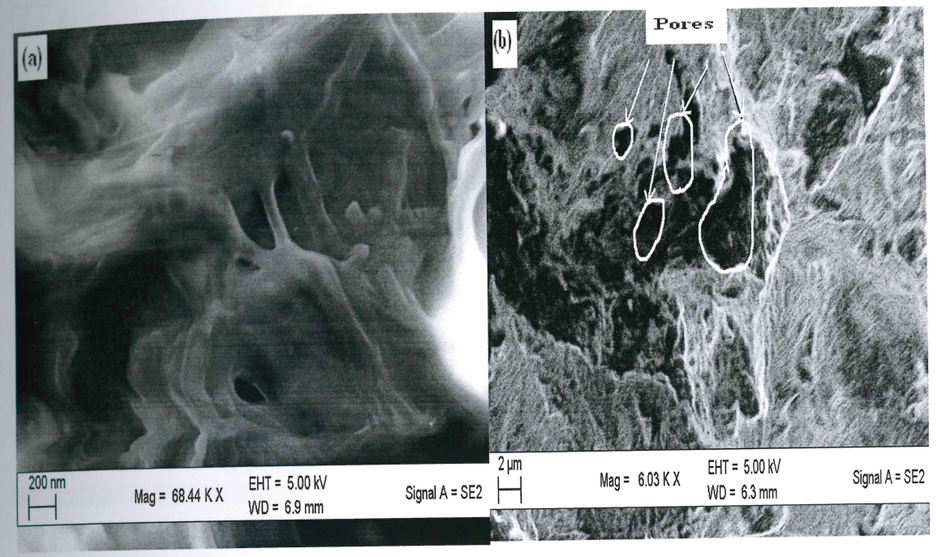


Figure 4.1: SEM images for (a) UMAS and (b) MAS

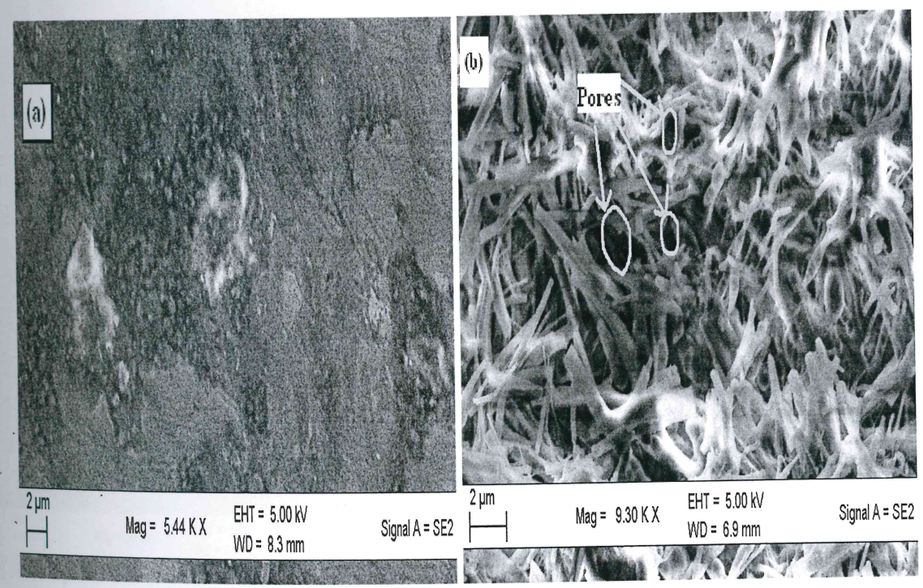


Figure 4.2: SEM image for (a) UMLP and (b) MLP

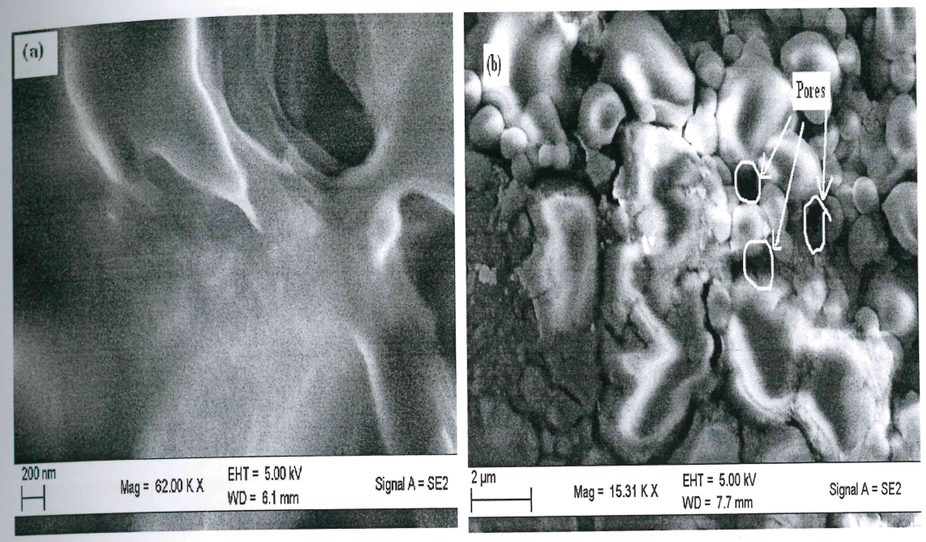


Figure 4.3: SEM images for (a) UMWP and (b)MWP

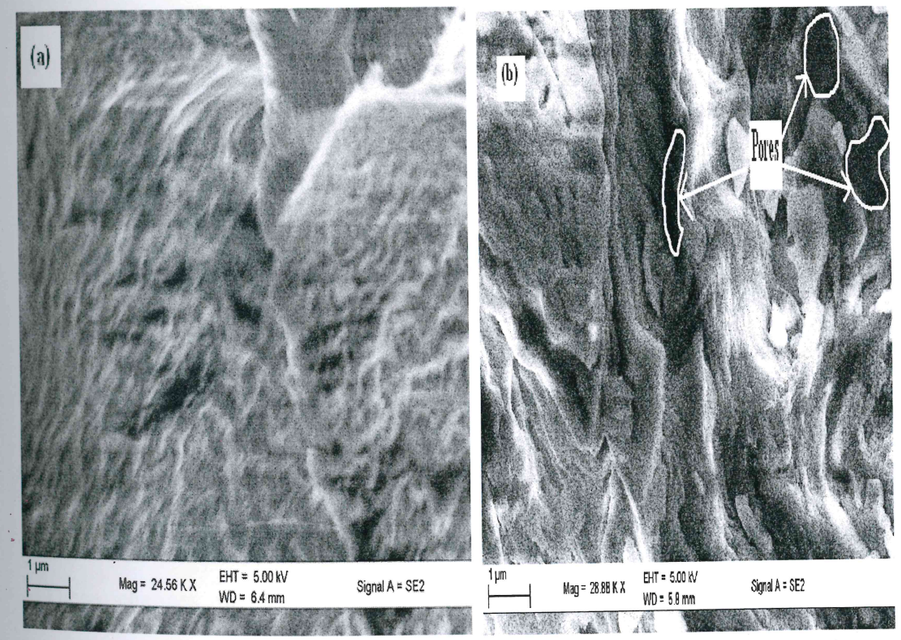


Figure 4.4: SEM image for (a) UMSYP and (b) MSYP

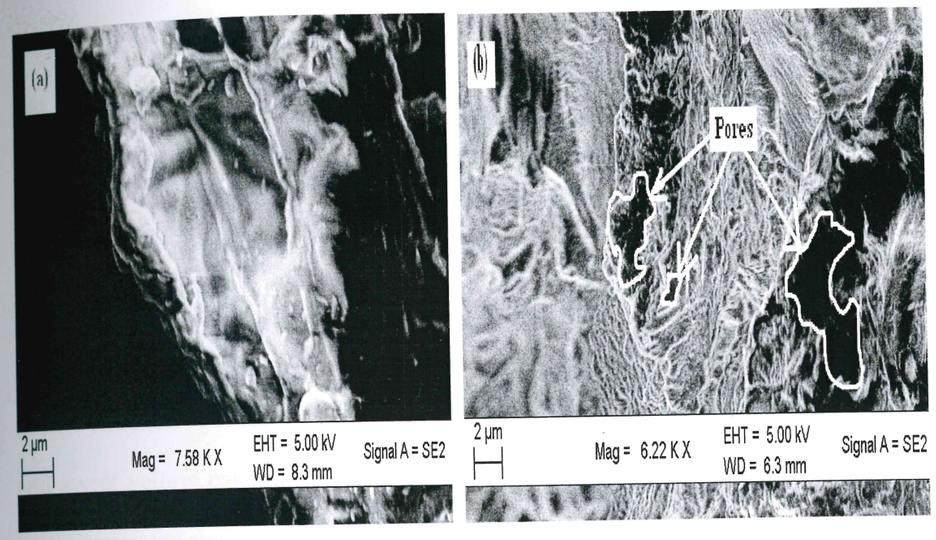


Figure 4.5: SEM image for (a) UMBP and (b) MBP

The SEM images clearly reveal the surface texture and morphology of the adsorbents as shown in figure 4.1 - 4.5. Figures 4.1 - 4.5 (a) shows that prior to H_2SO_4 treatment, the powdered avocado seeds, lemon peels, watermelon peels, sweet yellow passion peels and banana peels have rigid, rough and constricted surface. However, after H_2SO_4 activation, as can be seen in figures 4.1 - 4.5 (b) well developed pores occurred on the surface of the powdered (avocado seeds, lemon peels, watermelon peels, sweet yellow passion peels and banana). After acid treatment the biomass suffers morphological changes in its structure. This can be attributed to the partial destruction of cellulose, hemicellulose and lignin induced by sulphuric acid treatment (Pandey and Negi, 2015). These changes in morphological on acid treated biomass can contribute to the improvement of their sorption properties. Similar results were reported by Kumar *et al*.

(2014) on acid activated sawdust, bagasse and sea weed, acid treated orange peel (Feng and Guo, 2012) and raw banana peel (Hossain *et al.,* 2012).

4.2.2 The MIR Spectroscopy

The FT-IR technique was an important tool to identify some important functional groups, which are capable of adsorbing pollutant ions (Hanif *et al*., 2009; Han *et al*., 2010). The MIR spectrum of (powdered avocado seeds, lemon peels, watermelon peels, and sweet yellow passion and banana peels) samples, before and after sulphuric acid modification are shown in figures 4.6 - 4.10.

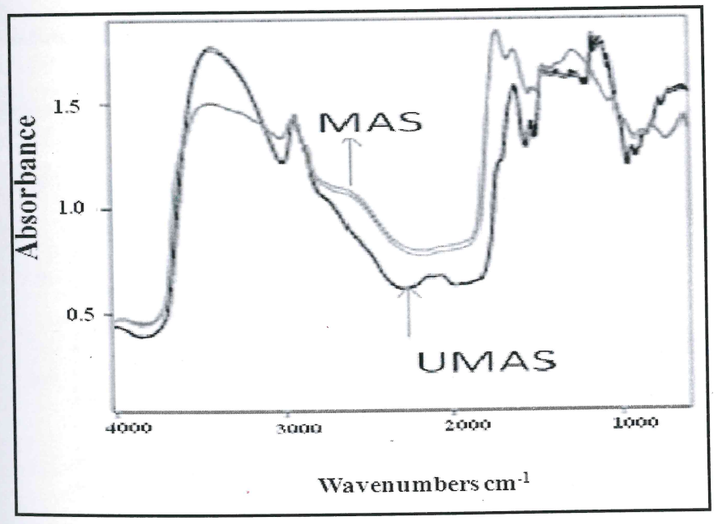


Figure 4.6: FT-IR spectra for UMAS and MAS

Figure 4.6 shows presence of broad absorption peaks 3455 and 3480 cm^{-1} of raw and acid treated avocado seeds respectively. This can be atributed to existence of stretching vibrations of surface hydroxyl group (O-H) from intermolecular hydrogen bonds of

alcohols and phenols in lignin and cellulose. Absorbance at 2935 cm^{-1} are indicative of CH_3CH_2 with -CH symmetrical and antisymetrical stretch and hydroxyl group in carboxylic acid. This is the same for both treated and raw powdered avocado seeds. The absorption peak at 1388 cm^{-1} is assigned to COO^- group in carboxylic salts and C=O symmetric stretch broadband in the raw avocado seeds and 1307 cm^{-1} in the acid treated avocado seeds is indicative of C-O stretch which shows presence of alcohols, carboxylic acids, esters and ethers (Han *et al*., 2010). A broad peak at 1390 cm^{-1} indicative of phosphate groups in the treated powdered avocado seeds. The hydroxyl, carboxylic, alcohols, esters and ethers are responsible for binding the heavy metals (Ferreira *et al.,* 2012). These groups in powdered avocado seeds can be involved in chemical bonding and are responsible for the cation exchange capacity.

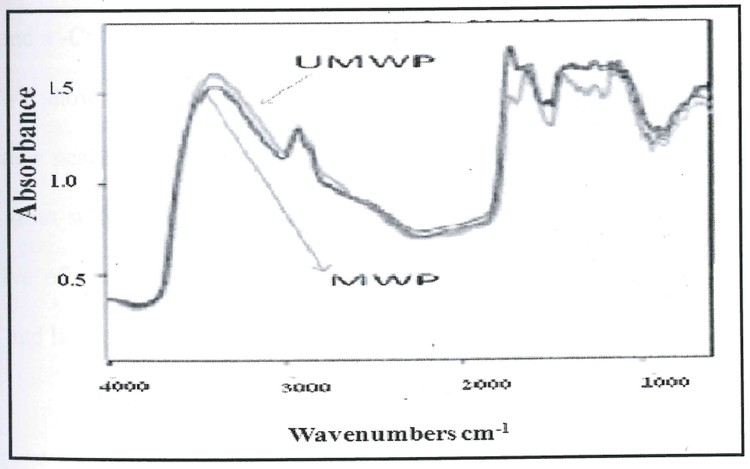


Figure 4.7: MIR results for MWP and UMWP

In the region between 3400-3300 cm^{-1} spectra of raw and acid treated watermelon peels (Figure 4.7) show strong band that appears with different intensity, which can be indicative of existence of OH-groups which shows presence of phenols and alcohols (Han *et al*., 2010). The peak observed at 2929 cm^{-1} is assigned to $-CH_3$ and $-CH_2$- from aliphatic groups which is a CH antisymmetric and symetric stretch. It is the same for both UMWP and MWP. Absorbance at 1737 cm^{-1} and 1735 cm^{-1} in UMWP and MWP is assigned to C=O stretch in aldehyde and saturated aliphatic compounds. The peak at 1627 cm^{-1} in the UMWP is assigned to C=O stretch and NH_2 deformation in primary amindes.

The peak at 1633 cm^{-1} appearing in the MWP is indicative of N-H bond in primary amine and a -C=C- stetch (Gupta *et al.,* 2013). At 1440 amd 1438 cm^{-1} peaks in UMWP and MWP show the presence of OH stretch in carboxilic acids. At 1390 cm^{-1} and 1176 cm^{-1} a new peaks emerges in the modifed peels which is assigned to $^{-}SO_2$ symmetrical stretch from sulfonyl chlorides. The peaks at 1272 cm^{-1}, 1278 cm^{-1} and 1106 cm^{-1} are indicative of presence of C-O stretch and C-O-C antisymmetric strecth from esters, ethers and lactones (Merkel *et al*., 2014).

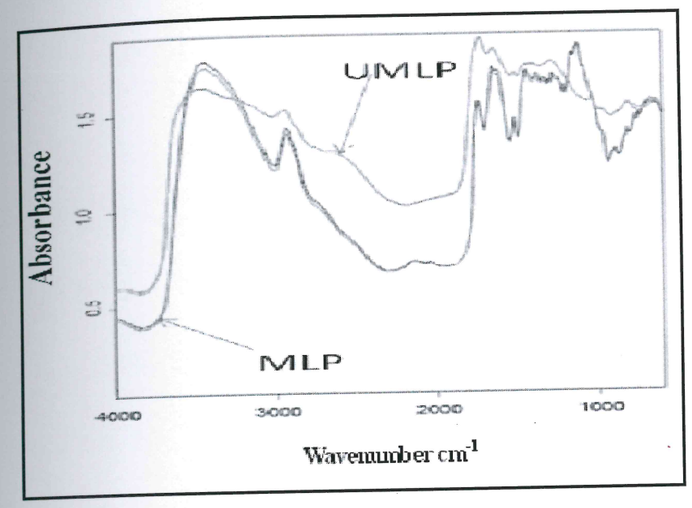


Figure: 4.8 MIR results for MLP and UMLP

An MIR spectrum of powdered MLP and UMLP was recorded to identify functional groups responsible for the metal ion co-ordination and results recorded in figure 4.8. The broad peaks at 3475 cm^{-1} and 3440 cm^{-1} in UMLP and MLP respectively are assigned to OH stretching in phenols and alcohols. The absorption band around 2942 cm^{-1} in MLP can be assigned to $-CH_3$ and $-CH_2$ stretch from aliphatic groups which is a CH symetric stretch. A peak at 2192 cm^{-1} assigned to C≡C which is absent in the acid treated lemon peels.

Absorbance at 1747 $cm^{-1}$and 1739 cm^{-1} in UMLP and MLP is assigned to C=O stretch in esters, carboxilic group and saturated aliphatic compounds. The absorption band around 1652 cm^{-1} and 1662 cm^{-1} in the UMLP and MLP are assigned to C=O stretch and NH_2 deformation in primary amindes. The peak at 1641 cm^{-1} appearing in the MLP is

indicative of N-H bond in primary amine and a -C=C- stetch. The absorption band around 1467 cm^{-1} from MWP is indicative of the presence of OH stretch in carboxilic acids. At 1282 cm^{-1} peak assigned to Ar-O in alkyl aryl ether and a C-O strecth in unmofied lemon peels. A new peaks emerges at 1164 cm^{-1} in the modifed peels which is assigned to -SO_2 symmetrical stretch from sulfonyl chlorides (Gupta *et al.*, 2013).

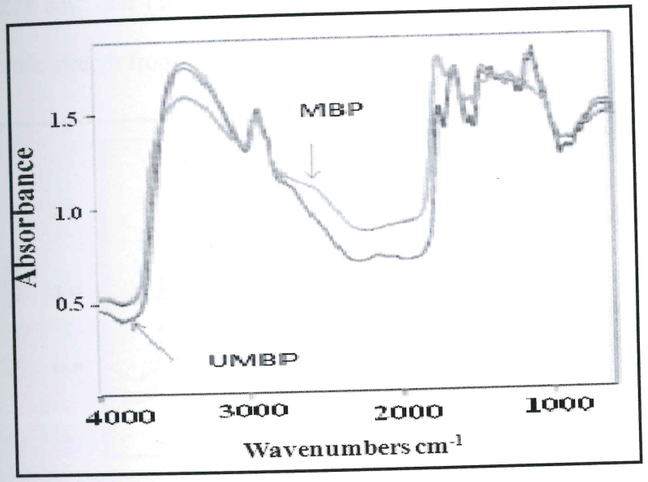


Figure 4.9: MIR results for MBP and UMBP

Results in figure 4.9 show that in powdered banana peels the absorption peaks at around 3400- 3450cm^{-1} in UMBP and MBP are indicative of existence of OH-groups which shows presence of phenols and alcohols. The peak observed at 2999 cm^{-1} is assigned to $–CH_3$ and $–CH_2$- from aliphatic groups which is a CH anti-symmetric and symmetric stretch. It is the same for both UMBP and MBP. Absorbance at 1741 $cm^{-1}$and 1743 cm^{-1} in UMBP and MBP is assigned to C=O stretch in aldehyde and saturated aliphatic compounds. The peak at 1639 cm^{-1} in the UMBP is assigned to C=O

stretch and NH_2 deformation in primary amindes. The peak at 1646 cm^{-1} appearing in the MBP is indicative of N-H bond in primary amine and a -C=O- stetch. At 1423 amd 1419 cm^{-1}peaks in UMBP and MBP are indicative of the presence of OH stretch in carboxilic acids. At 1375 cm^{-1} and 1176 cm^{-1} a new peaks emerges in the modifed peels which is assigned to $-SO_2$ symmetrical stretch from sulfonyl chlorides. The peaks at 1272 cm^{-1}, 1278 cm^{-1} and 1106 $cm^{-1}$are indicative of presence of C-O stretch and C-O-C anti-symmetric strecth from esters, ethers and lactones (Merkel *et al.*, 2014).

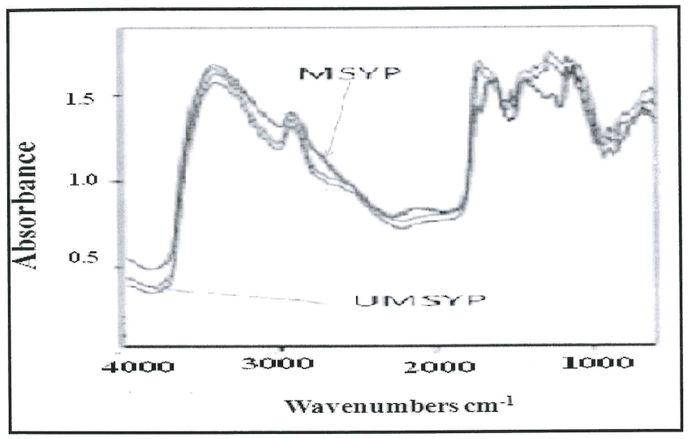


Figure 4.10: MIR spectra for MSYP and UMSYP

The absorption bands (Figure 4.10) at 3459 and 3450 cm^{-1} can be assigned to streching vibrations of surface hydroxyl group (OH) and H-bond in alcohols and phenols. The peak is broader and has reduced intensity after acid treatment of powdwered sweet yellow passion peels. At 2948 cm^{-1} and 2942 in UMSYP and MSYP are peaks assigned to C-H stretch in alkane. The peak at 2175 cm^{-1} in UMSYP is assined to a -NC stretch and is absent in the MSYP. The peaks appearing in 1743 cm^{-1} are assigned to –CO

stretch in esters and ketone in the UMSYP and 1733 cm^{-1} is assigned to a C-O stretch in aldehydes in MSYP. Peaks in 1673 cm^{-1} and 1700 cm^{-1} in UMSYP and MSYP are assigned to C=O stretch in carboxilic acid. A broad peak at 1390 cm^{-1} indicative of phosphate groups in the treated powdered sweet yellow passion peels. The hydroxyl, carboxylic, alcohols, esters and ethers are responsible for binding the heavy metals (Ferreira *et al.,* 2012). Results reported in this study were similar to those reported on acid activated sawdust, bagasse and sea weed (Kumar *et al*., 2014), acid treated orange peel (Feng and Guo, 2012), banana peel (Hossain *et al.,* 2012) and maize tassels (Mwangi *et al.,* 2012).

After acid treatment the biomasses present structural changes in their FTIR spectra see figure 4.6-4.10, the band at 1520 cm^{-1} is absent or decreased in acid modified samples, which suggests a reaction of depolymerization of aromatic ring of lignin that could lead to a lignin removal (Merkel *et al*., 2014). Additionallly the band at 935 cm^{-1} is absent in acid treated samples and these confirms the structural degredation of lignocellulosic material (Pandey and Negi, 2015). The bands at 3400-3300 cm^{-1} (OH groups); 1620, 1321 and 1150 cm^{-1}(C-O group) and 1430 cm^{-1}(CH groups) decreased in intensity after acid treatment. Reduction of FTIR peaks can be related to condensation reactions and splitting of lignin aliphatic as well as removal of part of cellulose and hemicellulose(Merkel *et al*., 2014). Biomass treatment could expose some new groups due to structural degredation (Lim *et al*., 2013).

4.3 Effect of initial metal ion concentration on sorption of Cu (II), Pb (II) and Cd (II)

The effects of initial metal concentration on sorption of metal ions was investigated for UMLP, MLP, UMAS, MAS, UMBP, MBP, UMWP, MWP, UMSYP and MSYP. All the batch sorption experiments reported at a constant temperature of 25±1°C.

