USE OF MAIZE COBS DERIVED PRODUCTS FOR REMOVAL OF SELECTED INORGANIC IONS, COLOUR AND TURBIDITY FROM CONTAMINATED WATER

DANIEL MUVENTGEI MWANGANGI (B.Ed. Sc)

I56/CE/21443/2010

A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science (Applied Analytical Chemistry) in the School of Pure and Applied Sciences of Kenyatta University

DECEMBER 2015
DECLARATION

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

Signature. ........................................ Date 22/12/2015

Daniel Muvengei Mwangangi (156/CE/21443/2010)
Department of Chemistry

SUPERVISORS

We confirm that the work reported in this thesis was carried out by the candidate and has been submitted with our approval as University Supervisors.

Signature. ........................................ Date 22/12/15

Dr. Harun Mbuvi
Department of Chemistry
Kenyatta University

Signature. ........................................ Date 22/12/2015

Dr. Margaret M. Ng’ang’a
Department of Chemistry
Kenyatta University
DEDICATION

I dedicate this work to my parents Mwangangi Muvengei and Elizabeth Mwangangi. Dad and Mum I love you always.
ACKNOWLEDGEMENTS

I would like to thank the almighty God for enabling me finish post graduate studies at Kenyatta University.

I would also like to extend my gratitude to my supervisors Dr. Harun Mbuvi and Dr. Margaret Ng’ang’a of Kenyatta University for their generous support, guidance, advice and their valuable suggestions they gave me during entire period.

I extend my gratefulness to lecturers and technical staff of Chemistry Department of Kenyatta University for the support they gave during data collection and research period. Specifically I wish to thank Mr. Dennis Osoro for guidance he gave during data analysis.

To my fellow students, especially Gerald Mbugua. I appreciate the advice and encouragement you gave me during the research period.

My appreciation goes to Agnes Mwaura, Maurine Mwangi and Raphael Njoroge for your encouragement and prayers.

To my brothers and sisters (James, John, Lenah and Janet) I can’t forget the moral support you gave me. God bless you
TABLE OF CONTENTS

TITLE PAGE ........................................................................................................... i

DECLARATION ........................................................................................................ ii

DEDICATION ........................................................................................................... iii

ACKNOWLEDGEMENTS ......................................................................................... iv

TABLE OF CONTENTS ........................................................................................... v

LIST OF FIGURES .................................................................................................. ix

LIST OF TABLES .................................................................................................... x

ABBREVIATIONS AND ACRONYMS ...................................................................... xi

ABSTRACT ............................................................................................................. xii

CHAPTER ONE ....................................................................................................... 1

INTRODUCTION ..................................................................................................... 1

1.1. Background to the study ................................................................................ 1

1.2. Statement of the Problem and Justification .................................................... 4

1.3. Hypothesis ...................................................................................................... 4

1.4 General Objective ............................................................................................ 5

1.4.1. Specific Objectives .................................................................................... 5

1.5. Significance of the study ................................................................................ 5

1.6. Scope and limitation of study ......................................................................... 6

CHAPTER TWO ..................................................................................................... 7

LITERATURE REVIEW ........................................................................................ 7

2.1 Water scarcity .................................................................................................. 7

2.2 Global Water Pollution .................................................................................... 8

2.3 Heavy metals ................................................................................................... 9

2.3.1 Lead and its effects .................................................................................... 10

2.3.2 Cadmium and its effects ............................................................................ 12
2.4 Water treatment methods .......................................................... 13
2.4.1 Ion exchange ........................................................................ 13
2.4.2 Electrodialysis ...................................................................... 14
2.4.3 Flotation ................................................................................ 14
2.4.4 Adsorbents ............................................................................ 15
2.5 Maize cob .................................................................................. 16
2.6 Water colour .............................................................................. 18
2.7 Water turbidity ......................................................................... 18
2.8 Sorption studies .......................................................................... 19
2.8.1 Factors affecting adsorption ................................................... 20
2.8.1.1 Effect of shaking speed ...................................................... 20
2.8.1.2 Effect of adsorbent dose ................................................... 20
2.8.1.3 Effect of initial metal ion concentration ............................ 21
2.8.1.4 Effect of temperature ......................................................... 21
2.8.1.5 Effect of contact time ......................................................... 21
2.9 Adsorption equilibrium ............................................................... 22
2.9.1 Langmuir isotherm ................................................................. 22
2.9.2 Freundlich isotherm ............................................................... 23
2.10 Techniques for metal analysis .................................................... 23
2.10.1 Atomic absorption spectrometry (AAS) ................................. 23
2.10.2 Turbidimeter ........................................................................ 25
2.10.3 Uv-visible spectrometer ......................................................... 26

CHAPTER THREE ........................................................................... 27
MATERIALS AND METHODS ......................................................... 27
3.1 Apparatus and reagents ............................................................. 27
3.1.1 Instrumentation ..................................................................... 27
3.1.2 Reagents ............................................................................................................. 27
3.1.3 Optimization of contact time ........................................................................... 28
3.1.4 Optimization of initial metal ion concentration ............................................... 29
3.1.5 Optimization of temperature ............................................................................. 29
3.1.6 Optimization of adsorbent dose ....................................................................... 29
3.1.7 Optimization of shaking speed .......................................................................... 29
3.1.8 Optimization of pH .......................................................................................... 30
3.2 Collection of raw materials and preparation of activated charcoal ............. 30
3.3 Removal of colour ............................................................................................... 31
3.4 Removal of suspended particles .......................................................................... 31
CHAPTER FOUR ........................................................................................................ 32
RESULTS AND DISCUSSION .................................................................................. 32
4.1 Carbonization and ashing ...................................................................................... 32
4.2 Elemental Composition of Ash ............................................................................. 32
4.3 Batch adsorption experiments .............................................................................. 33
4.3.1 Effect of initial metal ion concentration ......................................................... 34
4.3.2 Effect of contact time ......................................................................................... 36
4.3.3 Effect of dosage on percentage removal of metal ions .................................. 38
4.3.4 Effect of shaking speed ...................................................................................... 40
4.3.5 Effect of temperature ......................................................................................... 42
4.4 Removal of methylene blue .................................................................................. 44
4.5 Removal of suspended particles .......................................................................... 45
4.6 Adsorption isotherms ......................................................................................... 47
CHAPTER FIVE .......................................................................................................... 51
CONCLUSIONS AND RECOMMENDATIONS ...................................................... 51
5.1 CONCLUSION ...................................................................................................... 51
5.2 Recommendations ........................................................................................................ 52

REFERENCES ..................................................................................................................... 53

APPENDICES ...................................................................................................................... 60
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 2.1</td>
<td>AAS Instrumentation</td>
<td>25</td>
</tr>
<tr>
<td>Figure 2.2</td>
<td>Schematic diagram of a turbidity meter</td>
<td>25</td>
</tr>
<tr>
<td>Figure 4.1</td>
<td>Plate showing maize cob charcoal</td>
<td>32</td>
</tr>
<tr>
<td>Figure 4.2</td>
<td>Plate showing activated maize cob charcoal</td>
<td>32</td>
</tr>
<tr>
<td>Figure 4.3</td>
<td>Effect of initial metal concentration on percentage removal of lead (II) ions</td>
<td>35</td>
</tr>
<tr>
<td>Figure 4.4</td>
<td>Effect of initial metal ion concentration on percentage removal of cadmium (II) ions</td>
<td>36</td>
</tr>
<tr>
<td>Figure 4.5</td>
<td>Effect of contact time on the percentage removal of lead (II) ions</td>
<td>37</td>
</tr>
<tr>
<td>Figure 4.6</td>
<td>Effect of contact time on percentage removal of cadmium (II)</td>
<td>38</td>
</tr>
<tr>
<td>Figure 4.7</td>
<td>Effect of adsorbent dose on percentage removal of lead (II) ions</td>
<td>39</td>
</tr>
<tr>
<td>Figure 4.8</td>
<td>Effect of adsorbent dose on percentage removal of cadmium (II) ion</td>
<td>40</td>
</tr>
<tr>
<td>Figure 4.9</td>
<td>Effect of shaking speed on percentage removal of lead (II) ions</td>
<td>41</td>
</tr>
<tr>
<td>Figure 4.10</td>
<td>Effect of shaking speed on percentage removal of cadmium (II) ions</td>
<td>42</td>
</tr>
<tr>
<td>Figure 4.11</td>
<td>Effect of temperature on percentage removal of lead (II) ions</td>
<td>43</td>
</tr>
<tr>
<td>Figure 4.12</td>
<td>Effect of temperature on percentage removal of cadmium (II) ion</td>
<td>44</td>
</tr>
<tr>
<td>Figure 4.13</td>
<td>Effect of concentration on percentage removal of methylene blue</td>
<td>45</td>
</tr>
<tr>
<td>Figure 4.14</td>
<td>Effect of adsorbent dose on turbidity removal using ash from maize cobs</td>
<td>46</td>
</tr>
<tr>
<td>Figure 4.15</td>
<td>Langmuir isotherm for Cd\textsuperscript{2+} using MC</td>
<td>46</td>
</tr>
<tr>
<td>Figure 4.16</td>
<td>Freundlich isotherm for Cd\textsuperscript{2+} using MC</td>
<td>47</td>
</tr>
</tbody>
</table>
LIST OF TABLES