4. 3.1 Effect of initial Cu (II) ions concentration

Effect of initial copper (II) concentration on sorption of was carried out at optimum conditions identified during preliminery studies. The results were recorded as shown figure 4.11. Results in figure 4.11 show that sorption of Cu (II) ions on the peels and avocado seed is significantly influenced by the initial concentration of metal ion in aqueous solutions. The removal efficiency was found to increase with increase in amount of Cu (II) ions to a maximum of 50 mg/L in both acid treated and raw adsorbents. Further increase in concentration of metal ion had no effect on removal efficiency. The raw sorbents had low percentage removal of Cu (II) ions as observed in sorption plots in figure 4.11.

Uptake of copper (II) ions increases from 89.8 % to 97.7 % in lemon peels (a), 95.7 % to 98.9 % in avocado seeds (b), 96.6 % to 97.8 % in banana peels (c), 97.4 % to 98.4 % in watermelon peels (d) and 96.6 % to 99.3 % in sweet yellow passion peels (e) after acid modification. This confirms that the modification has a positive effect on sorption of copper (II) ions.

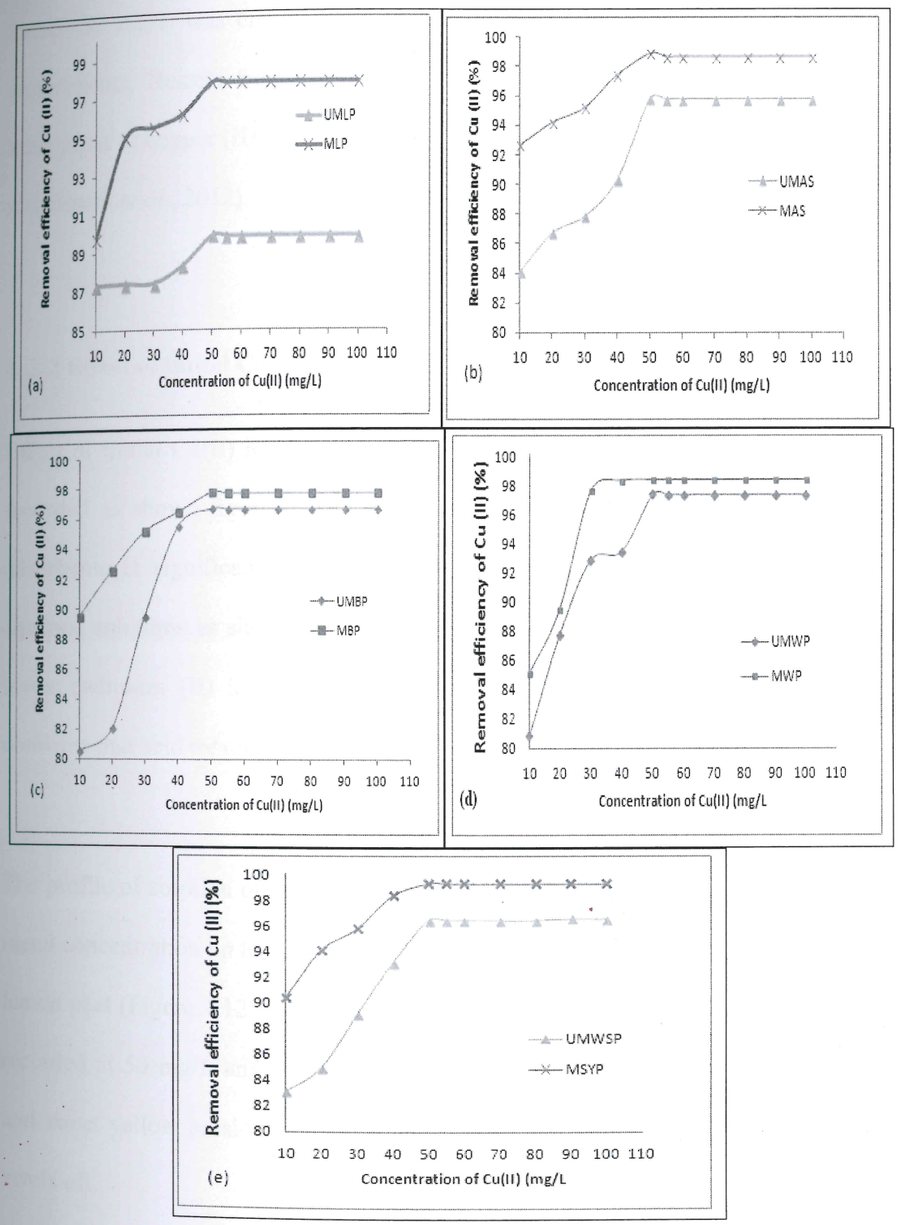


Figure 4.11: Effect of initial metal ion concentration on sorption of Cu (II) ions on (a) lemon peels, (b) avocado seeds, (c) banana peels, (d) watermelon peels and (e) sweet yellow passion peels (acid treated: 20 mg, 2 hrs and pH 5.9 and raw: 20 mg, 3 hrs and pH 4.2).

Hence 50 mg/L was chosen as the optimum initial concentration in the subsequent experiments. Results from this study are higher than those reported by a study on adsorption of copper (II) ions using raw banana peel which reported 88 % at 10 mg/L, 5 g (Hossain *et al*., 2012).

4. 3.2 Effect of initial Cd (II) ions concentration

Effect of initial Cd(II) ions concentration on sorption was carried out the results were recorded as shown figure 4.12. Adsorption of cadmium (II) ions on raw and treated adsorbents is significantly influenced by the initial concentration of metal ions in aqueous solutions as shown in figure 4.12. The results show that raw adsorbents had lower cadmium (II) ions uptake as compared to the acid treated adsorbents. This confirms that acid treatment had a positive effect on sorption of the metal ions.

The profile of sorption of cadmium was observed to increase with increase in the initial metal concentration up to 10 mg/L and 50 mg/L in raw and acid treated watermelon and lemon peel (Figure 4.12 (d) and (a)) respectively. Maximum sorption of cadmium was recorded at 50 mg/L and 10 mg/L in raw and acid treated avocado seed, banana peel and sweet yellow passion peel respectively (figure 4.12 (b), (c) and (d)) after which it levels off.

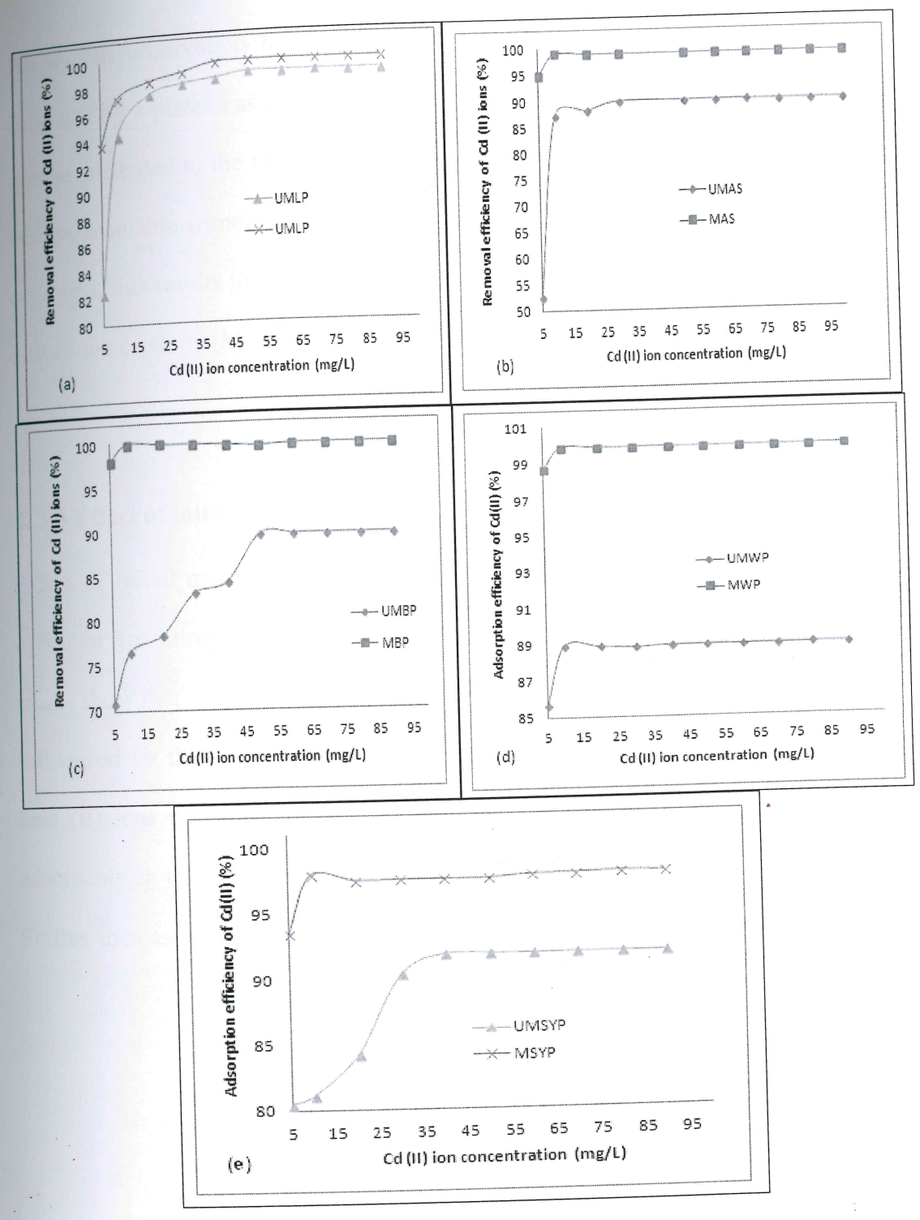


Figure 4.12: Effect of initial concentration on sorption of Cd (II) ions on (a) lemon peels (b) avocado seeds, (c) banana peels,(d) watermelon peels and (e) sweet yellow passion peel (acid mofidified: 10 mg, 2hrs, pH 5.9 and raw: 10 mg, 3 hrs, pH 5.8)

An overall observation for all the adsorbents shows a continuous cadmium uptake followed by a plateau as concentration of cadmium in the solution was increased. This can be attributed to the fact that concentration is the driving force for the metal ions to occupy available sorption sites. When most of the available sites on the adsorbent are occupied, this results in saturation and is said to have attained its operational maximum adsorption capacity (Mwangi *et al*., 2012).

4. 3.3 Effect of initial Pb (II) ions concentration

Effect of initial metal concentration on sorption of lead (II) ions was carried out at optimum conditions identified, the results were recorded as shown figure 4.13. The results show that sorption of lead (II) ions on raw and treated adsorbents is significantly influenced by the initial concentration of metal ions in aqueous solutions. Uptake of lead (II) ions was found to increase with increase in metal concentration in all the adsorbents up to a maximum of 20 mg/L and 50 mg/L raw and acid treated adsorbents. Further increase in concentration of lead (II) ions had no effect on removal efficiency.

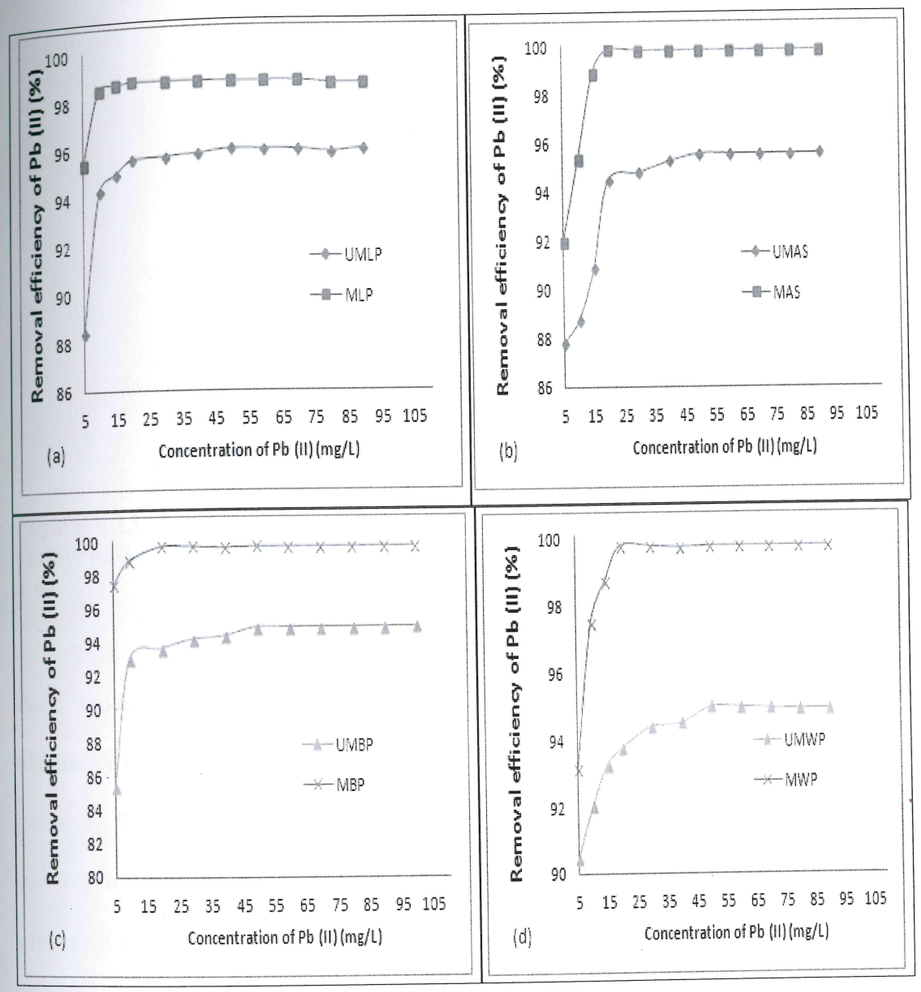


Figure 4.13: Effect of initial concentration on sorption of Pb (II) ions on (a) lemon peels, (b) avocado seeds, (c) banana peels and (d) watermelon peels (acid mofidified: 20 mg, 2 hrs, pH 5.9 and raw: 50 mg, 3 hrs, pH 5.8)

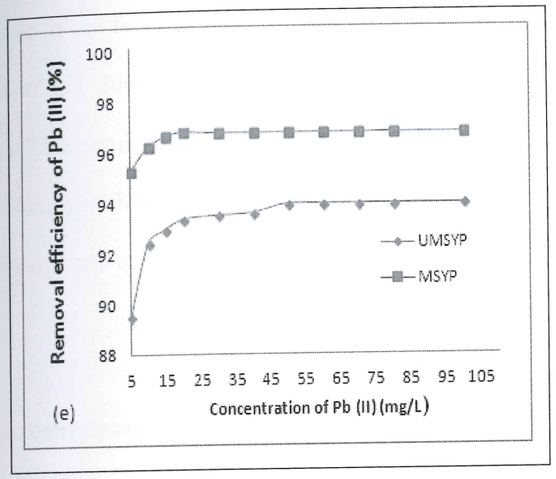


Figure 4.13(e)**:** Effect of initial concentration on sorption of Pb (II) ions on sweet yellow passion peels (acid mofidified: 20 mg, 2 hrs, pH 5.9 and raw: 50 mg, 3 hrs, pH 5.8)

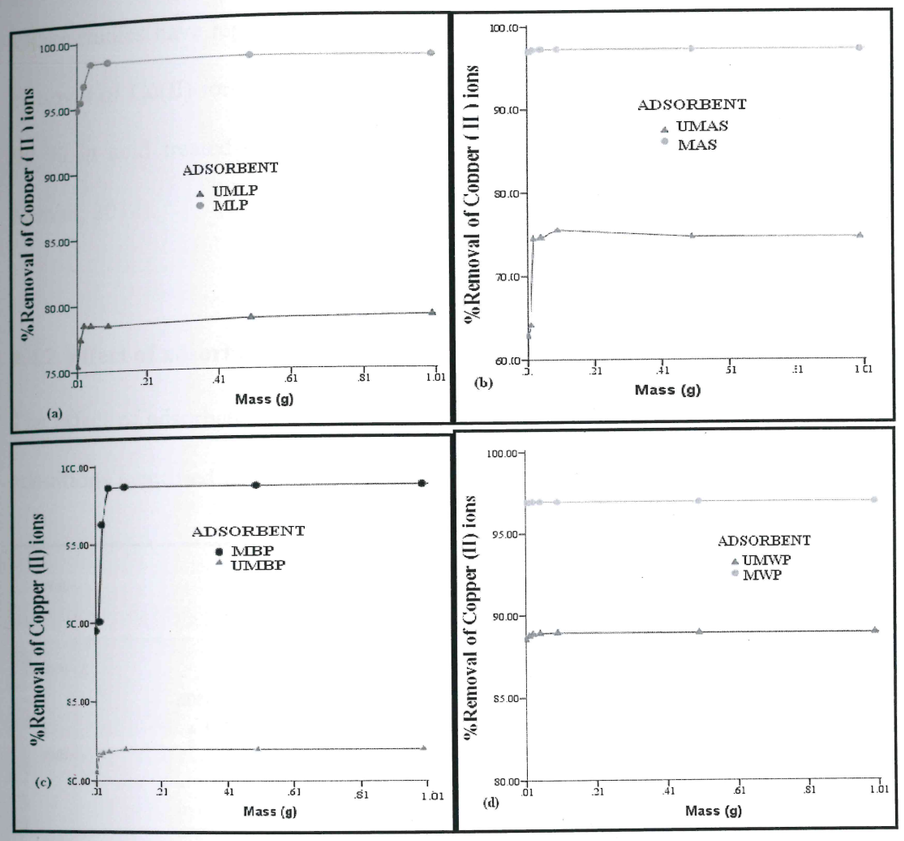
Acid modification was found to have effect on the sorption of lead. Maximum efficiency removal of lead (II) ions was found to increase from 96.0 % to 98.8 % lemon peels (a), 95.6 % to 99.9% avocado seeds (b), 94.8 % to 99.7 % banana peels (c), 95 % to 99 % in watermelon peels (d) and (93.6 % to 96.8 % sweet yellow passion peels (e) after acid modification. The raw sorbents had lower percentage removal as compared to the acid treated sorbents on the metals ions (Cu (II), Cd (II) and Pb (II)). This is an indication that modification has a positive effect on sorption of metals. This can be attributed to the micro-rough texture and the porous surface after modication as shown in figures 4.1- 4.5. Generally metal ions uptake increases continuously up to a maximum and thereafter levels off as the concentration of metal ions is increased. At low initial metal concentration almost all the metal ions have been removed from aqueous solution. As the initial metal concentration is increased the adsorpion eficiency

does not change due to the fact that the available active sites become limited (Ilhan *et al*., 2004; Arshad *et al*., 2008; Koel *et al*., 2012; Mwangi *et al.,* 2012; Moyo and Chikazaza., 2013,). This results compare with those reported in the study of watermelon shell in removal of copper (Koel *et al*., 2012) and removal of lead from polluted waste waters employing sulphuric acid treated maize tessel (Moyo and Chikazaza., 2013).

4.4 Effect of adsorbent dosage on sorption of Cu (II), Pb (II) and Cd (II)

4.4.1 Effect of adsorbent dosage on sorption of Cu (II) ions

To determine the effect of adsorbent dosage on removal of copper (II) ions the results are shown in figure 4.14. The results show that uptake of copper (II) ions increased with increase in adsorbent doses. Maximum uptake was attained at 10 mg for all the acid treated and raw adorbents with exception of sweet yellow passion where maximum removal was attained at 50 mg. Beyond this mass there was no further increase in percentage removal of copper (II) ions recorded. Acid treated adsorbents were found to have a higher efficiency on copper removal than raw adsorbents as shown in figure 4.14. Maximum percentage removal copper (II) was found to increase from 78.9 % to 98.4 % in lemon peels (a), 74.6 % to 97.3 % in avocado seeds (b), 81.7 % to 98.6 % in banana peels (c), 88.9 % to 97.0 % in watermelon peels (d) and 80.1 % and 97.6 % in sweet yellow passion (e) after acid modification.



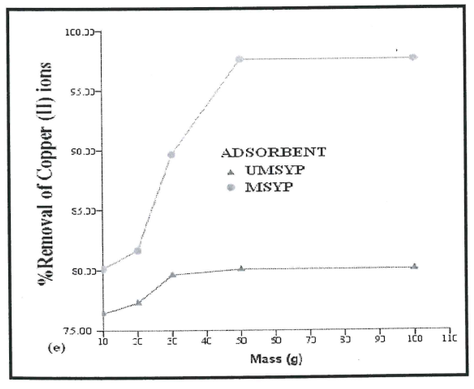


Figure 4.14: Effect of dosage of (a) lemon peels and (b) avocado seeds c) banana peels, (d) watermelon peels, and (e) sweet yellow passion peels on the adsorption of Cu (II) ions (acid treated: 2 hrs and pH 5.9, 20 mg/L and raw: 3 hrs and pH 4.2, 20 mg/L).

Other studies have reported similar results, for example a 61.29 % (0.8 g) in study of removal of Cu(II) ions in orange peel activated carbon (Benard and Jimoh, 2013) and 99 % in acid treated orange peel and 75 % in raw on orange peel (Khalfaoui and Meniai, 2012).

4.4.2 Effect of adsorbent dosage on sorption of Pb (II) ions

The effect of adsorbent dosage on removal of lead (II) ions was conducted at optimum conditions identified results recorded in figure 4.15.

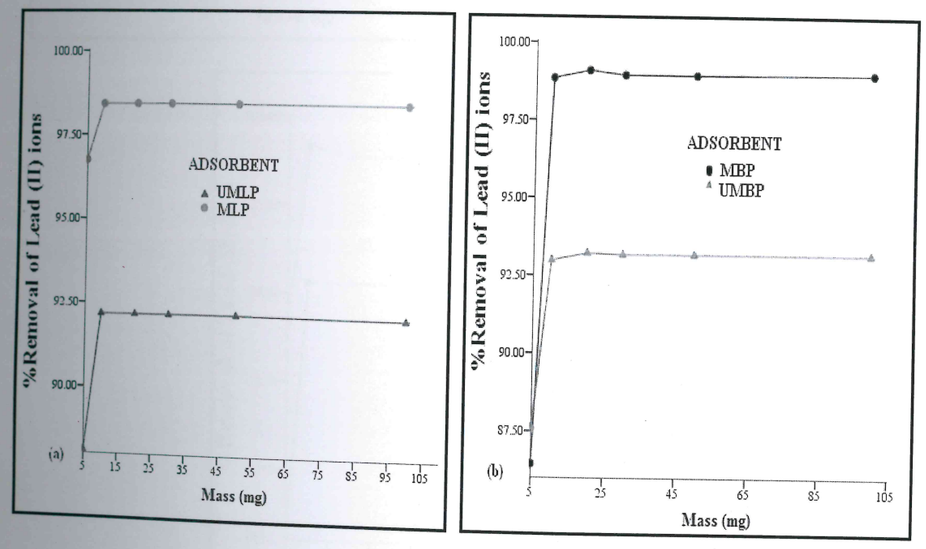
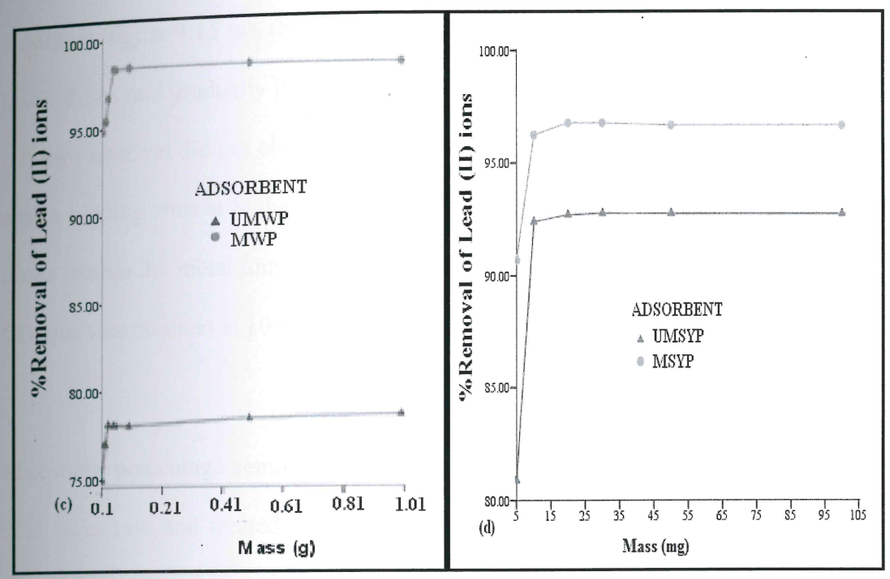


Figure 4.15: Effect of dosage on the adsorption of Pb (II) ions on (a) lemon peels and (b) banana peel (acid mofidified: 50 mg/L, 2 hrs, pH 5.9 and raw: 50 mg/L, 3 hrs, pH 5.8)



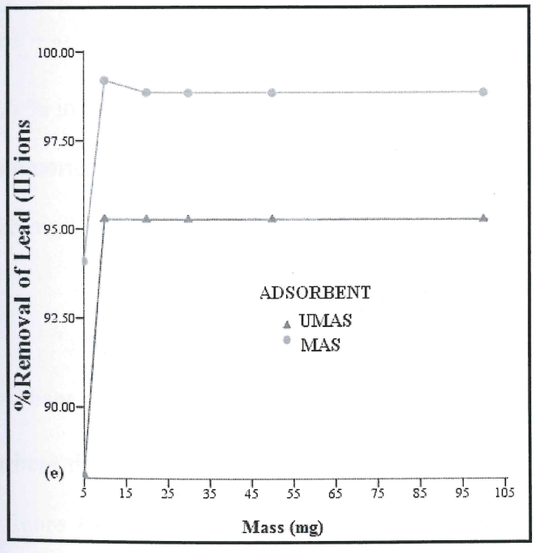


Figure 4.15: Effect of dosage on the adsorption of Pb (II) ions on (c) watermelon peels, (d) sweet yellow passion peels , and (e) avocado seed (acid mofidified: 50 mg/L, 2 hrs, pH 5.9 and raw: 50 mg/L, 3 hrs, pH 5.8)

Results in figure 4.15 (a), (b), (c), (d) and (e) show that lead (II) ions uptake was low at lower doses and gradually increased with increasing dosage. Latter at higher doses, lead (II) ions removal did not change greatly. The partial aggregation of among the available active binding sites at higher doses and limited number of active binding sites at lower doses retards the metal ions adsorption (Hossain *et al*., 2012). Maximum uptake of lead (II) ions was attained at 10 mg in both raw and acid treated adsorbents.

Maximum percentage removal of lead (II) ions was found to increase from 91.3% to 98.5 % in raw and treated lemon peels (a), from 93.3 % to 98.8 % in raw and acid treated banana peels (b), form 77.9 % to 98.3 % in raw and treated watermelon peels (c), from 92.8 % 96.7 % in raw and acid treated sweet yellow passion peels (d) and from 95.4 % to 99.6 % in raw and acid teated avocado seed (e). Percentage removal of 92.3 % (2.5 g) was reported on acid treated maize tassels (Moyo and Chikazaza., 2013) and 94.8 % (0.5g, 25 mg/L) on study of banana peel (Muhammad *et al*., 2011).

4.4.3 Effect of adsorbent dosage on sorption of Cd (II) ions

The effect of adsorbent dosage on removal of cadmium (II) ions was conducted and results recorded in figure 4.16.

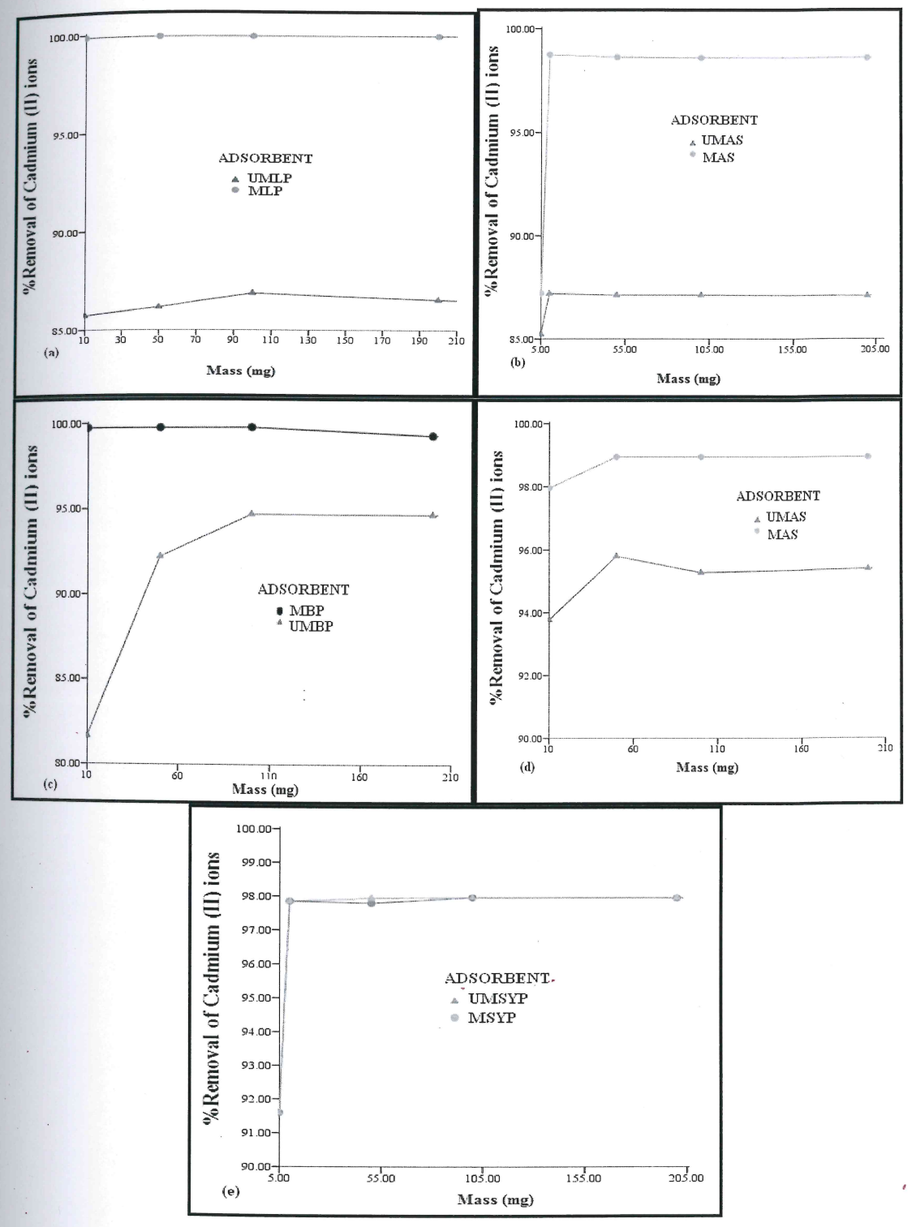


Figure 4.16: Effect of dosage of (a) lemon peels, (b) avocado seeds, (c) banana peels and (d) watermelon peels and (e) sweet yellow passion peels on sorption of Cd (II) ions (acid mofidified: 10 mg, 2 hrs, pH 5.9 and raw: 10 mg, 3 hrs, pH 5.8).

Results from figure 4.16 show that uptake of cadmium (II) ions was influenced by adsorbent dosage. Uptake of cadmium (II) ions increases with increase in mass of the adsorbent to a maximum of 86.2 % (50 mg) and 99.9 % (10 mg) in lemon peels (a), 87.2 % (10 mg) and 98.7 % (10 mg) in avocado seeds (b), 94.6 % (100 mg) and 98.9 % (10 mg) in banana peels (c), 95.8 % (50 mg) and 98.9 % (50 mg) in watermelon peels (d) and 97.9 % (10 mg) in sweet yellow passion (e) for raw and treated adsorbents respectively. Acid modification improved the uptake of cadmium in all the adsorbents except in sweet yellow passion peel.

The increase in percentage removal oberved in all adorbents and metal ions after acid modification can be attributed to improved surface texture and micro pore structure after acid modification as shown in figures 4.1- 4.5 making easier penetration of ions to the adsorption sites (Anwar *et al*., 2010). Uptake of metal ions increased with increase in adsorbent dosage to a maximum and thereafter percentage removal of the metal ions did not change significantly in all the adsorbents. This phenomenon can be attributed to greater the availability of active binding sites at higher doses and lack of active binding site at lower doses which retards the metal ion adsorption onto the adsorbent (Karthikeyan *et al*., 2007; Anwar *et al*., 2010). Increasing the dosage had no effect at higher doses (Moyo and Chikazaza., 2013). These results are in agreement to those reported in the literature (Dekhil *et al*., 2011; Hossain *et al.*, 2012; Koel *et al.*, 2012; Moyo and Chikazaza., 2013; Srinivasa and Kesava, 2013)

4.5 Effect of contact time on sorption of Cu (II), Pb (II) and Cd (II)

The effect of contact time on sorption of metal ions was investigated for raw and treated lemon peels (UMLP and MLP), and treated avocado seeds (UMAS and MAS), raw and acid treated banana peels (UMBP and MBP), and acid treated watermelon peels (UMWPand MWP), raw and acid treated sweet yellow passion peels (UMSYP and MSYP) in this study and the results are discussed in the following subsections. Optimum conditions for each metal ion were adopted in this section while temperature was kept constant at 25±0.5°C. From different plots of metal sorption against time, the optimum contact time for each metal was obtained.

4.5.1 Effect of contact time on sorption of Cu (II) ions

Effect of contact time on sorption of copper was carried out at optimum conditions identified the results were recorded as shown figure 4.17. Uptake of copper ions was influenced by adsorbate residence time as shown in figure 4.17. From the graphs (a), (b), (c),and (d), the rate of copper adsorption was very rapid during first 60 minutes in the acid treated and 90 minutes in unmodifed lemon peels, avocado seeds, banana peels and watermelon peels. However, maximium adsorption of copper (II) ions was achieved at 60 minutes in sweet yellow passion peel as in figure 4.17 (e). Thereafter, the rate of copper removal approached a steady state, indicating attainment of equilibrium (Karthikeyan *et al*., 2007). Optmum adsorption time for copper (II) ions in all experiments was taken to be 120 and 180 minutes for the acid treated and raw adsorbents respectively.

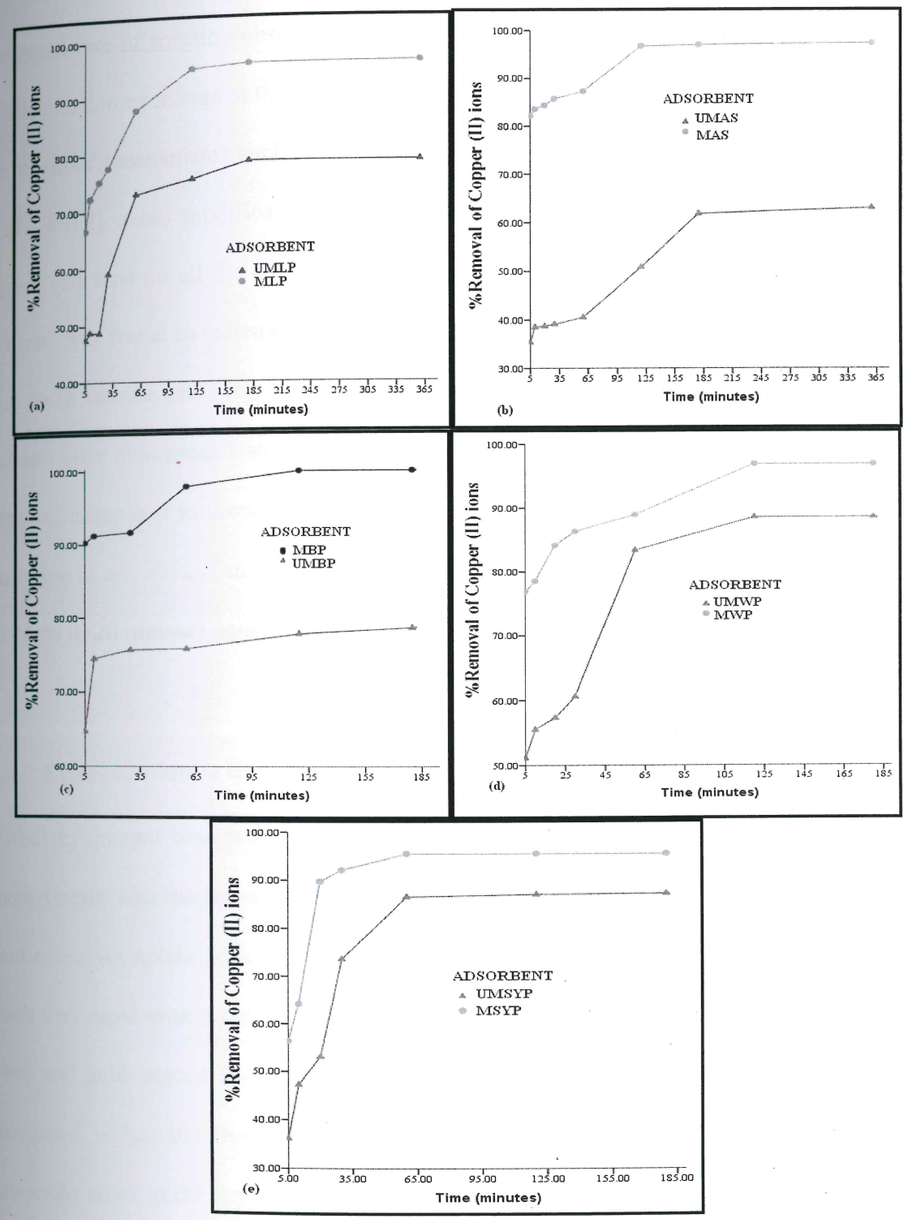


Figure 4.17: Effect of contact time on sorption Cu (II) ions on (a) lemon peels and (b) avocado seeds, c) banana peels, (d) watermelon peels and (e) sweet yellow passion peels (acid treated: 20 mg, pH 5.9, 20 mg/L and raw: 20 mg, pH 4.2, 20 mg/L).

The rapid rate of sorption observed at lower contact time may be attributed to physical sorption or ion exchange at the surface of the adsorbents and the subsequent slower rate due to other mechanisms such as complexation or saturation of binding sites (Mwangi *et al*., 2012). Acid modification was found to have a positive effect on sorption of copper (II) ions on all the adsorbents. At optimum time percentage removal of copper (II) ions was found to increase by 16.8 % in lemon peels (a), 35 % in avocado seeds (b), 21.8 % in banana peels (c), 18.4 % in watermelon peels (d) and 8.5 % in sweet yellow passion after acid modification. Results obtained in this study show greater percentage removal compared to those reported for raw watermelon peel (84 %) in 120 minutes (Bunarjee *et al*., 2012; Cm, 2015) and lower than those reported by (Castro *et al*., 2011) of 94 % in 20 minutes using solid phase extraction colunm procedure.

4.4.2 Effect of contact time on sorption of Pb (II) ions

Effect of contact time was carried out at optimum conditions identified in the batch experiments and results recorded in figure 4.18. The results indicate that agitation time had effect on uptake of lead (II) ions. In figure 4.18 (a) the rate of sorption of lead (II) ions was rapid within the first 60 minutes attaining maximum of 91.9 % and 96.9 % in raw and acid treated lemon peels. Maximum uptake of of 92.8 % lead (II) ions was recorded within the first 120 minutes in raw avocado seed and 99.5 % acid treated avocado seeds in the first 30 minutes.

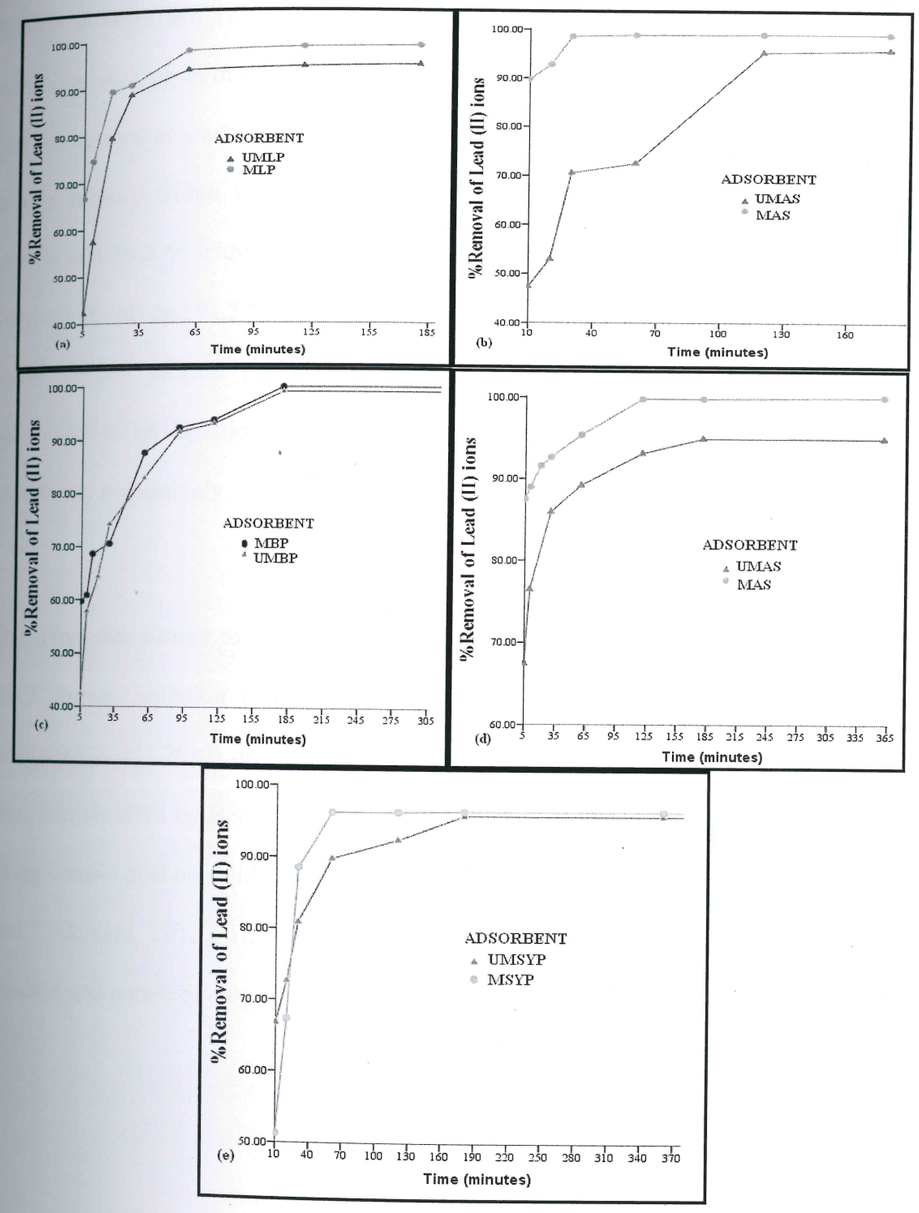


Figure 4.18: Effect of contact time on sorption Pb (II) ions on (a) lemon peels, (b) avocado seeds (c) banana peels, (d) watermelon peels and (e) sweet yellow passion peels (acid mofidified: 50 mg/L, 10 mg, pH 5.9 and raw: 50 mg/L, 50 mg, pH 5.8)

first 60 minutes and 100 % in 120 minutes for raw and acid treated lemon peel, a maximum adsorption of 88.5 % and 99.2 % were attained after 120 and 30 minutes in raw and treated avocado seed respectively (b), percentage removal of 80.2 % and 98.5 % was achived within 120 minutes in raw and treated banana peels respectively (c), 83.4 % and 99.8 % within the first 120 minutes for raw and treated watermelon peels respectively (d) and 91.3 % and 95.9 % within the first 120 minutes for raw and treated sweet yellow passion peels respectively (e). The subsequent experiments were conducted at an agitation time of 180 and 120 minutes for raw and acid treated adsorbents respectively.

The trend was similar to that observed in copper (II) and lead (II) in section 4.4.1 and 4.4.2 above. Agitation time obtained in this study compare with that reported by (Bunarjee *et al.,* 2012) on study of adsoption of lead by watermelon peel but is more than that reported by Benard and Jimoh (2013) using orange peel, Castro *et al*., (2011) using banana peel on solid phase colunm procedure and acid treated maize tassel (Moyo and Chikazaza, 2013). This can be attributed to difference in experimental conditions, method and nature of adsorbents.

Maximum removal in lead (II) ions of 99.0 % and 99.2 % was achieved by 180 minutes in raw and acid treated banana peels (c). However, maximum revoval of 98.8% and 100.0 % were attained after 180 and 120 minutes in raw and acid treated watermelon peels respectively (d) and 95.8 % and 96.3 % within 180 and 60 minutes in raw and acid treated sweet yellow passion peel respectively. After attainment of maximum percentage removal there was no further increase with increase in time in all the adsorbents. The trend was similar to that observed in copper (II) in section 4.4.1. Acid modification had a great influence in agitation time. Acid treated adorbents attained equillibrium within a shorter time as compared to the raw adorbents and also improvement in efficiency was also noted after acid treatment in all the adorbents. Adequate external surface area on the acid treated adsorbents may have boosted the rate of asorption. Similar trend was reported in treated maize tassels (Mwangi *et al.,* 2012; Moyo and Chikazaza, 2013).