Table 2.1 Some of the biomasses that have been investigated for their ability to remove heavy metals from aqueous solutions…………………16

Table 4.1 Elemental composition of Ash……………………………………………………………33

Table 4.2 Langmuir and Freundlich constants for removal of lead………………..48

Table 4.3 Langmuir and Freundlich constants for removal of cadmium………49

Table 4.4 Langmuir and Freundlich constants for removal of methylene blue…50
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMC</td>
<td>Activated maize cob charcoal</td>
</tr>
<tr>
<td>BOD</td>
<td>Biochemical oxygen demand</td>
</tr>
<tr>
<td>COD</td>
<td>Chemical oxygen demand</td>
</tr>
<tr>
<td>FAAS</td>
<td>Flame atomic absorption spectroscopy</td>
</tr>
<tr>
<td>MC</td>
<td>Maize cob charcoal</td>
</tr>
<tr>
<td>NCAR</td>
<td>National Center for Atmospheric Research</td>
</tr>
<tr>
<td>NTU</td>
<td>Nephelometric turbidity units</td>
</tr>
<tr>
<td>RPM</td>
<td>Revolutions per minute</td>
</tr>
<tr>
<td>UN</td>
<td>United Nations</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environment Programme</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra violet</td>
</tr>
<tr>
<td>WHO</td>
<td>World health organization</td>
</tr>
<tr>
<td>DO</td>
<td>Dissolved oxygen</td>
</tr>
<tr>
<td>SS</td>
<td>Suspended solids</td>
</tr>
<tr>
<td>IQ</td>
<td>Intelligent quotient</td>
</tr>
<tr>
<td>CDC</td>
<td>Centre for disease control</td>
</tr>
<tr>
<td>IARC</td>
<td>International agency for research on cancer</td>
</tr>
</tbody>
</table>
ABSTRACT

Majority of Kenyans lack access to clean water due to increased population growth, high rate of industrialisation and poor waste management. The situation may worsen if immediate measures are not taken. Lead and cadmium are the main heavy metals in contaminated water and their harmful effects such as lung cancer, mental retardation and nerve disorder cannot be underestimated. Available methods for removing these metal ions from water such as use of activated carbon are very expensive and unaffordable to low income earners. Maize cobs have minimal use after maize harvesting can be utilised to reduce environmental pollution. The primary aim of this study was to investigate the ability of maize cobs derived products to adsorb both lead (II) and cadmium (II) ions and remove methylene blue and turbidity from contaminated water. Maize cobs charcoal was prepared by heating dry maize cobs in a furnace in limited air. Activation was done by use of 1.0 M sulphuric acid and heating the mixture in a closed vessel. Maize cob ash was generated by heating dry maize cobs in a furnace. Ability of these sorbents to adsorb lead (II) and cadmium (II) ions from the solution was investigated by carrying out batch experiment and varying parameters such as contact time, initial metal ion concentration, adsorbent dose, temperature and shaking speed. The data obtained was fitted into Langmuir and Freundlich models. Activated charcoal gave the best fit in Langmuir for lead ions with maximum adsorption capacity of 13.0 mg/g. For removal of cadmium (II) ions, all the adsorbents fitted in Freundlich with maize cob charcoal having the highest adsorption capacity of 24.3 mg/g and \( r^2 = 0.997 \). Among the three adsorbent only ash was found to have the ability of removing turbidity from water. This implies that maize cob derived products can be used to remove lead (II) and cadmium (II) ions from waste water.
CHAPTER ONE

INTRODUCTION

1.1. Background to the study

The world population has increased three times in the 20th century, increasing the need of renewable water resources. This population progression coupled with industrialization and urbanisation has led to increased demand for clean water leading to its shortage worldwide (UNWWAP, 2006). Contamination of water is highly pronounced currently due to inappropriate waste management in most of part of our country (UNEP, 1996). At present, 1.1 billion people don’t have access to safe drinking water and 2.6 billion people lack suitable and proper sanitation (WHO/UNICEF, 2000) while 3900 children lose their lives daily from water borne diseases (UNEP, 1996).