4.5.3 Effect of contact time on sorption of Cd (II) ions

Effect of contact time on sorption of cadmium (II) ions was investigated at optimum condition. The results were recorded as shown in figure 4.19. Initially there was rapid increase in adsorption of cadmium (II) ions upto a maximum time in all the adsorbents, beyond this time the percentage of reoval was almost constant indicating the attainnment of equillibrium conditions as shown in figure 4.19 (a), (b), (c),and (d) and (e). figure 419 (a) shows that maximum adsorption of 85.2 % was attained within the

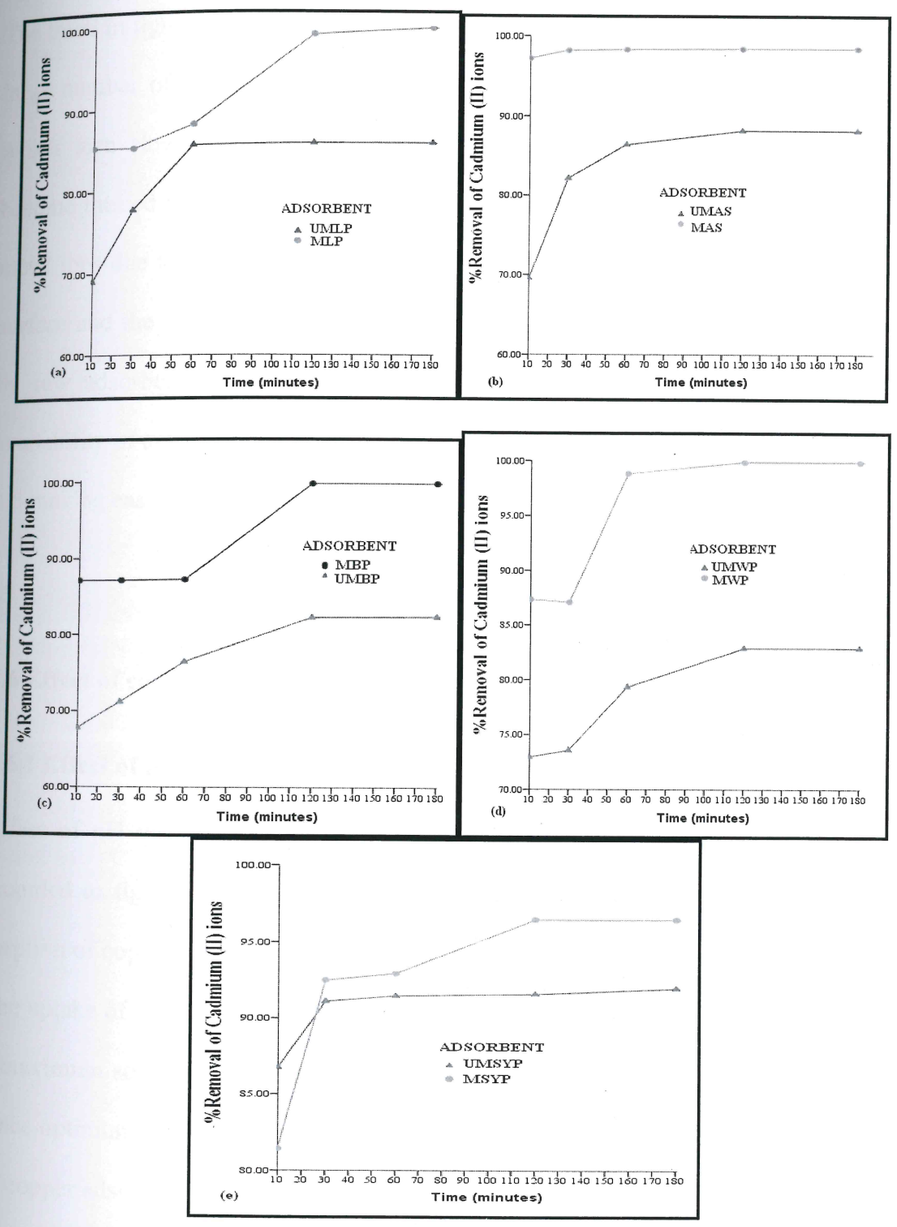


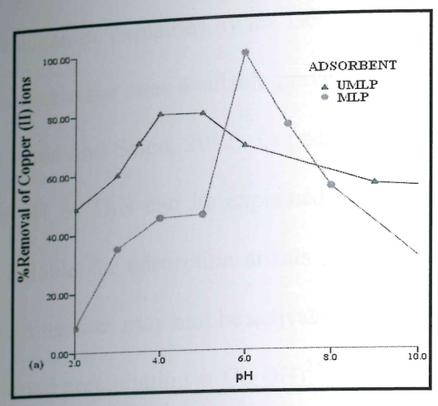
Figure 4.19: Effect of contact time on sorption Cd (II) ions on (a) lemon peels, (b) avocado seeds,(c) banana peels, (d) watermelon peels and (e) sweet yellow passion peels (acid mofidified: 10 mg, 50 mg/L, pH 5.9 and raw: 10 mg, pH 5.8, 50 mg/L).

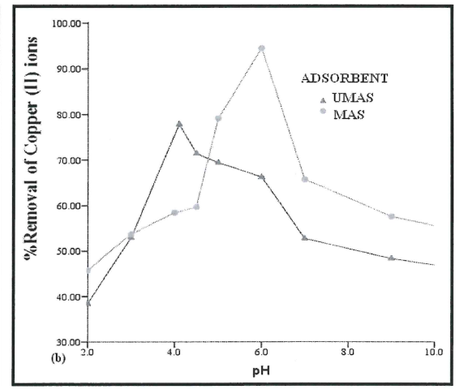
The trend in figures 4.16-4.19 can be explained by the fact initially due to presence of a large number of vacant active binding sites, the adsorption rate was relatively high, which then slowed down and levelled off. As time increased the adsorption sites become limited and the remaining vacant surface sites were difficult to be occupied by metal ions due to the formation of repulsive forces between the metal ions on the solid surface and the liquid phase (Anwar *et al*., 2010). The increase in percentage removal by raw adsorbents observed in all adorbents and metal ions can be attributed to availability of enhanced surface porarity after acid modification as shown in figures 4.1-4.5 making easier penetration of ions to the adsorption sites.

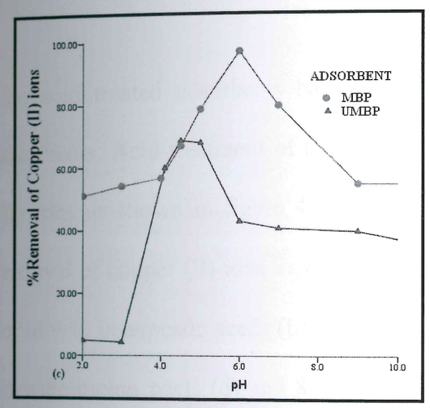
4.6 Effect of contact pH on sorption of Cu (II), Pb (II) and Cd (II)

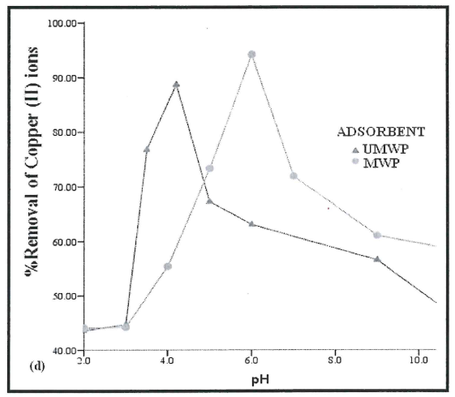
4.6.1 Effect of pH on sorption of copper (II) ions

Effect of pH was carried out on optmum condition identified and the results were recorded in figure 4.20. The results in figure 4.20 (a), (b), (c), (d) and (e) show that sorption of copper (II) ions as a function of pH by both acid treated and raw adsorbents. The uptake of copper (II) ions was low at low pH and increases with inncrease in pH to a maximum sorption at pH 6.0 and 4.1 in acid treated and raw adsorbents respectively. Once optimum pH is reached, further increase in pH results in reduction of the amount of copper adsorbed.









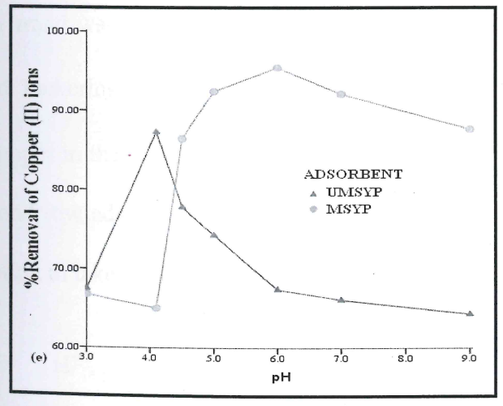


Figure 4.20: Effect of pH on the adsorption of Cu (II) ions on (a) lemon peels, (b) avocado seeds, (c) banana peels, (d) watermelon peels and (e) sweet yellow passion peels (acid treated: 20 mg, 2 hrs and 20 mg/L and raw: 20 mg, 3 hrs and 20 mg/L)

This can be explained by the fact that at low pH value, H^+ ions compete with Cu^{2+} for the exchange sites available preventing copper ions from approaching the binding sites (Gönen and Selen, 2012). Copper (II) adsorption was significantly high between pH 4 to pH 6. This can be explained by the fact that Cu^{2+}, $Cu(OH)^+$, and $Cu(OH)_2$ are available for adsorption at this pH range (Wang and Qin, 2005). Beyond pH 6 the binding sites may mot be activated in basic conditions (Hossain *et al*, 2012) and copper started precipitating as $Cu(OH)^{2+}$ resulting in the decline in amount of copper adsorbed.

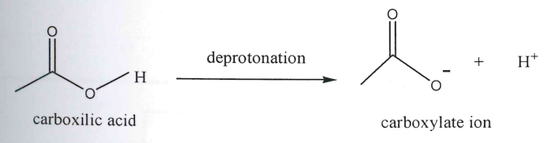
The acid treated adsorbents had a higher adsorption at optimum pH than the raw adsorbents. Acid treatment of adsorbent has a significant effect on sorption of copper (II) ions as shown in figure 4.20 (a), (b), (c) and (d) and (e). Maximum percentage removal of copper (II) ions increased from 79.4 % to 98.6 % in lemon peels (a), 79.9 % to 98.9 % in avocado seeds (b), 68.7 % to 97.1 % in banana peels (c), 88.7 % to 94.3% in watermelon peels (d) and 87.3 % to 95.5 % in sweet yellow passion (e) after acid modification. Similar trend was reported in acid treated maize tassel (Tranford *et al.,* 1952; Beveridge and Pickering, 1984; Mwangi *et al.,* 2012; Moyo and Chikazaza, 2013). Sorption of copper in the subsequent experiments was carried out at pH 6.0 and 4.2 for acid treated and raw adsorbents respectively. Dissociation of active sites must take place for adsorption to take place as shown in equation 4.1;

$$HL_{(aq)} \rightleftharpoons H^+_{(aq)} + L^-_{(aq)} \qquad \text{Equation. 4.1}$$

Where, HL is the sorbent and dissociates by splitting into L^-, conjugate base of the acid and H^+ proton.

4.6.2 Effect of pH on sorption of lead (II) ions

Effect of pH on sorption of lead (II) ions was investigated at optimum condition. The results were recordeds in figure 4.21. The results in figure 4.21 (a), (b), (c) and (d) and (e) show that percentage removal of lead (II) ions was low at low pH in all the adsorbents. As the pH was increased sorption lead (II) ions increased to a maximum pH 5.8 and 6.0 for raw and acid treated adsorbents respectively. This may be associated with the presence of carboxyl groups (-COOH) in the all the adsorbents as shown in figures 4.6 - 4.10. At pHs 5.8 – 6.0, the carboxylate ($-COO^-$) ligands attract the positively charged Pb^{2+}, binding occurs, indicating that the binding process is likely to be an ion-exchange mechanism that involves an electrostatic interaction between the negatively charged groups in the cell walls and the metallic cations (Moyo and Chikazaza., 2013) as shown in equations 4.2;



Equations 4.2

This phenomenon can be explained by the fact that at low pH presence of hydroxonium ions (H^+) which hinders the access of the metal ions to the surface functional groups (Low *et al*., 1995), the carboxyl groups retain their protons reducing the probability of binding to any positively charged ions (Low *et al*., 1995).

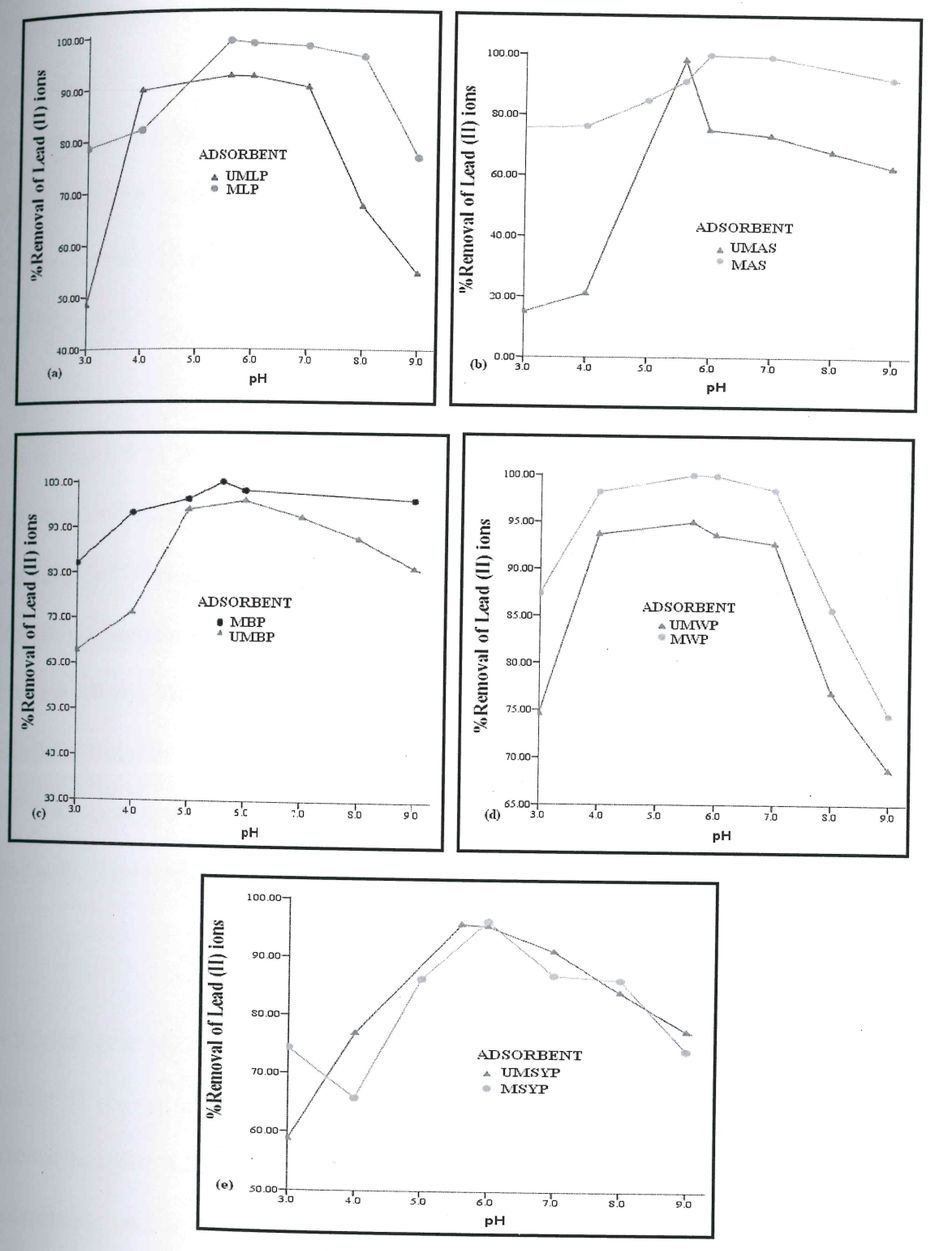


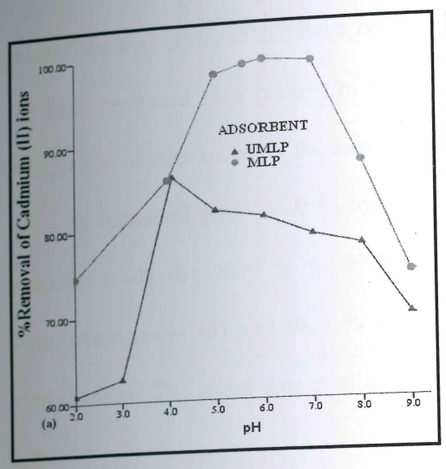
Figure 4.21: Effect of pH on sorption of Pb (II) ions on(a) lemon peels, (b) avocado seeds (c) banana peels, (d) watermelon peels and (e) sweet yellow passion peels (acid mofidified: 50 mg/L, 10 mg, 2 hrs and raw: 50 mg/L, 50 mg, 3 hrs)

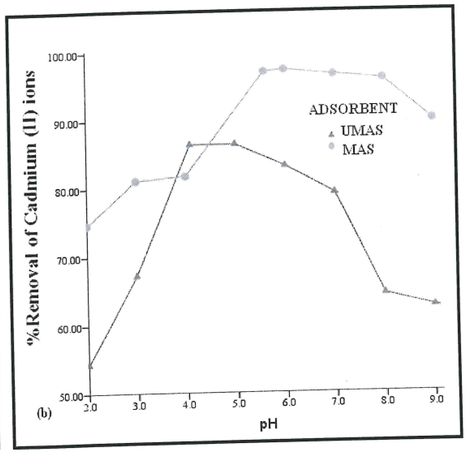
From the results (Figure 4.21) sorbent modification brought about improvement on efficiency of lead (II) ions which were found to increase from 92.3 % to 99.1 % in lemon peels (a), 98.0 % to 99.9 % in avocado seeds (b), 95.8 % to 99.9 % in banana peels (c), 82.9 % to 99.9 % in watermelon peels (d) and 95.8 % to 96.3% in sweet yellow passion (e) after acid modification. The trend was similar to the one recorded by copper in 4.4.1.

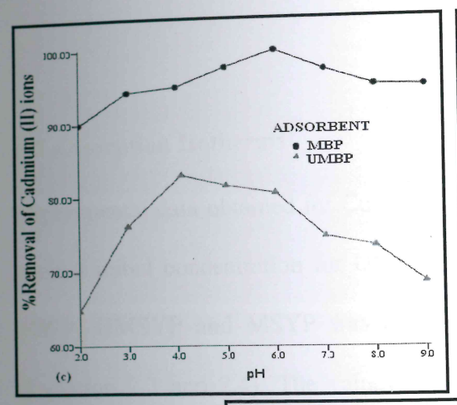
From figure 4.21 the percentage of lead (II) ions decreased beyond pH 6 the percentage removal of lead (II) ions reduced in all the adsorbents. This can be explained by the presence of ^{-}OH group in the adsorbents and lead (II) ions started precipitating as $Pb(OH)_2$ (Hossain *et al*., 2012, Wang and Qin, 2005). Phenolic compounds present in the adsorbents (figure 4.8) are also active sites for bio-sorption mechanism. Two adjacent phenolic hydroxyl groups can effectively bind with divalent heavy metal ion M^{2+} as shown in equation 4.3 (Khan *et al.*, 2013). The pH values of 5.8 and 6.0 for raw and acid treated adsorbens were used for the subsequent experiments.

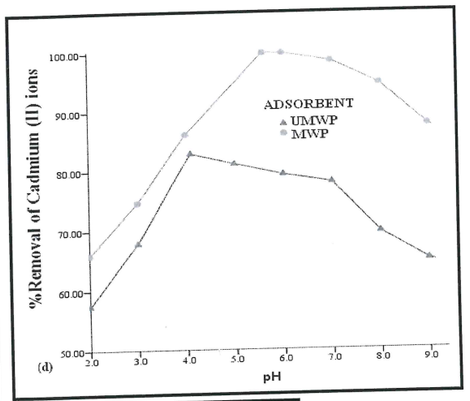
4.6.3 Effect of pH on sorption of cadmium (II) ions

Effect of pH on sorption of Cd (II) ions was caried out the results were recorded as shown in figure 4.22. The results in figure 4.22 (a), (b), (c),and (d) and (e) show raw adsorbents had a maximum sorption of pH 4.0 while the treated adsorbents had maximum adsorption at pH 5.8. Maximum sorption at pH 4.4 (Singh *et al.,* 2006), 4.2 and 6.1 in raw and acid treated maize









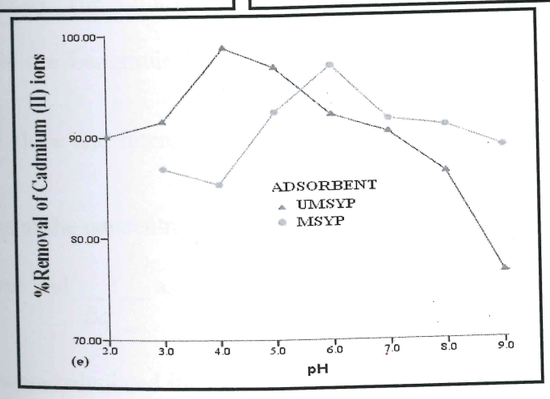


Figure 4.22: Effect of pH on the adsorption of Cd (II) ions on (a) lemon peels, (b) avocado seeds, (c) banana peels, (d) watermelon peels and (e) sweet yellow passion (acid mofidified: 10 mg, 2 hrs, 50 mg/L and raw: 10 mg, 3 hrs, 50 mg/L).

tassel (Mwangi *et al.,* 2012) have been reported. The percentage removal of cadmium (II) ions increased to a maximum at pH 4.0 – 6.0, further increase in pH lead to a decrease in adsorption in all the adsorbents. Maximum percentage removal of cadmium (II) ions increased from 86.0 % to 99.6 % in lemon peels (a), 88.2 % to 98.9 % in avocado seeds (b), 82.9 % to 99.7 % in banana peels (c), 95.2 % to 99.9 % in watermelon peels (d) and 98.8 % to 96.7 % in sweet yellow passion (e) after acid modification. The trend was similar to the one recorded by copper in 4.4.1 and lead 4.4.2.

4.7 Adsorption Isotherms

Experimental data obtained for Cu (II), Pb (II) and Cd (II) ions in single metal system against initial concentration for UMLP, MLP, UMAS, MAS, UMBP, MBP, UMWP, MWP, UMSYP and MSYP was analysed using Frendlich and Langmuir equation (Equation 2.3 and 2.4). The values of $q_{\max}$ and b (q_{max} is the monolayer sorption capacity (mg/g, b is the Langmuir constant related to affinity of binding sites) were computed from the slope and intercept of the Langmuir equation plot of $\frac{C_e}{q_e}$ versus C_e (C_e is the metal ions at the concentration at equilibrium) which gives a straight line with $\frac{1}{q_{\max}}$ as the intercept and $\frac{1}{bq_{\max}}$ as the slope, and hence $q_{\max}$ and b can be calculated.

While K_f and 1/n were calculated intercept and slope respectively from a linear plot of Freundlich equation Inq_e versus Inc_e (q_e is the maximum amount of adsorption (mg/g),

K_f the constant representing the adsorption capacity and n is the constant depicting the adsorption intensity). (See Appendix 2 and 3). The results discussed in the following subsections.

4.7.1 Adsorption isotherms for Cu (II) ions

Table 4.1: Langmuir and Freundlich constants for copper (II) ions adsorption using raw and acid treated adsorbents

Adsorbent	Langmuir			**Freundlich**			
	Q_{max} (mg/g)	**b (L/mg)**	**R^2**	**1/n**	**Kf (mg/g)**	**R^2**	**Best model**
UMAS	-	-	0.419	0.859	46.03	0.996	Freundlich
MAS	-	-	0.112	1.255	102.57	0.987	Freundlich
UMWP	108.498	0.587	0.995	0.845	5.636	0.795	Langmuir
MWP	114.234	0.798	0.997	0.429	9.977	0.944	Langmuir
UMLP	-	-	0.206	0.977	2.421	0.999	Freundlich
MLP	-	-	0.015	1.013	6.053	0.955	Freundlich
MBP	79.598	0.497	0.998	1.375	6.471	0.832	Langmuir
UMBP	37.893	0.347	0.995	0.978	3.365	0.799	Langmuir
UMSYP	58.458	0.238	0.993	0.657	38.94	0.937	Langmuir
MSYP	69.278	0 .563	0.997	1.255	102.57	0.838	Langmuir

The sorption of copper (II) ions with acid treated and raw watermelon peel, banana peel and sweet yellow passion peel gave $R^2 > 0.993$ indicating the data fitted well in

Langmuir model. R^2 values (0.419, 0.112, 0.206 and 0.0150) obtained from avocado seed and lemon peel show lack of fit of the data in this model. This model prescribes a monolayer adsorption and it indicates a chemisorptions mechanism (Deng *et al*., 2003; Hossain *et al.,* 2012, Mwangi *et al.,* 2012). Lower values of b (< 1) were noticed from the all the adsorption processes which indicates the high affinity of the adsorbent for copper (Hossain *et al.,* 2012). Adsorption capacities (Q_{max}) recorded by raw adsorbents were lower than those recorded by acid treated adsorbents (watermelon peel, banana peel and sweet yellow passion peel). This clearly shows that acid modification improved the sorption capacities of these adsorbents. These results compare with those reported in study of watermelon peel (Koel *et al*., 2012), banana peel (Hossain *et al*., 2012) and orange peel (Liang *et al*., 2012).