More than a quarter of the world’s population will be living in regions that are experiencing severe clean waters scarcity as we approach the next century (Rosegrant et al., 2002). A good clean water supply and adequate sanitation system are considered to be the most important factors in ensuring good health in a community (Fewtrell et al., 2005).

Kenya’s natural water resources do not offer equitable provision of water to the various regions of the country (UNWWAP, 2006). Rapid urban migration has pushed majority of low income urban residents to the slums, with no access to clean
or safe to drink water and appropriate sanitation. This has aggravated the already perilous health conditions (WHO/UNICEF, 2000).

In Kenya, especially the arid regions such as the North Eastern, the water shortage has resulted to a large population of women and children spending up to one-third of their daytime fetching water from the nearest fresh water source (Banks et al., 1997). This strenuous work leaves approximately half of the country's inhabitants susceptible to serious vulnerabilities and risk of attack by predators, the principal water collectors are also the most prone to water-borne diseases (Ward, 1996).

Today, water fetched from rivers is increasingly being used for drinking and irrigation particularly in more urbanized and highly industrialized areas. In addition to water pollution by organic compounds and nutrients, the heavy metal concentration levels in water majorly in rivers has become one of the principal problems since their toxicity have lethal consequences even at low concentrations. However, high concentrations of heavy metals are known to produce a range of toxic effect and also have a potentially damaging effect on human physiology and other biological systems. For example, lead can cause encephalopathy, cognitive impairment, behavioural disturbances, kidney damage, anaemia, and toxicity to the reproductive system. At high exposure level, cadmium can cause nephrotoxic effect, while after long term exposure it can cause bone damage. Other study reported that copper can cause weakness, lethargy, anorexia, and gastrointestinal tract (El-said et al., 2010). In general, suspended matter and sediment work as a trap for dissolved heavy metals, butremobilization has been observed (Ward et al., 1996).
Higher turbidity increases water temperature because suspended particles absorb more heat. This, in turn, reduces the concentration of dissolved oxygen (DO) because warm water holds less DO than cold (Mitchell and Stapp, 2003). Higher turbidity also reduces the amount of light penetrating the water, which reduces photosynthesis and the production of DO. Dyes are also extensively used in many industries including printing process, textile, plastics and cosmetics to add colour for their final products. Most of unreacted dyes generate undesirable effluents and are usually discharged to the environment without treatment (Wang et al., 2008). The release of dyes into water by industries is undesirable and cause serious environmental problem. Coloured water can limit the penetration of light. Thus highly coloured body water cannot sustain aquatic life which can lead to long term impairment of ecosystem.

There are several ways that dissolved heavy metals can be removed from water that include ion exchange, reverse osmosis, precipitation, ultrafiltration, electro dialysis and adsorption (Burton and Tchnobanoglous, 1991). Most of them require high energy and advanced operations that are out of reach to many low income earners. Consequently, new approaches based on the use of natural inexpensive adsorbents such as orange peels and rice husk for treatment have been reported (Badmus et al., 2007). In general, an adsorbent can be termed as a low cost adsorbent if it requires minor processing, is abundant in nature, or is a by-product or waste material from another industry (Nasim et al., 2004). Therefore there is a growing need for the development of new, innovative and cost effective methods for the removal of heavy metals from waste water (Sayeda et al., 2010). This study explores
possibilities of developing cheap and reliable water treatment adsorbent from maize cobs derived products. Maize cobs are one of the agricultural wastes.

1.2. Statement of the Problem and Justification

With rapid development in agriculture, industry, commerce, hospital and health-care facilities, there is large amount of hazardous waste being deposited in rivers and water bodies. Available water treatment methods are expensive to low income earners. Due to increased industrialisation in Kenya, the rate of water contamination is also increasing which is majorly caused by discharge from industries. Organic compounds such as methylene blue produce unpleasant odour and taste in water making it unsafe for human consumption. Suspended particles in drinking water affect its turbidity. It is therefore necessary to remove heavy metals, methylene blue and suspended particles from wastewater. Poor waste management in Kenya is also another factor contributing greatly in water pollution. Although Maize is the main subsistence crop grown in Kenya, very little is done to maize cobs after harvesting. Consequently they pile up in our homesteads. This project utilised maize cobs in production of charcoal and ash for cleaning contaminated water.

1.3. Hypothesis

Activated charcoal and ash generated from maize cobs provide an effective absorbent for removal of heavy metals, turbidity and colour from contaminated water.
1.4 General Objective

The general objective was to determine the efficiency and capacity of maize cobs derived products for removal of selected inorganic ions, colour and turbidity from contaminated water.

1.4.1. Specific Objectives

i. To determine the adsorption efficiency and capacity of ash and charcoal derived from maize cobs for removal of Pb²⁺ and Cd²⁺ ions from contaminated water.

ii. To determine the efficiency and capacity of ash, charcoal and activated charcoal from maize cobs to remove turbidity and colour from contaminated water.

iii. To determine percentage removal of Pb²⁺ and Cd²⁺ from water using maize cob derived products while varying parameters of adsorbent dose, contact time, shaking speed, initial concentrations and temperature.

1.5. Significance of the study

Available water treatment methods are expensive. This leaves many Kenyans vulnerable to water borne diseases hence spending so much money in treatment of these diseases which includes cholera, typhoid and amoeba which are caused by microbes and those caused by heavy metals like lung cancer. This study utilizes locally available material to make adsorbents for water treatment. Environmental pollution brought about by these waste would be minimized. Potential of the low cost adsorbent from maize cob to remove lead (II) and cadmium (II) ions from
waste water will greatly help in reducing the number of people affected with lung cancer, nerve disorders and mental retardation.

1.6. Scope and limitation of study

The study was limited to Pb$^{2+}$ and Cd$^{2+}$ ions. The interfering ion effect was not investigated. The study was limited to usage of maize cobs as one of the agricultural waste.
CHAPTER TWO

LITERATURE REVIEW

2.1 Water scarcity

Water is already over-utilised in many regions of the world. More than one-third of the world’s population – roughly 2.4 billion people – live in water-stressed countries and by 2025 the number is expected to rise to two-thirds (UNEP, 1996). Groundwater tables and river levels are receding in many parts of the world due to human water use. In India, for example, farmers are now using nearly 80 percent of the country’s available water, largely from groundwater wells; the World Bank estimates that at current rates, India will have exhausted available water supplies by 2050 (Stumm et al., 1980). Regions affected by drought also are increasing. The percentage of global land classified as “very dry” has doubled since the 1970s, including large parts of Africa and Australia (NCAR, 2005) Natural water storage capacity and long-term annual river flows are also declining, especially in the Northern Hemisphere, due to glacial/snow cap melting.

Glacial melting is one of the reasons that many of Asia’s largest rivers are projected to recede in coming decades leading to water shortage, and reduced snowpack in the rocky mountains is the explanation given by scientists who say that Lake Mead, a key water source for millions of people in the south western United States, could dry up by 2021 if future water use is not limited (UNEP, 1996). Kenya has a land mass area of approximately 592,000 sq.km, of which 2/3 are permanent pastures, 1/5 wilderness, and comparatively low land proportions occupied by either forests
or cropland, it is mainly an agricultural country with an expanding economy whose basic element for development is water. The annual quantity of renewable fresh water resources is estimated at 20.2 billion m$^3$ comprising 19.59 m$^3$ of surface water and 0.62 billion m$^3$ of ground water (Felmy et al., 1984). The amount of water actually available for utilisation in any one year (among other factors) depends on the rate of run-off, the aridity of the catchment area and the methods of interception at various points in the hydrological cycle. Given the country’s population of about 40 million (David, 2010) people, per capita supply is approximately 696 m$^3$/person per year, which makes Kenya a water scarce country.

The major development challenge that Kenya faces is creating conditions for rapid and sustained economic growth. Prudent management of water resources is an essential component of the whole process (UNICEF/WHO, 2008). As Kenya hopes to transform into a newly industrialised country by the year 2030, the twin challenges it will face will be to provide water to both agriculture (irrigation) and urban areas and to promote industrialization without undermining its water resource base (Banks et al., 1997). The availability and demand for clean water resources in Kenya varies from one region to another.