The $R^2 > 0.987$ values obtained in raw and acid treated avocado seed and lemon peel indicate applicability of Freundlich model for adsorption of copper (II) ions in these adsorbents. Freundlich model prescribes a multilayer adsorption which is a descriptive of both chemisorptions and physical sorption of copper as a result of weak Vander Waal forces (Deng *et al*., 2003; Hossain *et al.,* 2012; Mwangi *et al.,* 2012). The constant K_f is an approximate indicator of adsorption capacity, while 1/n is a function of the strength of adsorption in the adsorption process (Voudrias *et al.*, 2002).

From Table 4.1 the value of 1/n observed in all the metal ions is greater than 0.859, this indicates that the adsorption is favorable for removal of Cu (II) ions by both acid treated and raw adsorbents. The values of 1/n obtained for raw avocado seed and lemon peel

are below one which indicates a normal adsorption. On the other hand, 1/n values recorded by acid treated avocado seed and lemon peel being above one which indicates cooperative adsorption or interaction between the adsorbate and adsorbent molecules (Dada *et al*., 2012). If n = 1 then the partition between the two phases are independent of the concentration. The values for K_f for acid treated adsorbents are higher than those of the raw adsorbents as shown in table 4.1, thus indicating the efficiency of the sulphuric acid modification process.

4.7.2 Adsorption isotherms for Cd (II) ions

This study analyzed the equillibrium data obtained from adsorption of Cd(II) onto raw powderd and acid treated adsorbents using the langmuir and Freundlich isotherms and results recorded in table 4.2. correlation cofficients of > 0.997 (table 4.2) show that the experimental data on the adsorption of Cd (II) onto raw and acid treated avocado seed, watermelon peels and sweet yellow passion peel fitted well in Langmuir model. Adsorption capacities for the acid treated adsorbents was higher than that of the raw adsorbent. Adsorption data for cadmium (II) ions for raw and acid treated lemon and banana peel fitted well in Freundlich model with R^2 values (> 0.916). The calculated values of '1/n' lies between 0.429 and 1.105 (table 4.2) indicating favourable sorption of cadmium onto raw and acid treated watermelon peels (Achak *et al*., 2009).

Table 4.2: Langmuir and Freundlich constants for cadmium (II) ions adsorption using raw and acid treated adsorbents

Adsorbent	Langmuir			Freundlich			
	Q_{max} (mg/g)	b (L/mg)	R^2	1/n	K_f (mg/g)	R^2	Best model
UMAS	30.231	0.032	0.997	1.248	11.78	0.851	Langmuir
MAS	72.362	0.545	0.999	1.125	23.74	0.872	Langmuir
UMWP	28.369	0.023	0.999	1.105	18.53	0.722	Langmuir
MWP	97.149	0.634	1.000	0.999	2.183	0.993	Langmuir
UMLP	58.231	0.078	0.136	1.006	2.244	0.988	Freundlich
MLP	63.234	0.223	0.751	0.956	32.14	0.999	Freundlich
UMBP	23.125	0.098	0.789	1.371	35.63	0.916	Freundlich
MBP	44.145	0.039	0.978	1.089	14.26	0.999	Freundlich
UMSYP	16.325	0.023	0.998	1.248	11.78	0.851	Langmuir
MSYP	24.236	0.054	0.999	1.125	27.14	0.872	Langmuir

Efficiency of acid treated adsorbents in uptake of cadmium (II) ions is higher than that of the raw adsorbents, this is reflected in the K_f values obtained for the utreated lemon peels which increased after modificationfrom from 2.244 to 32.14 mg/g and 14.76 to 35.63 mg/g in banana peels after modification. This increase can be attributed to the porosity of the surface of watermelon peels after adsorption as shown in figure 4.7 indicating the efficiency of the sulphuric acid modification process. The K_f values obtained in this study are higher than those reported for orange peels (Husain *et al*., 2012), minced raw banana peel (Castro *et al*., 2011).

4.7.3 Adsorption isotherms for Pb (II) ions

Table 4.3: Langmuir and Freundlich constants for the adsorption of Pb (II) onto raw and acid treated adsorbents

Adsorbent	Langmuir			Freundlich			
	Q (max)	B (L/mg)	R^2	1/n	Kf (mg/g)	R^2	Best model
UMAS	-	-	0.309	1.03	21.48	1.000	Freundlich
MAS	-	-	0.226	1.333	71.02	0.998	Freundlich
UMWP	71.45	0.789	0.999	1.092	14.76	0.991	Langmuir
MWP	130.23	0.956	0.998	0.93	66.74	0.925	Langmuir
UMLP	53.122	0.145	0.999	1.287	11.72	0.928	Langmuir
MLP	87.238	0.793	0.999	1.035	72.11	0.995	Langmuir
MBP	69.785	0.469	0.997	1.371	35.63	0.916	Langmuir
UMBP	32.366	0.236	0.995	1.089	14.26	0.999	Langmuir
UMSYP	-	-	0.084	1.042	12.88	0.953	Freundlich
MSYP	-	-	0.226	1.333	32.12	0.997	Freundlich

Results in table 4.3 show that the experimental data on the adsorption of Pb(II) onto raw and acid treated avocado seed and sweet yellow passion peels, fitted well in Freundlich model as it poses higher R^2 values (> 0.953). The calculated values of '1/n' (table 4.3) prove that the adsorption of lead(II) onto these adsorbents is favourable as the magnitude lies between 0.956 and 1.287 (Achak *et al*., 2009). The sorption of lead (II) ions onto treated and raw watermelon peel, banana peel and lemon peel gave $R^2 > 0.995$

indicating the data fitted well in Langmuir model. R^2 values (0.309, 0.226, 0.084 and 0.226) obtained from avocado seed and sweet yellow passion peel) show lack of fit of the data in this model.

Sorption capacites of lead (II) was higher in acid treated adsorbents as compared to the the acid treated adsorbents. This increase can be attributed to the porosity of the surface of lemon peels after acid modification as shown in figure 4.13 indicating the efficiency of the sulphuric acid modification process. The adsorption capacities obtained in this study are higher than those reported for orange peels (Husain *et al*., 2012).

4.8 Adsorption kinetic studies

Kinetic study of adsorption fives an inportant insight to understand the mechanism. The present study is an attempt to understand the asorption rate and sorption capatity. Kinetics is investigated using Pseudo first order and Pseudo second order models. Linear plots of Equation 2.5 and 2.6 were applied to explore the best fit model and to analyse the adsorption kinetics parameters for copper, cadmium and lead (see Apendix XI). The theoritical (calculated) values of q_e ($q_{e(cal)}$) of Pseudo first order and Pseudo second order models are compared to the experimental q_e ($q_{e(exp)}$) calculated using Equation 3.1 using data obtained as described in section 3.9. The rates of adsorption K_1 and K_2 values were calculated also obtained from linear plots Pseudo first order and Pseudo second order models and. Results discussed in the following subsections.

4.8.1 Adsorption kinetic studies for cadmium

Kinetic parameters for cadmium in all the adsorbents are recorded in table 4.4.Pseudo first order and Pseudo second order adsorption kinetics models were used to shed light on the adsorption kinetics of the adsorbents, correlation coefficients (R^2 values) were calculated from these plots.

The results (table 4.4) indicate that the Pseudo second order models is best fit to explain the adsorption of Cd(II) ions by the adsorbents. The Pseudo second order models recorded R^2 values > 0.998 in all the adsorbents. Secondly, pseudo second order model experimental quantity adsorbed $q_{e,(exp)}$ for all the adsorbents were close to the calculated $q_{e,(cal)}$ values. The difference can be attributed to experimental uncertainties. The model is based on the assumption that chemisorption is the rate limiting step (Bernard and Jimoh, 2013, Mekonnen *et al.*, 2015).

Table 4.4: Kinetic parameters for asorption of Cd (II) onto adsorbents

Adsorbent	Pseudo –first –order			Pseudo –second –order			
	$q_{e(\exp)}$	$k_1(mg/g\,\min^{-1})$	R^2	$q_{e(cal)}$	$k_2(mg/g\,\min^{-1})$	$q_{e(cal)}$	R^2
UMLP	31.976	0.435	0.009	0.129	25.641	$1.1\text{x}10^{-4}$	0.999
MLP	32.921	6.295	0.028	0.654	33.333	$1.332\text{x}10^{-4}$	0.998
UMAS	31.892	0.520	0.014	0.202	26.316	$1.105\text{x}10^{-4}$	0.999
MAS	33.200	0.053	0.002	0.013	29.412	$3.4\text{x}10^{-5}$	1.000
MBP	31.157	2.275	0.007	0.122	30.303	$1.5\text{x}10^{-4}$	0.998
UMBP	31.203	1.786	0.007	0.294	25.000	$2.37\text{x}10^{-4}$	0.999
UMWP	29.596	0.114	0.009	0.199	25.000	$1.552\text{x}10^{-4}$	1.000
MWP	33.225	1.622	0.002	0.128	30.303	$6.32\text{x}10^{-5}$	0.999
UMSYP	30.108	0.315	0.002	0.088	27.778	$2.2\text{x}10^{-4}$	0.999
MSYP	31.588	0.853	0.012	0.180	29.412	$6.59\text{x}10^{-4}$	0.998

Lower values were recorded by pseudo first order therefore, it was concluded that data fitted well in pseudo- second order than first order. The values of the adsorption capacity qe(cal) were higher in the acid treated forms of adsorbents as compared to the raw form. For example, lemon peels recorded the highest difference for the acid treated (33.333 mg/g) compared to raw form (23.641 mg/g). The rates of adorption was also higher in the acid treated forms as compared to the raw forms. Sweet yellow passion peels recorded the highest value of $6.59x10^{-4}$ mg/g/min and $2.2x10^{-4}$ mg/g/min in acid treated peels and raw peels respectively. Similar results were recorded by Benard and Jimoh (2013).

4.8.2 Adsorption kinetic studies for copper

table 4.5 gives kinetics parameters for copper (II) ions. The results in table 4.5 show that the correlation coefficient, R^2, values pseudo second order fits better to the experimental data than pseudo first order model. For this reason only Pseudo second order results are discussed in this section. For second order model experimental quantity of copper (II) ions adsorbed $q_{e,(exp)}$ for all the adsorbents were close to the calculated $q_{e,(cal)}$ values. The difference can be attributed to experimental uncertainties. Lower values were recorded by pseudo first order therefore, it was concluded that data fitted well in pseudo- second order than first order.

Table 4.5: Kinetic parameters for asorption of Cu (II) onto adsorbents

Adsorbent	Pseudo- First- Order				Pseudo- Second- Order		
	$q_{e(\exp)}$	$q_{e(cal)}$	$k_1 (mg/g\,\min^{-1})$	R^2	$q_{e(cal)}$	$k_2 (mg/g\,\min^{-1})$	R^2
UMLP	29.132	5.212	$1.382\ X10^{-2}$	0.440	24.390	$5.27x10^{-3}$	0.999
MLP	32.036	4.375	$9.21\ X10^{-3}$	0.397	29.412	$7.136\ x10^{-3}$	1.000
UMAS	31.568	7.534	$6.91\ X10^{-3}$	0.629	19.608	$2.969\ x10^{-3}$	0.990
MAS	32.734	2.742	$6.91\ X10^{-2}$	0.309	29.412	$1.080\ x10^{-2}$	1.000
MBP	32.586	0.847	$4.61\ X10^{-3}$	0.080	30.303	$2.593\ x10^{-2}$	1.000
UMBP	30.379	6.266	$1.382\ X10^{-2}$	0.641	25.641	$7.313\ x10^{-3}$	0.998
UMWP	31.160	5.559	$2.073\ X10^{-2}$	0.595	27.027	$4.907\ x10^{-3}$	0.999
MWP	32.887	3.899	$4.61\ X10^{-3}$	0.662	29.412	$1.145\ x10^{-2}$	1.000
UMSYP	31.385	2.924	$1.152\ X10^{-2}$	0.235	27.027	$5.127\ x10^{-3}$	0.999
MSYP	32.234	2.999	$4.61\ X10^{-3}$	0.261	28.571	$1.591\ x10^{-2}$	1.000

The R^2 values for all adsorbents were >0.998, this shows the suitability of this model indicating the process mechanism to be chemical adsorption (Liang *et al.*, 2012). The acid treated forms of the adsorbents recorded the higher values of q_e and K_2 as compared to the raw forms of the adorbents. For example, acid treated banana peels adsorbent recorded 30.303 mg/g and 2.593 $x10^{-2}$ mg/g/min q_e and K_2 values respectively.

4.8.3 Adsorption kinetic studies for lead

The results in table 4.6 indicate that the correlation coefficient, R^2, values pseudo second order fits better to the experimental data than pseudo first order model. For this reason only Pseudo second order results are discussed in this section. The R^2 values for all adsorbents were >0.940, this shows the suitability of this model, this implies that the asorption process for Pb (II) ions onto the fruit waste products was chimical in nature. The R^2 values for all adsorbents were < 0.932 and the qe calculated values greatly deviated from the experimental values. This means that pseudo-first order did not fit well. The qe calculated values from pseudo second order model were closer to the experimental qe (exp) values showing suitability of this modedl. the acid modied forms of the adsorbents recorded the higher values of q_e and K_2 as compared to the raw forms of the adorbents. For example, acid treated banana peels adsorbent recorded 30.303 mg/g and 1.13 $x10^{-2}$ mg/g/min q_e and K_2 values respectively.

Table 4.6: Kinetic parameters for asorption of Pb (II) onto adsorbents

Adsorbent	**Pseudo- First- Order**				**Pseudo- Second- Order**		
	$q_{e(\exp)}$	R^2	$q_{e(cal)}$	$k_1(mg/g\,\min^{-1})$	R^2	$q_{e(cal)}$	$k_2(mg/g\,\min^{-1})$
UMLP	32.822	0.856	10.568	0.039	0.999	24.390	$8.89\text{x}10^{-3}$
MLP	33.023	0.913	7.798	0.037	1.000	30.303	$1.13\ \text{x}10^{-2}$
UMAS	32.999	0.822	0.528	0.253	0.940	13.514	$5.24\ \text{x}10^{-3}$
MAS	29.911	0.491	0.432	0.025	1.000	29.412	$1.05\ \text{x}10^{-1}$
MBP	29.933	0.932	10.423	0.021	0.998	24.390	$9.66\ \text{x}10^{-3}$
UMBP	33.255	0.720	17.783	0.039	0.998	23.256	$9.11\ \text{x}10^{-3}$
UMWP	33.290	0.571	3.698	0.021	1.000	28.571	$2.50\ \text{x}10^{-2}$
MWP	29.596	0.471	2.065	0.030	1.000	29.412	$3.50\ \text{x}10^{-2}$
UMSYP	30.108	0.451	3.055	0.012	1.000	22.727	$2.4\ \text{x}10^{-2}$
MSYP	31.588	0.219	1.875	0.007	0.999	29.412	$2.96\ \text{x}10^{-2}$

4.9 Comparison of efficacy of adsorbents

The results in table 4.7 indicate that treated adsorbents recorded significantly higher percentage removal of lead (II) ions as compared to the raw adsorbents. The treated watermelon peel had the highest percentage removal, followed by treated lemon peel, treated banana peel and treated avocado seed.

Adsorption efficacy of cadmium (II) ions were highest in acid treated adsorbents as compared to raw adsorbents with watermelon peels recording the highest followed by banana peels, lemon peels, avocado seeds and sweet yellow passion in that order (Table 4.7), Pb (II) ions, watermelon peels, followed by banana peels, avocado seeds and lemon peels in that order ($p< 0.001$) (Table 4.8) and Cu (II) ions, acid treated watermelon peels, sweet yellow passion peels, avocado seeds and lemon peels (table 4.9). The high percentages recorded by the acid treated adsorbents can be attributed to their porosity as discussed in sections 4.1.1.

Table 4.7: A comparative representation of biosorption efficiency (%) of various biosorbents varying concentration of Pb (II) ions

	C_o (mg/L)	10	20	50	100	200	500
		Mean±SE % Removal	**Mean±SE % Removal**	**Mean±SE % Removal**	**Mean±SE % Removal**	**Mean±SE % Removal**	**Mean±SE % Removal**
Adsorbent	UMLP	86.28±0.11^{a}	94.32±0.08^{c}	95.00±0.06^{d}	95.93±0.00^{e}	95.92±0.00^{f}	95.81±0.00^{c}
	MLP	**98.42±0.01^{g}**	**98.51±0.00^{f}**	**98.73±0.00^{g}**	**98.76±0.00^{f}**	**98.77±0.00^{g}**	**98.55±0.00^{e}**
	UMAS	95.28±0.01^{e}	95.68±0.00^{d}	95.69±0.00^{e}	95.74±0.01^{d}	95.90±0.00^{e}	95.82±0.00^{d}
	MAS	**98.84±0.01^{h}**	**99.27±0.01^{g}**	**99.58±0.00^{h}**	**99.60±0.00^{g}**	**99.65±0.00^{h}**	**99.61±0.00^{f}**
	MBP	**98.84±0.01^{h}**	**99.35±0.00^{g}**	**99.69±0.00^{i}**	**99.68±0.00^{h}**	**99.70±0.00^{i}**	**99.69±0.00^{f}**
	UMBP	92.99±0.01^{d}	93.61±0.01^{b}	94.16±0.02^{b}	94.36±0.00^{b}	94.87±0.00^{c}	94.73±0.00^{b}
	UMWP	92.03±0.03^{b}	94.25±0.12^{c}	94.93±0.00^{c}	94.90±0.01^{c}	94.77±0.00^{b}	94.76±0.00^{b}
	MWP	**99.78±0.00^{i}**	**99.94±0.00^{h}**	**99.87±0.00^{j}**	**99.88±0.00^{i}**	**99.88±0.00^{j}**	**99.86±0.02^{g}**
	UMSYP	92.39±0.02^{c}	92.43±0.00^{a}	93.91±0.00^{a}	93.57±0.00^{a}	93.48±0.00^{a}	93.33±0.17^{a}
	MSYP	96.22±0.03^{f}	96.79±0.00^{e}	96.63±0.01^{f}	95.74±0.00^{d}	95.46±0.01^{d}	95.28±0.02^{d}
	p-value	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

*Mean values followed with the same small letter within the same column do not differ significantly from one another (one-way ANOVA, SNK-test, α=0.05). *C_o (Initial concentration)

Table 4.8: A comparative representation of biosorption efficiency (%) of various biosorbents for Cd (II) ions

	C_o (mg/L)	10	50	100	200	500
		Mean±SE	**Mean±SE**	**Mean±SE**	**Mean±SE**	**Mean±SE**
		% Removal	**% Removal**	**% Removal**	**% Removal**	**% Removal**
Adsorbent	UMLP	98.39±0.00^{g}	98.88±.01^{f}	98.81±0.01^{f}	98.79±0.00^{f}	98.47±0.00^{f}
	MLP	**99.14±0.02^{h}**	**99.16±.00^{g}**	**99.07±0.00^{g}**	**99.04±0.00^{h}**	**99.00±0.00^{h}**
	UMAS	87.20±0.00^{b}	89.95±.01^{d}	89.73±0.13^{b}	89.74±0.00^{c}	89.92±0.00^{d}
	MAS	**98.95±0.00^{h}**	**98.92±.00^{f}**	**99.00±0.00^{g}**	**98.95±0.00^{g}**	**98.93±0.00^{g}**
	MBP	**99.73±0.01^{i}**	**99.77±.00^{h}**	**99.91±0.00^{h}**	**99.79±0.01^{i}**	**99.77±0.00^{i}**
	UMBP	78.37±0.32^{a}	89.52±.02^{c}	90.89±0.01^{d}	89.80±0.01^{d}	89.76±0.03^{c}
	UMWP	88.89±0.00^{c}	88.89±.01^{b}	88.86±0.01^{a}	88.79±0.00^{b}	85.89±0.00^{a}
	MWP	**99.87±0.00^{i}**	**99.87±.00^{i}**	**99.87±0.00^{h}**	**99.87±0.00^{j}**	**99.86±0.00^{j}**
	UMSYP	91.77±0.00^{d}	87.80±.06^{a}	90.32±0.02^{c}	84.19±0.02^{a}	89.53±0.00^{b}
	MSYP	97.94±0.00^{e}	93.53±.00^{e}	94.76±0.00^{e}	93.82±0.00^{e}	95.90±0.00^{e}
	P-value	<0.001	<0.001	<0.001	<0.001	<0.001

*Mean values followed with the same small letter within the same column do not differ significantly from one another (one-way ANOVA, SNK-test, α=0.05). *C_o (Initial concentration)

Table 4.9: A comparative representation of biosorption efficiency (%) of various biosorbents for Cu (II) ions

C_o (mg/L)		10	50	100	200	500
		Mean±SE	**Mean±SE**	**Mean±SE**	**Mean±SE**	**Mean±SE**
		%Removal	**%Removal**	**%Removal**	**%Removal**	**%Removal**
Adsorbent	UMLP	87.39±0.08^{c}	89.93±0.02^{a}	89.83±0.07^{a}	87.40±0.86^{a}	87.31±0.76^{b}
	MLP	**89.75±0.00^{d}**	97.71±0.00^{e}	96.11±0.00^{f}	95.48±0.02^{e}	94.94±0.06^{f}
	UMAS	89.07±0.02^{d}	95.74±0.05^{b}	94.70±0.10^{d}	90.29±0.06^{b}	87.84±0.44^{c}
	MAS	**92.67±0.05^{e}**	**98.41±0.00^{f}**	**98.20±0.14^{i}**	**98.20±0.03^{g}**	**98.02±0.01^{i}**
	MBP	89.51±0.01^{d}	97.71±0.01^{d}	**97.76±0.01^{h}**	**97.78±0.00^{g}**	**97.69±0.00^{h}**
	UMBP	80.54±0.01^{b}	96.61±0.01^{c}	91.14±0.05^{b}	91.75±0.26^{c}	91.36±0.13^{d}
	UMWP	88.74±0.01^{d}	97.38±0.00^{d}	93.48±0.00^{c}	92.90±0.80^{d}	86.85±0.13^{a}
	MWP	**98.76±0.00^{h}**	**99.40±0.01^{e}**	**98.66±0.04^{j}**	**97.68±0.27^{g}**	**97.55±0.30^{h}**
	UMSYP	**80.42±0.03^{f}**	**95.11±0.02^{g}**	95.88±0.00^{e}	95.82±0.00^{e}	94.16±0.08^{e}
	MSYP	**98.27±0.00^{g}**	**98.32±0.00^{h}**	**96.70±0.00^{g}**	**97.07±0.00^{f}**	96.35±0.00^{g}
	P-value	<0.001	<0.001	<0.001	<0.001	<0.001

*Mean values followed with the same small letter within the same column do not differ significantly from one another (one-way ANOVA, SNK-test, α=0.05). *C_o (Initial concentration)

The acid treated watermelon peels demonstrated the highest efficiency for removal of the three metal ions (Cu, Cd and Pb) followed by banana peels, avocado seeds, lemon peels and sweet yellow passion in that order. Acid treated adsorbents had higher efficacy as compared to their raw counterparts; this was demonstrated in all the metal ions as shown in tables 4.7 - 4.9. Therefore, these four efficient adsorbents were chosen for further adsorption and desorption studies.

4.10 Competitive adsorption

Studies were conducted to determine the sorption of lead, cadmium and copper in binary systems and ternary metal system on MAS, MLP and MWP. The adsorption data for adsorption of lead, cadmium and copper ions in binary and tertiary metal system was modeled using Freundlich and Langmuir equations (Equations 2.3 and 2.4). The linear plots were used to calculate the model parameters and constants (see Appendix IX and X). Interaction effects were also calculated (Equation 2.7). The results are discussed in the following subsections.

4.10.1 Cadmium adsorption in multi-metal system (binary and tertiary metal system)

The effect of Pb (II) and Cd (II) on Cu (II) ion removal was studied at different co-cation concentration in binary and tertiary metal system results recorded in figure 4.23. The results show that as the concentration of cadmium (II) ions decreased as the concentration of co-cation was increased from 10 mg/L to 200 mg/L in solution in the

three adsorbents (Figure 4.23). The decrease was highest in tertiary mixture (Figure 4.23 (c)) as compared to binary mixtures (Figure 4.23: (**a**) and **b**).