2.2 Global Water Pollution

Every day, 2 million tonnes of sewage, industrial and agricultural waste are discharged into the world’s water (UN WWAP, 2003), the equivalent of the weight of the entire human population of 6.8 billion people. The UN estimates that the amount of waste water produced annually is about 1,500 km$^3$, six times more water
than exists in all the rivers of the world (UN WWAP, 2003). Water is mostly contaminated by suspended solids (SS) that can lead to development of sludge deposits and anaerobic conditions when untreated wastewater is discharged to the aquatic environment (UNWWAP, 2009).

Biodegradable organics are principally made up of proteins, carbohydrates and fats. They are commonly measured in terms of biological oxygen demand (BOD) and chemical oxygen demand (COD). If discharged into inland rivers, streams or lakes, their biological stabilization can deplete natural oxygen resources and cause septic conditions that are detrimental to aquatic species. Pathogenic organisms found in waste-water can cause infectious diseases. Priority pollutants, including organic and inorganic compounds, may be highly toxic, carcinogenic, mutagenic or teratogenic (David et al., 1997). Refractory organics that tend to resist conventional waste-water treatment include surfactants, phenols and agricultural pesticides. Common water pollutants are listed in the following sub sections

2.3 Heavy metals
The criteria used to define a heavy metal include density, atomic weight and atomic number as the toxicity of a metal is connected to its atomic weight (Duffus, 2002). Heavy metals are chemical elements with a specific gravity that is at least 5 times the specific gravity of water and have atomic weight greater than that of sodium (23) (Hawkes, 1997). Among the major heavy metals in waste water include cadmium, lead, arsenic, iron and mercury, their toxicity can result in damaged or reduced mental and central nervous function, lower energy levels, and damage to blood composition, lungs, kidneys, liver, and other vital organs. Long-term
exposure may result in slowly progressing physical, muscular, and neurological degenerative processes that mimic Alzheimer's disease, Parkinson's disease, muscular dystrophy, and multiple sclerosis. Allergies are not uncommon and repeated long-term contact with some metals or their compounds may even cause cancer (Ward, 1996). Some of the heavy metals include lead and cadmium.

2.3.1 Lead and its effects

Lead is one of the toxic heavy metals in our environment. It occurs naturally in the earth crust inform of lead sulphide (galena), lead anglesite (lead sulfite) or cerussite (lead carbonate). Inorganic form of lead is found in old paints, soil, dust and various consumer products. Organic form of lead occurs in leaded gasoline in form of tetra – ethyl lead (Landrigan, 2007)

There are many different health effects associated with elevated blood lead levels. Young children under the age of six are especially vulnerable to lead's harmful health effects, because their brains and central nervous system are still being formed. For them, even very low levels of exposure can result in reduced IQ, learning disabilities, attention deficit disorders, behavioural problems, stunted growth, impaired hearing, and kidney damage (WHO, 2009). At high levels of exposure, a child may become mentally retarded, fall into a coma, and even die from lead poisoning. In adults, lead can increase blood pressure and cause fertility problems, nerve disorders, muscle and joint pain, irritability, and memory or concentration problems (Igwe and Abia, 2007).
It takes a significantly greater level of exposure to lead for adults than it does for kids to sustain adverse health effects. Most adults who are lead poisoned get exposed to lead at work. Occupations related to house painting, welding, renovation and remodeling activities, smelters, firing ranges, the manufacture and disposal of car batteries, and the maintenance and repair of bridges and water towers, are particularly at risk for lead exposure (Schwartz, 1990). Workers in these occupations must also take care not to leave their work site with potentially contaminated clothing, tools, and facial hair, or with unwashed hands. Otherwise, they can spread the lead to their family vehicles and ultimately to other family members (Schwartz, 1990).

When an expectant mother has an elevated blood lead level, that lead can easily be transferred to the foetus, as lead crosses the placenta. In fact, pregnancy itself can cause lead to be released from the bone, where lead is stored—often for decades—after it first enters the blood stream (Erdem, 2004). Once the lead is released from the mother's bones, it re-enters the blood stream and can end up in the foetus. In other words, if a woman had been exposed to enough lead as a child for some of the lead to have been stored in her bones, the mere fact of pregnancy can trigger the release of that lead and can cause the foetus to be exposed. In such cases, the baby is born with an elevated blood lead level (Erdem, 2004).