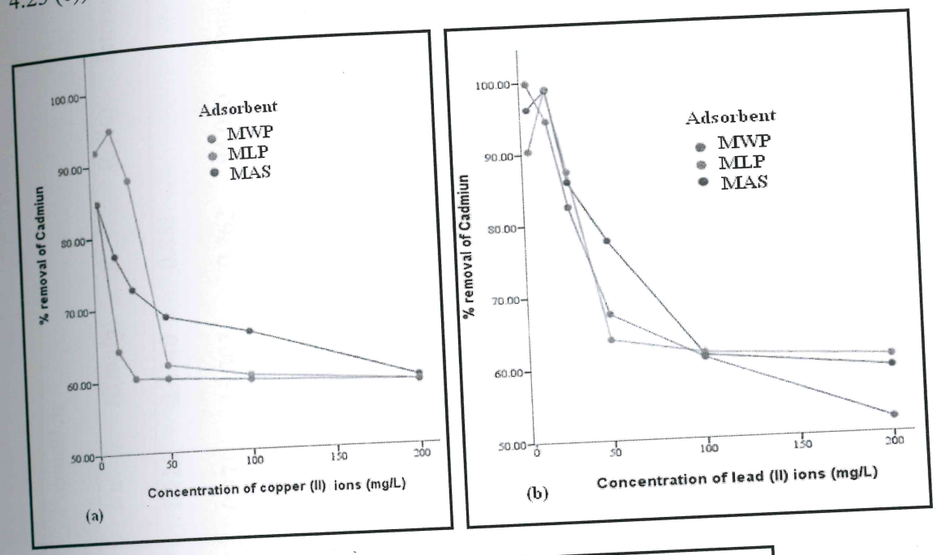


Figure 4.23: Effect of; (a) Cu (II), (b) Pb II) and (c) Pb (II) and Cu (II) on adsorption Cd (II) onto MAS, MLP and MWP

Table 4.10: Langmuir and Freundlich parameters for Cd (II) in mono, binary and tertiary systems by MAS, MWP and MLP and interactive effect of mixture of metal ions

		Langmuir			Freundlich				
Adsorbent	Metal combinations	Q_{max} (mg/g)	b(L/mg)	R^2	1/n	K(mg/g)	R^2	R_i (%)	Interactive effect
MAS	Cd^{2+}	72.362	0.345	0.997	1.125	23.740	0.851		
	Cd^{2+}/Pb^{2+}	58.027	0.051	0.994	0.371	15.307	0.762	94.010	Antagonistic
	Cd^{2+}/Cu^{2+}	67.568	0.092	0.996	0.913	14.818	0.863	93.374	Antagonistic
	$Cu^{2+}/Cd^{2+}/Pb^{2+}$	22.283	0.011	0.998	0.287	41.461	0.791	58.433	Antagonistic
MWP	Cd^{2+}	97.149	0.634	1.000	0.999	2.183	0.993		
	Cd^{2+}/Pb^{2+}	66.667	0.113	0.997	0.351	20.137	0.470	68.623	Antagonistic
	Cd^{2+}/Cu^{2+}	86.207	0.121	0.991	0.399	17.053	0.644	88.737	Antagonistic
	$Cu^{2+}/Cd^{2+}/Pb^{2+}$	32.080	0.069	0.987	1.012	10.236	0.235	78.120	Antagonistic
MLP	Cd^{2+}	63.234	0.223	0.975	0.956	32.140	0.999		
	Cd^{2+}/Pb^{2+}	50.505	0.081	0.999	0.171	23.174	0.950	79.870	Antagonistic
	Cd^{2+}/Cu^{2+}	58.824	0.092	0.998	0.287	15.146	0.791	93.025	Antagonistic
	$Cu^{2+}/Cd^{2+}/Pb^{2+}$	26.235	0.078	0.989	0.478	10.125	0.326	57.303	Antagonistic

The Langmuir and Freundlich adsorption isotherms were applied for mono, binary and tertiary system (Table 4.10). The data fitted well in Langmuir isotherm model as compared to Freundlich model. The value of correlation coefficient R^2 for Langmuir isotherm was found to be > 0.95 for all the systems in the three adsorbents. The results (Table 4.10) indicate that the adsorption capacity MAS, MWP and MLP for binary and tertiary mixtures were lower than for the single metal system. For instance in MAS the adsorption capacity of cadmium reduced from 73.362 mg/g to 58.027 mg/g, 67.568 mg/g and 22.283 mg/mg when mixed with Pb, Cu and Pb/Cu respectively. The adsorption capacity of cadmium in MWP reduced from 97.149 mg/g to 66.667 mg/g, 86.207 mg/g and 22.080 mg/g in a mixture Pb, Cu and Pb/Cu respectively. While in MLP, adsorption capacity decreased from 63.234 mg/g to 50.505 mg/g, 58.824 and 26.235 mg/g in a mixture Pb, Cu and Pb/Cu respectively.

The *b* values for single metal ions were higher than those in binary and tertiary metal system suggesting a better affinity for cadmium in single metal ion onto MAS, MLP and MWP (Najiah *et al.*, 2014). The values of R_i< 100 in binary and tertiary metal system for all the adsorbents. So, it was inferred that the interactions between different metal ions are antagonistic in nature. This may be due to screening effect by the metals present in the solution (Sag and Kutsal, 1996; Jain *et al.*, 2016). The order of maximum adsorption capacity was found to be mono-component > binary component > tertiary component. Lead exerted a greater inhibitory effect on cadmium removal than copper in all the adsorbents. This can be attributed to the relative ionic radii of Pb (1.19 Å) and Cd (0.97Å), the smaller the ionic radius the greater the tendency to hydrate leading

o reduced sorption (Sheng *et al.*, 2007). Similar trend was reported in study of banana peels by Ashraf *et al.* (2011).

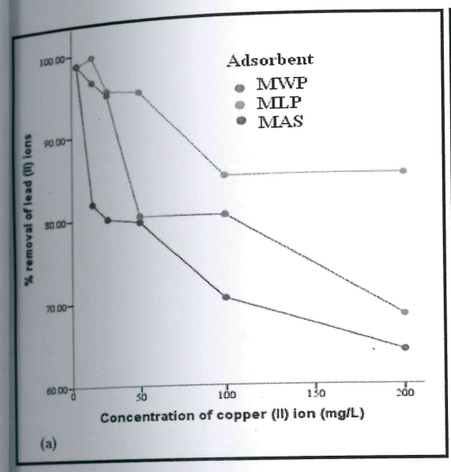
4.10.2 Lead adsorption in multi-metal system (Binary and tertiary)

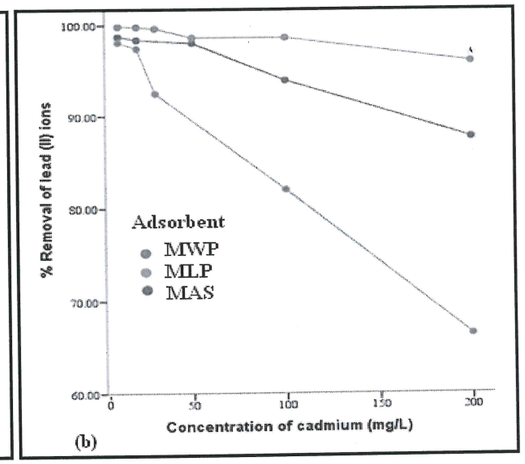
The effect of the presence of cadmium and copper on the removal of lead using acid treated avocado seeds was investigated and the results quantitatively demonstrated in figure 4.24. Uptake lead was found to decrease with increase in co ion concentration. The greatest reduction was recorded in tertiary metal system for all the adsorbents (Figure 4.24 (c)).

The Langmuir and Freundlich adsorption isotherms were applied in adsorption of lead in mono, binary and tertiary systems and results recorded in table 4.11. The adsorption data obtained from MAS fitted in Freundlich ($R^2 > 0.995$) as compared to Langmuir isotherm ($R^2 < 0.995$). The calculated values of $1/n < 1$ indicating that the adsorption is a favorable chemical process (Amna *etal*., 2011). Uptake of lead (II) ions by MAS reduced from 71.02 mg/g to 57.876 mg/g, 62.015 mg/g and 51.421 mg/g in a mixture of Cu, Cd and Cu/Cd respectively. The adsorption data obtained from MLP and MWP fitted well in Langmuir model ($R^2 > 0.995$) than Freundlich model.

The calculated values of *b* were higher in single metal system in the two adsorbents indicating a higher affinity for lead as compared to multiple metal systems. The adsorption capacity was reduced from 87.238 mg/g to 71.773 mg/g, 67.73 mg/g and 40.634 mg/g in a mixture Cu, Cd and

Cu/Cd respectively in MLP. While in MWP the adsorption capacity of lead reduced from 130.23 mg/g, 84.2 mg/g, 60.27 mg/g and 48.23 mg/g in a mixture Cu, Cd and Cu/Cd respectively





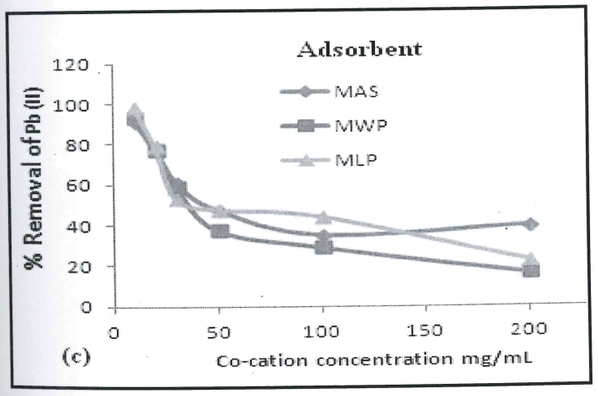


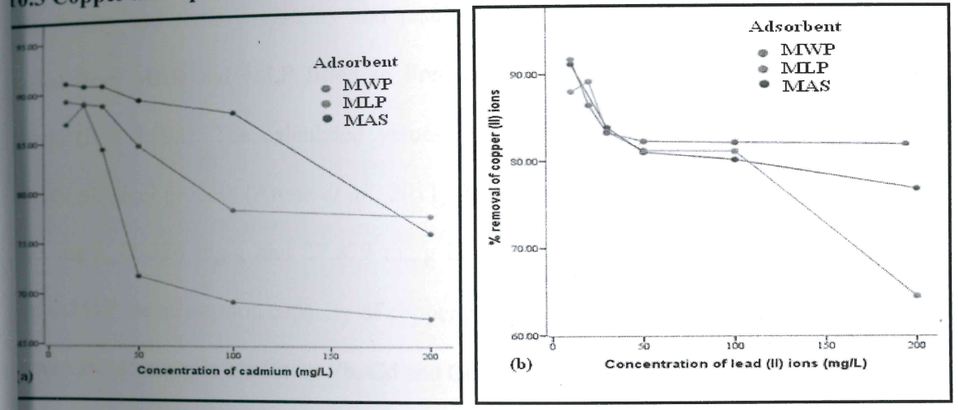
Figure 4.24: Effect of; (a) Cu (II), (b) Cd II) and **(c)** Cd (II) and Cu (II) on adsorption Pb (II) onto MAS, MLP and MWP

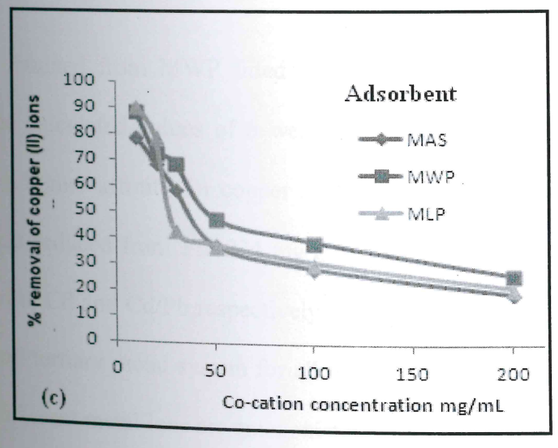
Table 4.11: *Langmuir and Freundlich parameters for Pb (II) in mono, binary and tertiary systems by MAS, MWP and MLP and interactive effect of metal ions*

	Langmuir model				Freundlich				
Adsorbent	Metal combinations	Q_{max} (mg/g)	b(L/mg)	R^2	K(mg/g)	1/n	R^2	R_i (%)	Interactive effect
MAS	Pb^{2+}	-	-	0.226	71.02	1.33	0.998		
	Pb^{2+}/Cu^{2+}	-	-	0.311	57.876	0.497	0.976	81.493	Antagonistic
	Pb^{2+}/Cd^{2+}	-	-	0.058	62.015	0.684	0.986	87.320	Antagonistic
	$Pb^{2+}/Cu^{2+}/Cd^{2+}$	-	-	0.012	51.421	0.471	0.996	16.081	Antagonistic
MLP	Pb^{2+}	87.238	0.793	0.999	72.11	1.035	0.998		
	Pb^{2+}/Cu^{2+}	71.773	0.061	0.985	70.194	0.7514	0.994	97.492	Antagonistic
	Pb^{2+}/Cd^{2+}	67.73	0.509	0.999	66.069	0.3705	0.997	91.763	Antagonistic
	$Pb^{2+}/Cu^{2+}/Cd^{2+}$	40.634	0.756	0.953	18.838	0.6491	0.993	26.164	Antagonistic
MWP	Pb^{2+}	130.23	0.956	0.998	66.74	0.93	0.925		
	Pb^{2+}/Cu^{2+}	84.2	0.781	0.997	62.89	0.453	0.997	94.23	Antagonistic
	Pb^{2+}/Cd^{2+}	60.27	0.586	0.993	47.228	0.741	0.992	70.764	Antagonistic
	$Pb^{2+}/Cu^{2+}/Cd^{2+}$	48.23	0.664	0.989	27.341	0.691	0.993	40.966	Antagonistic

he calculated values of R_i (< 100%) indicate that presence of copper (II) and cadmium (II) ions ad an antagonistic effect on sorption of lead (II) ions (table 4.11). Copper exerted a greater hibitory effect on lead removal than cadmium. This can be attributed to the fact that copper is ore electronegative (1.90) than cadmium (1.69) making it easier for it to compete faster for change sites. These results compare with those reported by (Li *et al.*, 2009; Ashraf *et al.*, 11).

10.3 Copper adsorption in multi-metal system (Binary and tertiary)





ure 4.25: Effect of; (a) Cd (II), (b) Pb II) and (c) Cd (II) and Pb(II) on adsorption Cu (II) onto S, MLP and MWP

The effect of presence of lead and cadmium in solution on removal of copper was investigated sing acid treated avocado seeds, lemon peels and watermelon peel and results recorded in figure .25 and table 4.12. Results in figure 4.25 indicate that as concentration of interfering ion was ıcreased from 10-200 mg/L uptake of copper ions decreased. Highest reduction was recorded in e tertiary mixture as compared to binary mixture (Figure 4.25 (c))

ıe Langmuir and Freundlich adsorption isotherms were applied in adsorption of copper in ıgle, binary and tertiary systems and results recorded in table 4.12. The adsorption data tained from MAS and MLP fitted in Freundlich ($R^2 > 0.995$) as compared to Langmuir otherm ($R^2 < 0.995$). The calculated values of $1/n > 1$ indicating that the adsorption is a vorable physical process (Amna *et al.*, 2011). Uptake of copper reduced from 102.57 mg/g to .803 mg/g, 86.126 mg/g and 37.879 mg/g in a mixture of Pb, Cd and Cd/Pb respectively. hile in MLP the adsorption capacity of copper reduced from 60.053 mg/g, 46.502mg/g, 52.356 /g and 38.145 mg/g in a mixture Pb, Cd and Cd/Pb respectively.

adsorption data obtained from MWP fitted well in Langmuir model ($R^2 > 0.995$) than undlich model. The calculated values of *b* were higher in single metal system in the two orbents indicating a higher affinity for copper as compared to multiple metal systems. The orption capacity was reduced from 114.234 mg/g to 90.091 mg/g, 96.154 mg/g and 42.369 g in a mixture Cu Pb, Cd and Cd/Pb respectively in MLP. Results in table 4.12 show values < 100 in binary and tertiary metal system for all the adsorbents. So, it was inferred that the ractions between different metal ions are antagonistic in nature. This may be due to screening ct by the metals present in the solution (Sag and Kutsal, 1996; Jain *et al.*, 2016).

Table 4.12: *Langmuir and Freundlich parameters for Cu (II) in mono, binary and tertiary systems by MAS, MWP and MLP and interactive effect of metal ions*

		Langmuir model			Freundlich				
Adsorbent	Metal combinations	Q_{max} (mg/g)	b(L/mg)	R^2	K(mg/g)	1/n	R^2	R_i (%)	Interactive effect
MAS	Cu^{2+}	-	-	0.112	102.57	1.255	0.987		
	Cu^{2+}/Pb^{2+}	14.438	0.016	0.792	57.803	1.002	0.998	56.35	Antagonistic
	Cu^{2+}/Cd^{2+}	14.398	0.025	0.799	86.126	1.013	0.984	56.36	Antagonistic
	$Cu^{2+}/Cd^{2+}/ Pb^{2+}$	-	-	0.478	37.879	0.978	0.997	36.93	Antagonistic
MLP	Cu^{2+}	-	-	0.015	60.053	1.013	0.955		
	Cu^{2+}/Pb^{2+}	14.398	0.132	0.002	46.502	0.913	0.997	77.43	Antagonistic
	Cu^{2+}/Cd^{2+}	20.059	0.060	0.799	52.356	0.327	0.984	87.18	Antagonistic
	$Cu^{2+}/Cd^{2+}/ Pb^{2+}$	16.672	0.123	0.678	38.145	1.120	0.999	63.52	Antagonistic
MWP	Cu^{2+}	114.234	0.587	0.997	9.977	0.429	0.944		
	Cu^{2+}/Pb^{2+}	90.091	0.114	0.997	14.914	0.342	0.644	67.11	Antagonistic
	Cu^{2+}/Cd^{2+}	96.154	0.113	0.998	15.146	0.287	0.791	71.63	Antagonistic
	$Cu^{2+}/Cd^{2+}/ Pb^{2+}$	42.369	0.174	0.999	9.236	0.789	0.745	59.91	Antagonistic

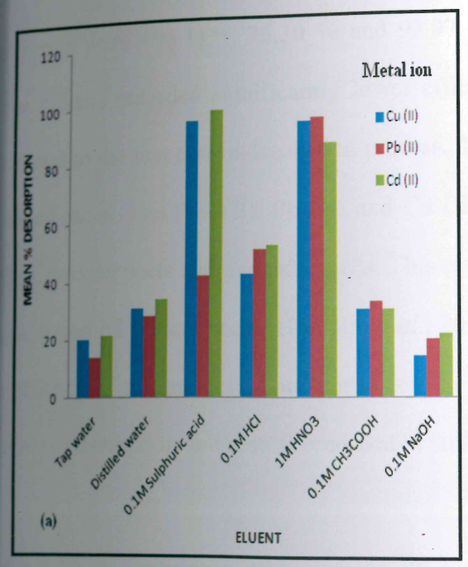
The results in table 4.12 shows lead (II) ions exerted a greater inhibitory effect on removal copper than cadmium in three adsorbents. The order of maximum adsorption capacity was found to be mono-component > binary component > tertiary component. This can be attributed to the ionic radius of Pb (1.19 Å) and Cd (0.97Å), the smaller the ionic radius the greater the tendency to hydrolyze leading to reduced sorption (Sheng *et al.,* 2007). Similar trend was reported in study of banana peels by Ashraf *et al.* (2011).

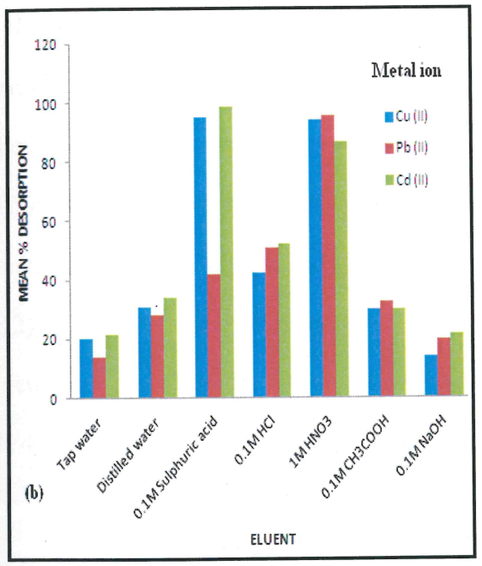
Experimental results in binary and tertiary systems (Tables 4.10-4.12) clearly showed that the combined action of multiple ions was antagonistic. The most likely reason for the antagonistic effect is the competition for adsorption sites on the cell surfaces and/or the screening effect by the competing metal ions (Sheng *et al*., 2007; Shoaib *et al*., 2011). From this study the results show that lead exerted the highest inhibitory effect on the adsorption of other metal ions followed by copper and cadmium in acid treated avocado seed, lemon peel and watermelon peel. The calculated values of *b* (Langmuir isotherm) in tertiary metal system in all the adsorbents were highest for Pb (II) ions compared to copper and cadmium, suggesting better affinity for metal binding onto MAS, MWP and MLP followed by Cu (II) and Cd (II). Secondly, lead recorded the highest adsorption capacities followed by copper and cadmium in tertiary metal system. Sheng *et al*. (2007) observed similar preference order of metal ions: Pb (II) > Cu (II) > Cd (II) onto algal biomass and attributed this uptake trend with the electro negativities of the metal-ion hydroxides.

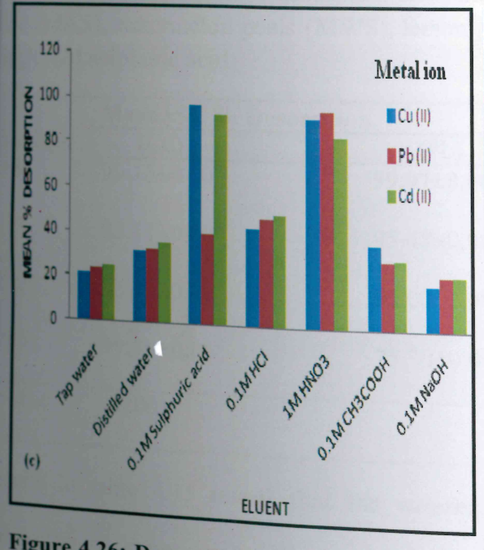
ıe electronegative value of Pb (II) is 2.33, Cu (II): 1.90 and Cd (II): 1.69. Higher ectronegativity corresponds to a higher adsorption capacity owing to higher attraction of metal ns for electrons (Wang *et al*., 2006). Shoaib *et al*. (2011) reported a competitive trend of b>Cd>Cu when they used fungi as an adsorbent. This preferential sorption behavior of dsorbents for metal ions acquired was explained in terms of ionic radii of the metal ions (Cu= .73 Å, Cd = 0.97 Å, Pb = 1.19 Å) (Shoaib *et al*., 2011). Thus, the element with larger ionic adius competes more effectively for exchange sites than those of smaller ionic radii. Adsorption nay be related to the loss of the entire hydration sphere. The smaller the ionic radius, the greater s its tendency to be hydrated leading to reduced sorption (Horsefall and Spiff, 2005). The bserved order indicates that Pb (II) may have greater accessibility to the surface of certain pores than Cd (II) and Cu (II) due to its higher electronegativity.

4.11 Regeneration of used adsorbents

The regeneration of used adsorbents is crucial to resuse and recovery of of valuable metals and to reduce operation cost for any type of treatment. Regeneration studies (Cu, Pb and Cd) were carried out on acid treated avocado seeds, lemon peels, watermelon peels and sweet yellow passion peels using seven eluents and results presented figure 4.26 (Appendix X).