Exposure to lead is estimated by measuring levels of lead in the blood (in micrograms of lead per deciliter of blood). The US Centers for Disease Control and Prevention (CDC) has set a "level of concern" for children at 10 micrograms per deciliter. At this level, it is generally accepted that adverse health effects can begin
to set in. However, recent research published in the New England Journal of Medicine provides new evidence that there could well be very harmful effects occurring at even lower levels of exposure, even as low as 5 micrograms of lead per decilitre of blood. In other words, science is now telling us that there is in fact no level of lead exposure that can be considered safe (WHO, 2009).

2.3.2 Cadmium and its effects

Cadmium is not essential to plants, animals and humans. Its presence in living organisms is unwanted and harmful. An increased level of cadmium in the air, water and soil increases its uptake by living organisms. It is taken up by plants and animals and through them also by humans. This leads to the cadmium cycle soil - plant - animal - man (Clemens, 2006). Cadmium can be released to the environment in a number of ways, including: natural activities, such as volcanic activity (both on land and in the deep sea), weathering and erosion, and river transport; human activities, such as tobacco smoking, mining, smelting and refining of non-ferrous metals (WHO, 2000), fossil fuel combustion, incineration of municipal waste (especially cadmium-containing batteries and plastics), manufacture of phosphate fertilizers, and recycling of cadmium-plated steel scrap and electric and electronic waste (UNEP, 2008).

The kidney is the critical target organ. Cadmium accumulates primarily in the kidneys, and its biological half-life in humans is 10–35 years (WHO, 2008). This accumulation may lead to renal tubular dysfunction, which results in increased excretion of low molecular weight proteins in the urine. This is generally
irreversible. High inhalation exposure to cadmium oxide fume results in acute pneumonitis with pulmonary oedema, which may be lethal. Long-term, high-level occupational exposure is associated with lung changes, primarily characterized by chronic obstructive airway disease (Bay and Bartkiewicz, 2009).

There is sufficient evidence that long-term occupational exposure to cadmium (e.g. through cadmium fume) contributes to the development of lung cancer. There is limited evidence that cadmium may also cause cancers of the kidney and prostate (Saravanne et al., 2002). The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as carcinogenic to humans (Group 1), meaning that there is sufficient evidence for their carcinogenicity in humans (WHO, 2008).

2.4 Water treatment methods

2.4.1 Ion exchange

Ion exchange is a water treatment method where one or more undesirable contaminants are removed from water by exchange with another substance. Both the contaminant and the exchanged substance must be dissolved and have the same type of electrical charge (Alguacil, 2003). When contaminants dissolve in water they form ions. Ions are electrically charged portions of a compound. There is a balance of positively and negatively charged ions in natural waters (Mollah et al., 2001).
Ion exchange method of water treatment has been efficiently used to removal cadmium from waste water (Bay et al., 2009). The disadvantage of this method is that it cannot handle concentrated metal solution as the matrix gets easily fouled by organics and other solids in the wastewater. Moreover ion exchange is nonselective and is highly sensitive to the pH of the solution (Babel et al., 2006).

2.4.2 Electrodialysis

Electrodialysis is an electrochemical process in which ions migrate through ion selective semi permeable membranes as a result of their attraction to two electrically charged electrodes able to remove most charged dissolved ions (Strathmann, 2001). The process uses direct current power to remove salts and other ionized species through cation and anion ion selective membranes. Electrodialysis is very useful for water treatment: removal of mineral salts, sulfate and nitrate from water and sea water (Amado et al., 2008). The disadvantage of electro-dialysis is the formation of metal hydroxides, which clog the membrane (Elmidaoui et al., 2001).

2.4.3 Flotation

Flotation is a process that involves producing small air bubbles in the water being treated (Emamjomeh and Sivakumar, 2009). The bubbles then attach to particles produced by coagulation and flocculation. The resulting particles float to the surface of the water where they accumulate as a floating layer of sludge, known as float, before being removed. Flotation in wastewater and domestic sewage treatment offers process advantages over filtration, precipitation, adsorption onto natural and
synthetic adsorbents. Advantages include better treated water quality, rapid start up, high rate operation, and a thicker sludge (Babel et al., 2003).