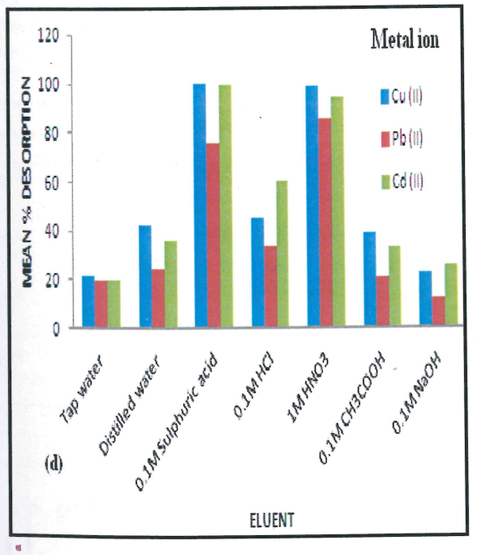


Figure 4.26: Desorption of metal ions Cu, Pb and Cd from (a): MAS, (b) MLP, (c) MSYP and (d) MWP

he results from figure 4.26 show that the highest recovery for Cu(II) and Cd (II) was achieved ith 0.1 M sulphuric acid and 1.0 M nitric acid for Pb (II). In all the adsorbents, percentage coveries were >95.11%, 75.30 % and 92.97 % of copper, lead and cadmium respectively. ther eluents recorded significantly lower efficacy ($p < 0.001$- See apendix X). This can be tributed to the fact that in desorption process, the H^+ released from the acids was likely to have placed metal ions (Cu (II), Pb (II) and Cd (II)) on the surface of lemon, watermelon, sweet ellow passion peels and avocado seeds. This results are in similar to those recorded by study of generation of banana peels (Hossain *et al.*, 2012). Further data analysis was carried out to on ie efficacy of sulphuric acid and nitric acid to determine the adsorbent that was most efficient nterms of desorption and results recorded in table 4.13.

able 4.13: A comparison of desorption efficiency of Cu (II), Pb (II) and Cd (II) from avocado eeds (MAS), watermelon peels (MWS), lemon peels (MLP) and sweet yellow passion(MSYP) sing 0.1M sulphuric acid

	Mean±SE % Desorption		
dsorbent	(Cu)	(Pb)	Cd)
AS	99.15±0.00^{c}	**99.97±0.00^{d}**	98.76±0.00^{c}
LP	95.11±0.00^{a}	95.48±0.00^{c}	98.31±0.00^{b}
SYP	96.73±0.00^{b}	95.00±0.00^{b}	92.97±0.00^{a}
WP	**99.79±0.00^{d}**	75.30±0.00^{a}	**99.23±0.00^{d}**
-value	<0.001		

esults in table 4.13 reveal that the watermelon peels recorded the highest efficiency in lesorption of copper and cadmium and avocado seeds recorded the highest efficiency in

desorption of lead ($p<0.001$). The recovery and resuse process was continued upto to nine time with minor deviations upto fifth times with as shown in figures 4.27-4.30 (Appendix X).

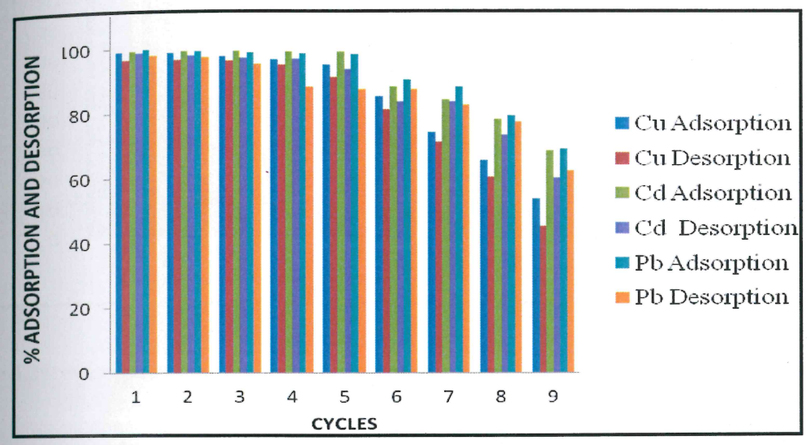


Figure 4.27: Adsorption desorption cycles for MAS

Adsorpion - desorption efficacy of > 80% were recorded upto the fifth cycle with minimal deviations(Figure 4.27) lowest efficiency for all the metal ions MAS. Beyond cycle five the decline is was for all the metal ions. This shows that the adsorbent can be reused upto five times with high efficiency.

Results in figure 4.28 indicate that adsorption and desorption efficacy of MWP for Cu (II), Cd(II) and Pb (II) decreased with increase in cycles. The efficiency was significantly high upto the fifth cycle beyond which the decline was high. This is an indication that the adsorbents are stable and can be resused with high efficiency upto the fifth cycle. and efficiency

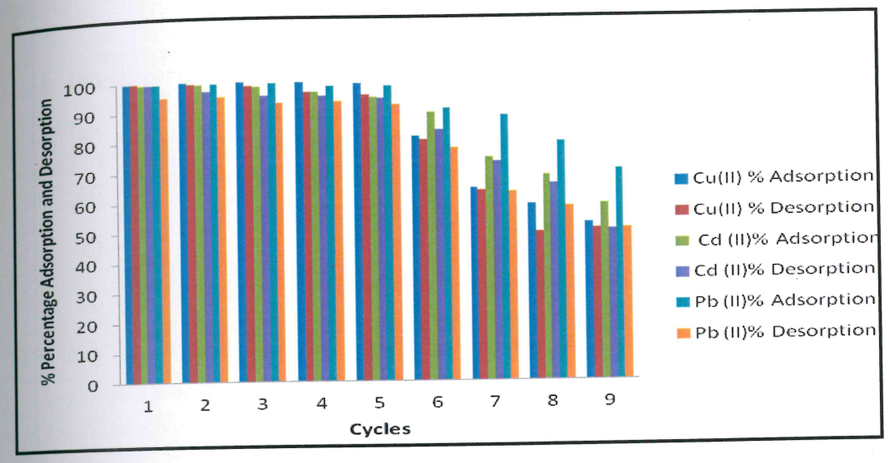


Figure 4.28: Adsorption desorption cycles for MWP

Results in figure 4.29 indicate that adsoption efficacy for MYSP for Pb(II) was the highest in all the cycles and it also recorded the lowest desorption efficacy in all the cyles. The the adsorption desorption efficincies decreased significantly with increase in number of cyles with high efficiency recorded by the first four cycles for copper (II) and cadmium (II) ions. Beyond cycle five the desoption efficacy were below 68 %, this is an indication that the adsorbent can be used and reused with high efficiency upto the fourth cycle.

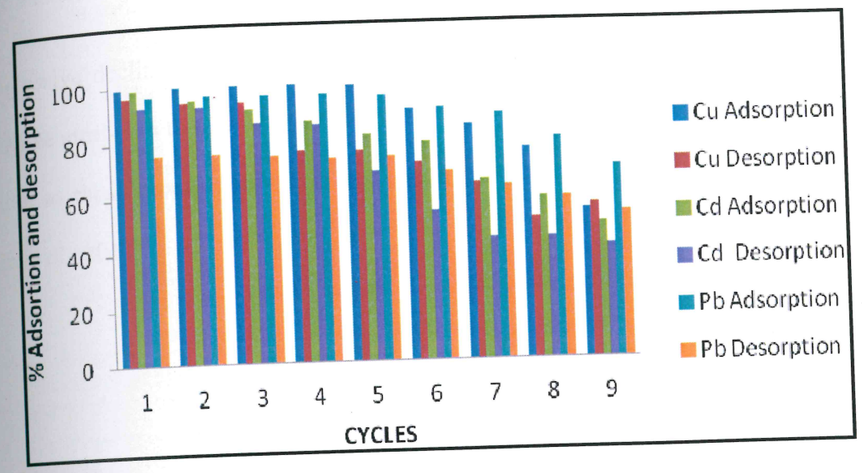


Figure 4.29: Adsorption desorption cycles for MSYP

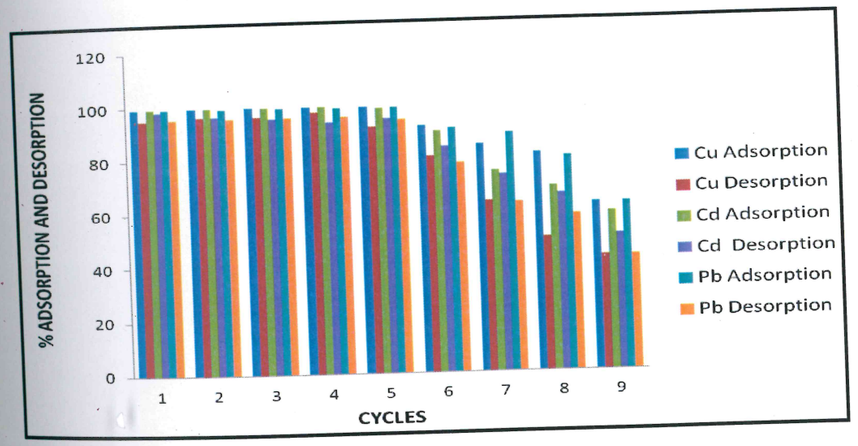


Figure 4.30: Adsorption desorption cycles for MLP

Results in figure 4.30 indicate that adsorption and desorption efficacy of MLP for Cu (II), Cd(II) and Pb (II) decreased with increase in cycles. The efficiency was significantly high (> 90 %)

o the fifth cycle beyond which the decline was high. This is an indication that the adsorbents stable and can be resused with high efficiency upto the fifth cycle. and efficiency

e progressive declined in the adsorption-desorption efficiecies with increase in number of :les can be attributed to biomass losses (Figure 4.27 - 4.30). The results recorded in this study : similar to those reported in sugar-beet peptin gels (Mata *et al*., 2010) and banana peels ossain *et al.*, 2012).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Based on the results of this study, it is concluded that: acid treated and raw lemon, watermelon, sweet yellow passion and lemon peels and avocado seeds show different levels of efficacy in removing lead, copper and cadmium ions in single, binary and multiple systems. Acid treated watermelon peels recorded the highest efficacy of 99.94% for lead (II) ions, 99.4 % for cadmium (II) ions and 99.87% for cadmium (II) in single metal ion systems. The operating parameters, including pH, initial metal concentration, dosage of the adsorbent and temperature greatly influence the efficacy of the adsorbents in the removal of lead, copper and cadmium ions. Adsorbents hold maximum efficiency for lead, followed by cadmium and copper. Adsorption capacities of adsorbents decreased in the presence of co-ions. The adsorption capacities were highest in single metal systems, followed by binary system and lowest in tertiary metal systems for each metal ion.

The interactive effect was found to be antagonistic in both binary and tertiary systems as indicated by values less than 100 in all adsorbents. Adsorption equilibrium was better described by Freundlich model than Langmuir isotherm models. Examination of the adsorption rates data of lead, copper and cadmium ions onto acid treated and raw lemon, watermelon, sweet yellow passion and lemon peels and avocado seeds show that these follow the pseudo second order kinetic model. Sorption of metal ions was reduced by the presence of

co-ions. Sulphuric acid treatment of natural fruit waste products improves their surface ligand binding sites and hence the adsorption efficiency. The FTIR analysis confirmed the presence of increased functional groups that acted as the binding sites for the adsorption of metals. Acid treated lemon peels, avocado seeds, watermelon peels and sweet yellow passion peels can be regenerated and reused for five times without reducing their efficacy. Desorption efficacy of 99.97% for lead (II) was achieved by use of acid treated avocado seed, 99.23 % for cadmium (II) ions from acid treated watermelon peel and 99.79% for copper (II) from acid treated avocado see. .

5.2 Recommendations

5.2.1 Recommendation from this work

Based on the findings of the present study, it is recommended that natural and acid treated fruit wastes be processed on larger scales for their downstream delivery to rural communities for removal of Cu (II), Pb (II) and Cd (II) ions in drinking and cooking water.

5.2.2 Recommendation for further research

i) High amounts of Cu (II), Pb (II) and Cd (II) ions can be removed from waste water using fruits wastes and we recommend their application at household level for treatment of drinking and cooking.

ii) Adsorption of other metals and microbes by fruit wastes should be investigated.

iii) Studies should be conducted on the efficacy of the fruit wastes in removing harmful anions such F^- from water consumed by humans.

iv) Studies should be done using combinations of different adsorbents to find out if removal of mixed metals from experimental solutions and natural water can be improved.

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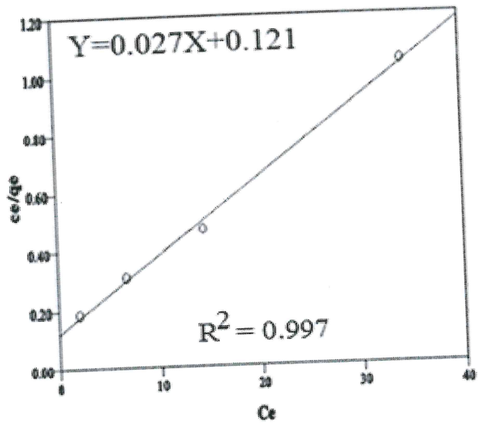
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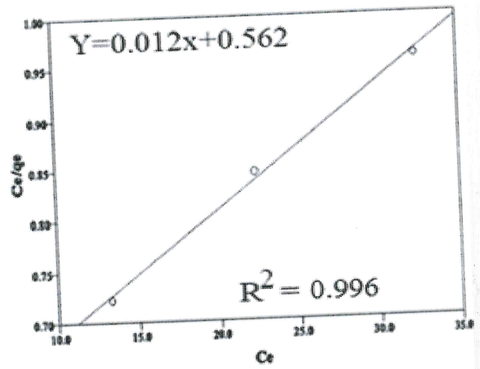
APPENDICES

APPENDIX 1: Langmuir isotherm model (Cd^{2+}) for avocado seed

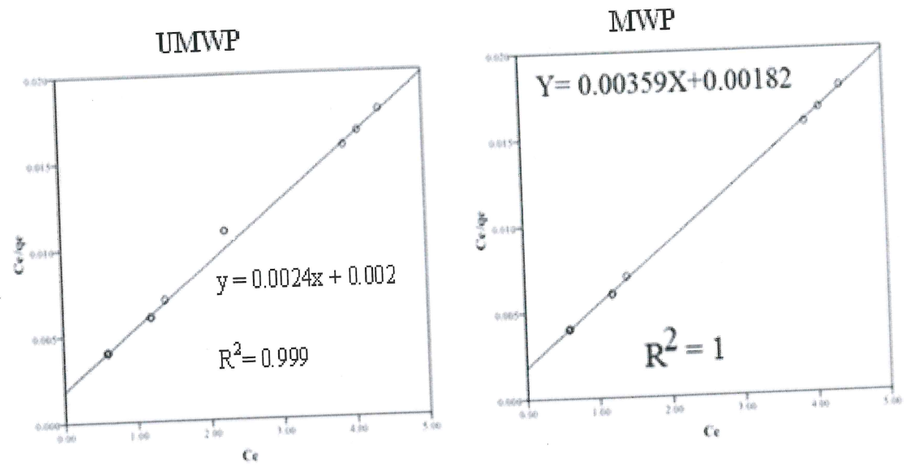
MAS



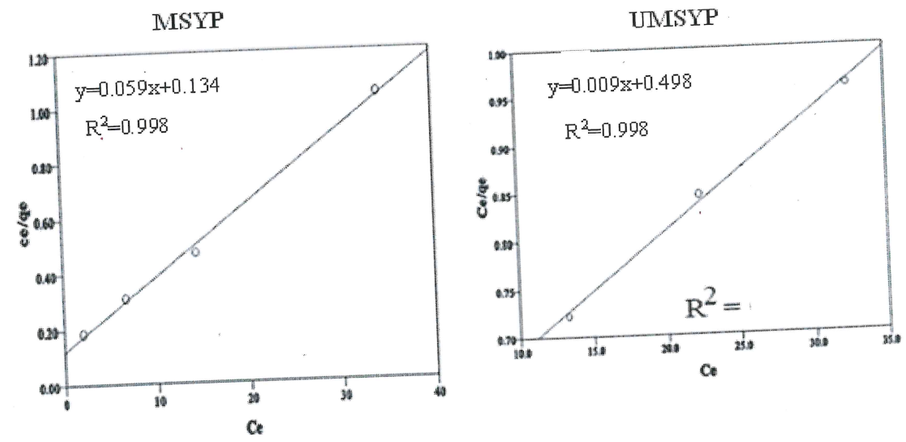
UMAS



APPENDIX II: Langmuir isotherm model (Cd^{2+}) watermelon peel

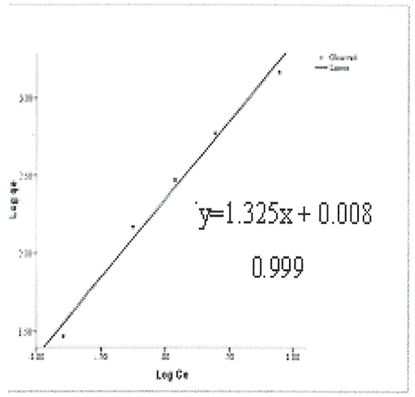


APPENDIX III: Langmuir isotherm model (Cd^{2+}) watermelon peel

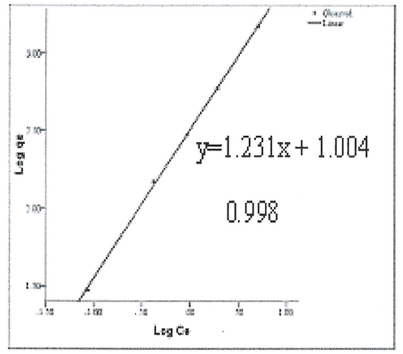


APPENDIX IV: Freundlich isotherm model (Cd^{2+}) lemon peel

MLP

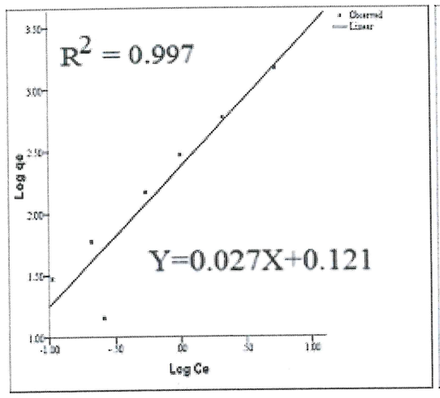


UMLP

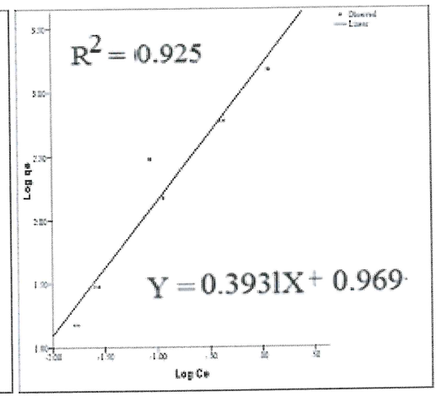


APPENDIX V: Freundlich isotherm model (Cd^{2+}) banana peel '

MBP

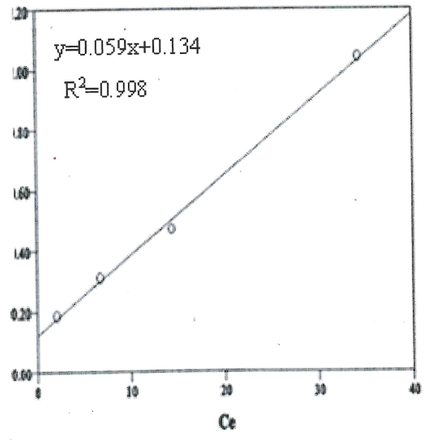


UMBP

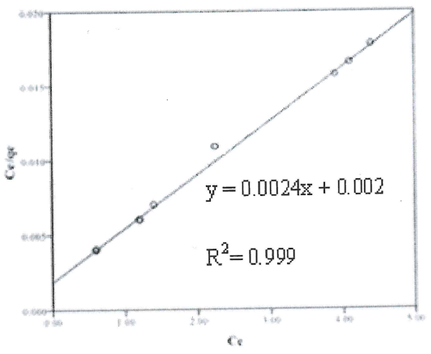


APPENDIX VI: Langmuir isotherm (pb^{2+}) for watermelon peel

MWP



UMWP



APPENDIX VII: Effect of changing initial metal concentration data

Table 1 (a): Mean percentage (%) removal of Cu (II) in adsorbents by varying initial Cu (II) ion concentration

C_o	UMWSP	MSYP	UMWP	MWP	UMAS	MAS	UMLP	MLP	UMBP	MBP
10	83.124±0.41	90.456±0.10	80.850±0.05	85.156±0.33	84.068±0.00	92.670±0.00	87.310±0.17	89.753±0.33	80.540±0.00	89.505±0.33
20	84.975±0.80	94.155±0.93	87.738±0.33	89.551±0.24	86.703±0.33	94.200±0.77	87.386±0.00	94.942±0.23	82.035±0.00	92.578±0.00
30	89.123±0.60	95.815±0.08	92.902±0.42	97.681±0.88	87.837±0.17	95.200±0.95	87.395±0.77	95.479±0.68	89.456±0.00	95.178±0.00
40	93.144±0.72	98.415±0.67	93.479±0.17	98.395±0.40	90.294±0.07	97.409±0.24	88.289±0.00	96.107±0.43	95.456±0.00	96.458±0.00
50	96.476±0.90	99.343±0.26	97.381±0.08	98.446±0.70	95.741±0.42	98.858±0.53	89.829±0.20	97.714±0.47	96.642±0.00	97.778±0.07
55	96.476±0.18	99.343±0.26	97.381±0.17	98.446±0.60	95.741±0.40	98.648±0.13	89.828±0.40	97.715±0.08	96.641±0.60	97.704±0.00
60	96.476±0.44	99.343±0.26	97.380±0.14	98.446±0.70	95.741±0.00	98.648±0.13	89.821±0.20	97.715±0.01	96.641±0.70	97.704±0.10
70	96.476±0.26	99.343±0.26	97.381±0.09	98.446±0.60	95.741±0.00	98.648±0.11	89.821±0.20	97.715±0.03	96.641±0.40	97.704±0.40
80	96.476±0.34	99.343±0.26	97.381±0.16	98.446±0.60	95.741±0.12	98.648±0.14	89.821±0.10	97.715±0.02	96.641±0.70	97.704±0.20
90	96.576±0.43	99.343±0.26	97.381±0.40	98.446±0.70	95.741±0.02	98.648±0.12	89.821±0.00	97.715±0.01	96.641±0.70	97.704±0.10
100	96.576±0.34	99.343±0.26	97.381±0.14	98.446±0.70	95.741±0.02	98.648±0.11	89.821±0.09	97.715±0.02	96.641±0.80	97.704±0.80

C_o: Initial metal concentration (mg/L)

Table 1 (b): Mean percentage (%) removal of Cd (II) in adsorbents by varying initial Cd (II) ion concentration

C_o	UMSYP	MSYP	UMWP	MWP	UMLP	UMLP	UMAS	MAS	UMBP	MBP
5	80.456±0.70	93.532±0.14	85.656±0.00	98.688±0.00	82.436±050	93.720±083	52.727±033	94.828±000	70.755±0.57	97.944±0.08
10	81.114±0.00	97.936±0.80	88.888±0.00	99.868±0.00	94.375±083	97.265±010	87.195±067	98.997±080	76.558±0.67	99.913±0.67
20	84.187±0.87	97.513±0.83	88.855±0.13	99.867±0.15	97.362±070	98.37±090	88.181±080	98.997±030	78.372±0.67	99.771±0.40
30	90.324±0.37	97.542±0.60	88.789±0.33	99.871±0.13	98.082±013	98.950±022	89.915±038	98.994±080	83.000±0.06	99.731±0.37
40	91.876±0.70	97.536±0.90	88.887±0.40	99.871±0.70	98.392±000	99.614±020	89.952±087	98.991±053	84.233±0.00	99.609±0.83
50	91.893±0.40	97.533±0.33	88.891±0.21	99.861±0.39	98.786±060	99.662±060	89.957±033	98.991±060	89.520±0.93	99.407±0.76
60	91.852±0.65	97.763±0.47	88.879±0.00	99.864±0.40	98.786±050	99.662±040	89.957±037	98.994±058	89.521±0.20	99.614±0.50
70	91.871±0.87	97.815±0.47	88.894±0.50	99.864±0.10	98.786±060	99.662±020	89.951±054	98.993±047	89.521±0.10	99.614±0.70
80	91.875±0.90	97.904±0.33	88.897±0.80	99.864±0.70	98.786±040	99.662±030	89.951±054	98.993±047	89.521±0.20	99.614±0.30
90	91.845±0.60	97.845±0.40	88.897±0.50	99.894±0.40	98.786±050	99.662±040	89.951±054	98.993±047	89.521±0.00	99.614±0.00

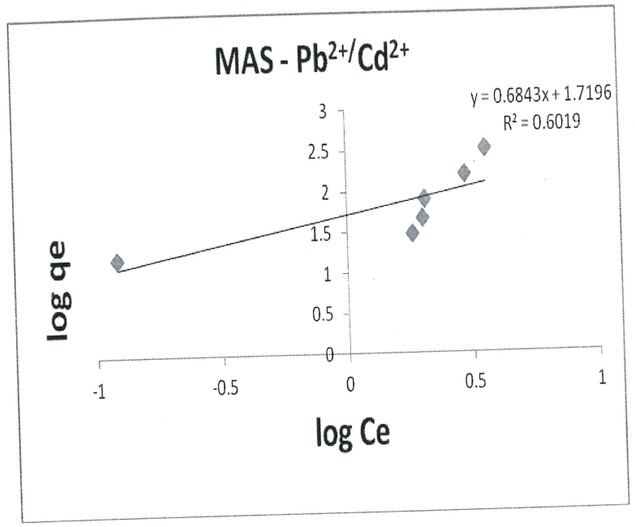
C_o: Initial metal concentration (mg/L)

Table 1 (c): Mean percentage (%) removal of Pb (II) in adsorbents by varying initial Pb (II) ion concentration

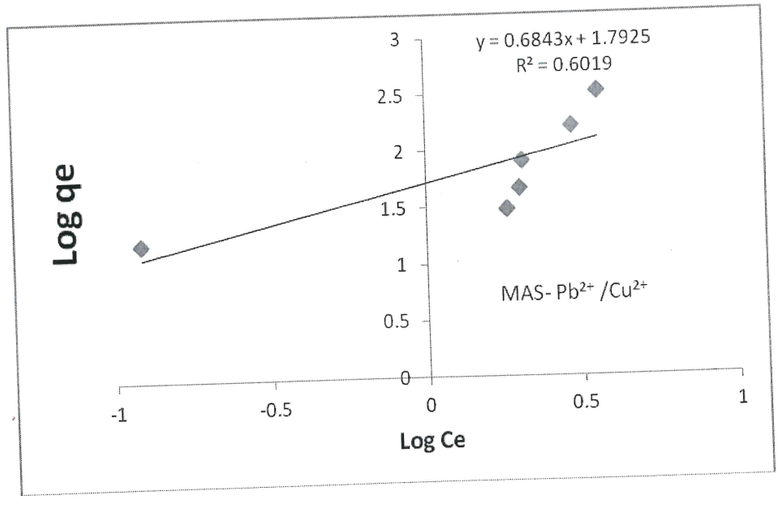
Co	UMLP	MLP	UMWP	MWP	UMAS	MAS	UMBP	MBP	UMSYP	MSYP
5	88.459±0.6	95.421±0.33	90.457±0.8	93.182±0.67	87.837±0.17	92.023±0.67	85.456±0.92	97.457±0.82	89.456±0.12	95.276±0.28
10	94.315±0.37	98.507±0.51	92.030±033	97.504±0.67	88.810±0.68	95.423±0.6	92.987±0.22	98.839±0.67	92.394±0.33	96.223±0.67
15	94.982±0.06	98.691±0.22	93.251±033	98.756±0.0	90.929±0.40	98.923±0.73	93.608±0.42	99.697±0.83	92.928±0.83	96.634±0.47
20	95.552±0.17	98.799±0.36	93.763±033	99.784±0.33	94.503±0.33	99.910±0.77	94.159±0.67	99.694±0.38	93.331±0.00	96.788±0.42
30	95.678±0.91	98.799±0.29	94.397±0.17	99.781±0.7	94.**843**±0.**14**	99.900±0.65	94.356±0.33	99.639±0.05	93.472±0.4	96.744±0.33
40	95.784±0.79	98.799±0.07	94.502±0.67	99.737±0.4	95.294±0.63	99.900±0.24	94.872±0.53	99.686±0.8	93.569±0.4	96.746±0.26
50	95.951±0.19	98.768±0.45	94.978±0.78	99.782±0.03	95.612±0.43	99.901±0.42	94.872±0.28	99.675±0.41	93.9132±0.6	96.746±0.34
60	95.928±0.1	98.763±0.53	94.978±0.24	99.782±0.24	95.613±0.01	99.900±0.54	94.872±0.19	99.675±0.44	93.912±0.78	96.746±0.65
70	95.922±0.33	98.763±0.56	94.942±0.34	99.782±0.14	95.612±0.29	99.903±0.44	94.872±0.09	99.675±0.61	93.913±0.47	96.747±0.24
80	95.808±0.73	98.650±0.66	94.912±0.61	99.783±0.12	95.614±0.52	99.900±0.47	94.872±0.34	99.674±0.6	93.915±0.46	96.750±0.00
90	95.931±0.24	98.645±0.78	94.921±0.24	99.782±0.11	95.614±0.78	99.900±0.08	94.8727±0.1	99.676±0.2	93.916±0.34	96.746±0.24

C_o: Initial metal concentration (mg/L)

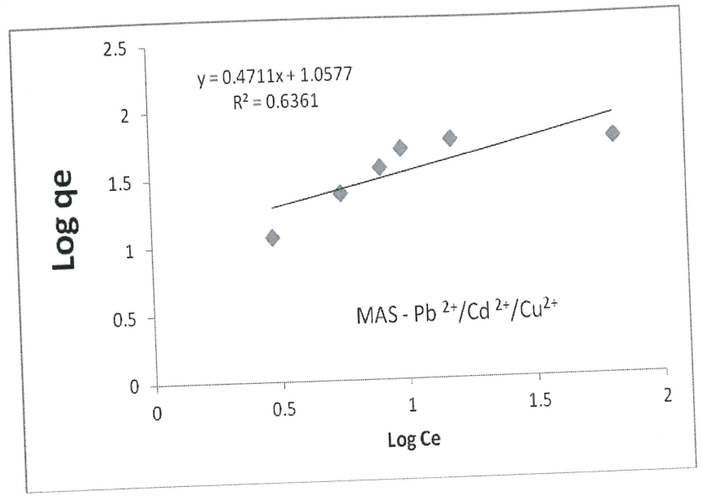
APPENDIX VIII (a): Freundlich isotherm model (Pb^{2+}/Cd^{2+}) MAS



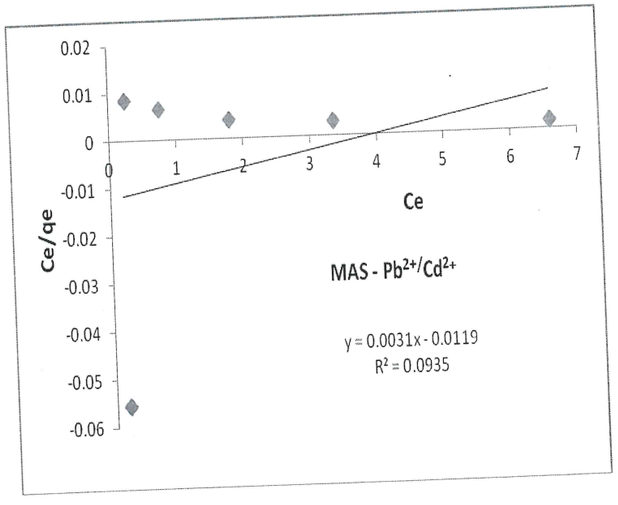
APPENDIX VIII (b): Freundlich isotherm model (Pb^{2+}/ Cu^{2+}) MAS



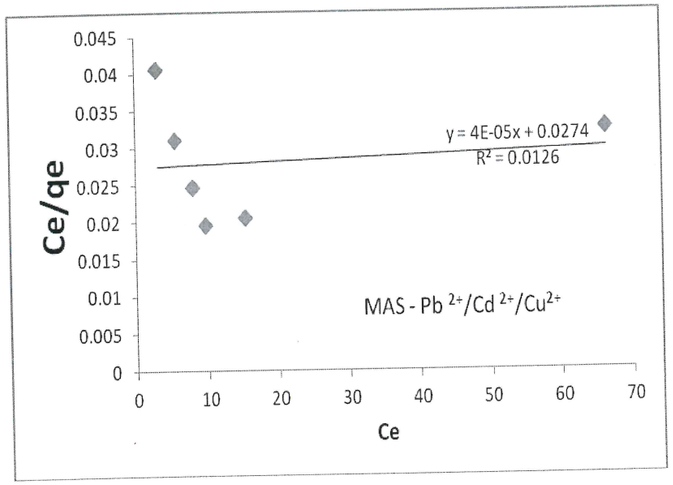
APPENDIX VIII (c): Freundlich isotherm model ($Pb^{2+}/Cd^{2+}/ Cu^{2+}$) MAS



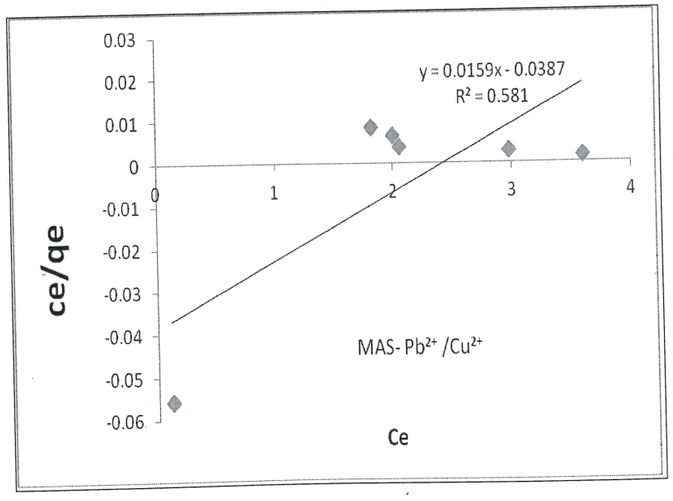
APPENDIX IX (a): Langmuir isotherm model (Pb^{2+}/ Cd^{2+}) MAS



APPENDIX IX (b): Langmuir isotherm model (Pb^{2+}/ Cd^{2+}/ Cd^{2+}) MAS



APPENDIX IX (c): Langmuir isotherm model (Pb^{2+}/ Cu^{2+}) MAS



APPENDIX X (a): Desorption data

Table 2: Desorption of Cu (II), Cd (II) and Pb (II) ions from acid treated avocado seeds (MAS), lemon peels (MLP), sweet yellow passion peels (MSYP) and watermelon peels (MWP)

Mean±SE % Desorption (Copper)				
ELLUENT /ADSORBENT	**MAS**	**MLP**	**MSYP**	**MWP**
Tap water	22.86 ± 0.00^{b}	20.28 ± 0.00^{b}	21.09 ± 0.00^{b}	21.42 ± 0.00^{a}
Distilled water	32.25 ± 0.00^{c}	30.86 ± 0.00^{d}	31.38 ± 0.00^{c}	42.34 ± 0.00^{d}
0.1M Sulphuric acid	99.15 ± 0.00^{g}	95.11 ± 0.00^{g}	96.73 ± 0.00^{g}	99.79 ± 0.00^{g}
0.1M HCl	43.92 ± 0.00^{e}	42.42 ± 0.00^{e}	42.88 ± 0.00^{e}	45.42 ± 0.00^{e}
0.1M HNO_3	59.22 ± 0.00^{f}	54.02 ± 0.00^{f}	61.49 ± 0.00^{f}	58.89 ± 0.00^{f}
0.1M CH_3COOH	33.19 ± 0.00^{d}	29.86 ± 0.00^{c}	36.57 ± 0.00^{d}	38.45 ± 0.00^{c}
0.1M NaOH	20.98 ± 0.07^{a}	13.97 ± 0.00^{a}	20.08 ± 0.00^{a}	22.65 ± 0.00^{b}
p-value	<0.001	<0.001	<0.001	<0.001
Mean±SE % Desorption (Lead)				
Tap water	12.47 ± 0.00^{a}	13.71 ± 0.00^{a}	23.30 ± 0.00^{a}	20.17 ± 0.00^{b}
Distilled water	30.17 ± 0.00^{e}	27.91 ± 0.00^{c}	32.72 ± 0.00^{d}	24.44 ± 0.00^{d}
0.1M Sulphuric acid	99.96 ± 0.00^{g}	95.48 ± 0.00^{g}	95.00 ± 0.00^{g}	75.30 ± 0.00^{g}
0.1M HCl	52.87 ± 0.00^{f}	50.51 ± 0.00^{f}	46.94 ± 0.00^{f}	33.33 ± 0.00^{f}
0.1M HNO_3	38.27 ± 0.00^{d}	41.75 ± 0.00^{e}	40.06 ± 0.00^{e}	25.47 ± 0.00^{e}
0.1M CH_3COOH	26.84 ± 0.00^{c}	32.55 ± 0.00^{d}	29.68 ± 0.00^{c}	20.61 ± 0.00^{c}
0.1M NaOH	18.03 ± 0.00^{b}	19.59 ± 0.00^{b}	23.52 ± 0.11^{b}	11.68 ± 0.03^{a}
p-value	<0.001	<0.001	<0.001	<0.001
Mean±SE % Desorption (Cadmium)				
Tap water	24.46 ± 0.00^{b}	21.49 ± 0.00^{a}	24.54 ± 0.00^{b}	20.02 ± 0.01^{a}
Distilled water	35.88 ± 0.00^{d}	33.82 ± 0.00^{c}	36.00 ± 0.00^{d}	35.92 ± 0.00^{d}
0.1M Sulphuric acid	98.76 ± 0.00^{g}	98.31 ± 0.00^{g}	92.97 ± 0.00^{g}	99.23 ± 0.00^{g}
0.1M HCl	53.56 ± 0.00^{e}	52.18 ± 0.00^{d}	49.68 ± 0.00^{e}	60.55 ± 0.00^{e}
0.1M HNO_3	62.66 ± 0.00^{f}	56.66 ± 0.00^{e}	53.16 ± 0.00^{f}	64.01 ± 0.00^{f}
0.1M CH_3COOH	31.42 ± 0.00^{c}	29.88 ± 0.00^{b}	30.54 ± 0.00^{c}	32.87 ± 0.00^{c}
0.1M NaOH	23.82 ± 0.00^{a}	21.49 ± 0.00^{a}	23.78 ± 0.00^{a}	25.81 ± 0.00^{b}
p-value	<0.001	<0.001	<0.001	<0.001

There was a significant interaction between pH and metal ion adsorption (Two-way ANOVA, $p<0.001$). $\alpha=0.05$,

APPENDIX X (b): Adsorption desorption cycles

Table 3(a): Cu^{2+} uptake and desorption performance of MAS, MWP, MLP and MSYP.

	Mean±SE % Adsorption and Desorption							
Cycles	**MAS**		**MLP**		**MSYP**		**MWP**	
	% Adsorption	% Desorption	% Adsorption	% Desorption	% Adsorption	% Desorption	% Adsorption	% Desorption
1	99.15±0.00	96.72±0.08	99.46±0.01	95.11±0.00	99.64±0.00	96.57±0.00	99.95±0.00	99.79±0.00
2	98.77±0.00	96.54±0.00	99.34±0.00	95.97±0.00	99.63±0.00	93.99±0.00	99.88±0.00	99.46±0.00
3	97.74±0.01	96.29±0.00	99.29±0.00	95.87±0.00	99.56±0.00	93.49±0.00	99.87±0.00	98.67±0.00
4	96.64±0.00	95.11±0.00	99.04±0.00	97.18±0.00	99.46±0.00	76.06±0.00	99.76±0.00	96.26±0.00
5	95.15±0.00	91.13±0.00	98.78±0.00	91.41±0.01	99.16±0.00	75.77±0.00	99.08±0.00	95.14±0.00
6	85.24±0.11	81.16±0.1	91.39±0.03	80.26±0.03	90.24±0.00	71.26±0.01	81.39±0.01	80.26±0.02
7	74.12±0.02	71.23±0.01	84.12±0.02	63.23±0.03	84.12±0.01	63.23±0.00	64.12±0.00	63.23±0.03
8	65.65±0.12	60.45±0.11	80.65±0.03	49.45±0.03	75.65±0.01	50.45±0.00	58.65±0.00	49.45±0.01
9	53.56±0.3	45.36±0.1	62.23±0.2	42.36±0.1	53.56±0.01	55.36±0.01	52.23±0.01	50.36±0.00
	p-value (<0.001)							

Table 3(b): Cd^{2+} uptake and desorption performance of MAS, MWP, MLP and MSYP

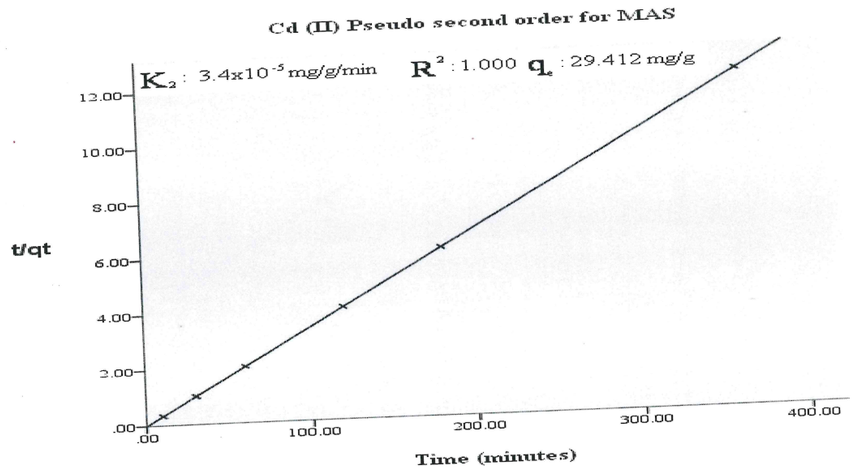
	Mean±SE % Adsorption and Desorption							
Cycles	**MAS**		**MLP**		**MSYP**		**MWP**	
	% Adsorption	% Desorption	% Adsorption	% Desorption	% Adsorption	% Desorption	% Adsorption	% Desorption
1	99.45±0.02	98.75±0.00	99.24±0.00	98.31±0.01	99.09±0.00	92.97±0.01	99.33±0.00	99.23±0.01
2	99.41±0.00	98.01±0.01	99.27±0.00	96.17±0.00	94.59±0.01	92.13±0.01	99.04±0.00	96.99±0.01
3	99.34±0.00	97.20±0.01	99.12±0.01	95.05±0.01	90.86±0.16	86.05±0.00	98.35±0.00	95.14±0.02
4	99.15±0.00	96.92±1.33	99.05±0.00	93.33±0.01	86.39±0.00	85.09±0.00	96.37±0.00	94.92±0.01
5	98.97±0.00	93.63±0.00	98.18±0.03	94.45±0.01	80.97±0.01	68.16±0.00	94.35±0.00	94.24±0.00
6	88.23±0.01	83.64±0.01	89.23±0.03	83.64±0.03	78.23±0.00	53.64±0.00	89.23±0.00	83.64±0.11
7	84.27±0.11	83.78±0.11	74.27±0.05	72.78±0.02	64.27±0.00	43.78±0.00	74.27±0.00	72.78±0.01
8	78.23±0.01	73.45±0.02	68.23±0.02	65.52±0.02	58.23±0.00	43.55±0.00	68.23±0.00	65.52±0.00
9	68.67±0.00	60.24±0.01	58.28±0.07	48.23±0.01	48.67±0.00	40.49±0.00	58.67±0.00	50.23±0.02
	p-value (<0.001)							

Table 3(c): Pb^{2+} uptake and desorption performance of MAS, MWP, MLP and MSYP

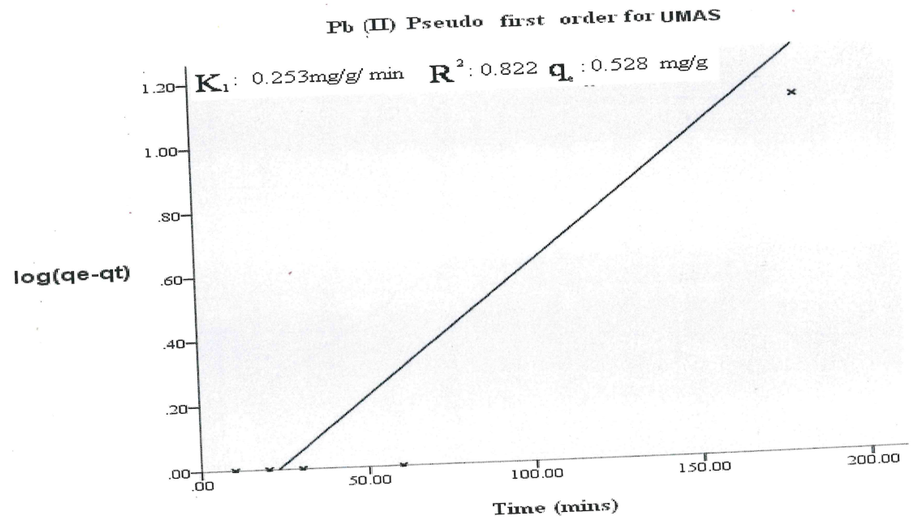
Cycles	**MAS**		**MLP**		**MSYP**		**MWP**	
	% Adsorption	% Desorption	% Adsorption	% Desorption	% Adsorption	% Desorption	% Adsorption	% Desorption
1	99.97±0.00	98.11±0.06	98.94±0.00	95.28±0.02	96.32±0.01	75.30±0.20	99.25±0.00	94.98±0.01
2	99.44±0.00	97.35±0.03	98.88±0.00	95.25±0.04	96.22±0.00	75.06±0.00	99.27±0.00	94.94±0.02
3	98.94±0.00	95.36±0.01	98.69±0.00	95.22±0.00	95.98±0.00	74.47±0.00	99.29±0.00	92.80±0.01
4	98.55±0.01	88.21±0.03	98.49±0.00	95.30±0.00	95.95±0.00	73.14±0.03	98.28±0.00	93.01±0.01
5	98.17±0.03	87.49±0.34	98.45±0.01	93.88±0.01	94.97±0.00	73.39±0.00	98.40±0.00	91.93±0.01
6	90.56±0.03	87.42±0.03	83.64±0.03	90.56±0.03	90.56±0.03	67.42±0.03	90.56±0.03	77.42±0.03
7	88.22±0.03	82.69±0.03	72.78±0.03	88.22±0.03	88.22±0.03	62.74±0.03	88.22±0.03	62.74±0.03
8	79.36±0.03	77.43±0.03	65.52±0.03	79.36±0.03	79.36±0.03	57.89±0.03	79.36±0.03	57.89±0.03
9	68.98±0.03	62.39±0.03	50.23±0.03	62.01±0.03	68.98±0.03	52.48±0.03	70.01±0.03	50.48±0.03
	p-value (<0.001)							

APPENDIX XI: Pseudo first and second order isotherms

APPENDIX XI (a): Cd (II) Pseudo second order for MAS



APPENDIX XI (b): Cd (II) Pseudo first order for UMAS



APPENDIX XI (e): Cd (II) Pseudo second order for MBP