2.4.4 Adsorbents

An adsorbent is a substance usually porous in nature with a high surface area that can adsorb substances onto its surface by intermolecular forces (Chaudhari et al., 2003). Adsorbent materials have an affinity to certain ions or ion groups and have shown high selectivity, resistance to degradation, high temperatures and high levels of radiation (Abdel et al., 2007). During adsorption, solutes distribute themselves between the adsorbent surface and the dispersing medium. Due to the presence of functional groups, sorbents can be derivertised to improve their efficiency and increase their adsorption capacity (Hong et al., 2002).

Adsorption techniques has become one of the most commonly used water treatment methods for removal of trace metals from wastewater and water supplies (Abasi et al., 2011). Adsorption reactions can be described by various models which include empirical models that provide descriptions of adsorption data without theoretical basis for example distribution coefficient, the Freundlich adsorption isotherm and Langmuir adsorption model (Goldberg et al., 1993). Chemical models provide a molecular description of adsorption using an equilibrium approach. Surface complexation models are chemical models designed to calculate values of thymodynamic properties mathematically (Pagnanelli et al., 2004). Most of agriculture wastes or by-products, are considered to be low value products. Different types of biomass have been investigated for their capacity to remove
heavy metals from aqueous solutions with a considerable degree of success. Some of them are given in table 2.1

**Table 2.1: Some of the biomasses that have been investigated for their ability to remove heavy metals from aqueous solutions.**

<table>
<thead>
<tr>
<th>Biomass</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Cassia grandis</em></td>
<td>Singh <em>et al</em>., 2007</td>
</tr>
<tr>
<td>Coffee husks</td>
<td>Oliveira <em>et al</em>., 2007</td>
</tr>
<tr>
<td>Orange peels</td>
<td>Benhima <em>et al</em>., 2008</td>
</tr>
<tr>
<td><em>Oscillatoria species</em></td>
<td>Katircioğlu <em>et al</em>., 2008</td>
</tr>
<tr>
<td>Sugar beet pulp</td>
<td>Pehlivan <em>et al</em>., 2008</td>
</tr>
<tr>
<td>Eucalyptus bark</td>
<td>Ghodbane <em>et al</em>., 2008</td>
</tr>
<tr>
<td><em>Bacillus Jeotgali</em></td>
<td>Ruiz <em>et al</em>., 2008</td>
</tr>
<tr>
<td><em>Lathyrus Sativa</em></td>
<td>Panda <em>et al</em>., 2008</td>
</tr>
</tbody>
</table>

**2.5 Maize cob**

Maize or corn is a common name for cereal grass grown for food or livestock folder (Muthusamy *et al*., 2012). Maize is one of the world’s chief grains. In Kenya it is grown in almost all parts of the country. After the maize grain has been harvested, the maize stalks are used to feed animals, maize cobs which are produced in large numbers in the country find very minimal use in our homesteads, low percentage of
the maize cobs are used as fuels the rest are found in large piles in our homesteads. Accumulation of these maize cobs leads to environmental pollution.

One common use of corn cobs is to make furfural, a 5-carbon ring (Tin Win, 2005). Furfural can be used directly in the manufacturing of resins for automotive brakes or fiberglass. It is an important solvent in the refining of lubricating oils. Resins are produced by reacting furfural with various phenolics. Furfural may also be used to generate furans and other important organic compounds.

Another more general use of corn cobs is for industrial cleaning purposes. Corn cobs are ground and used for sandblasting, polishing, paint removal, and grease removal (Grit O’Cobs, 2011). A company that specializes in industrial uses of corn cobs provides several different sizes of corn cob particles. Cob blast can be used to remove paint from metal, fiberglass, and wood surfaces and to clean log homes, electrical insulators, transformer substations, barns, boat hauls, wooden decks, and to remove smoke damage.

Grease and grime can be removed from equipment and tools of all sizes: motors, generators, construction equipment, oil rigs, mining equipment, gear housings and mechanical parts. Also, cobs can be used in factories for cleaning dampers and ventilation grates (Tin Win, 2005). In addition, cob particles can be used for polishing and de-burring items including: cartridges and casings, automotive parts,
plastic parts, nails, staples, nuts and bolts, and button rivets. Dry corn cobs have a high absorption capacity, higher than clay, and as such are used for spill clean ups (Grit O’Cob, 2011).

2.6 Water colour

Colour of water is commonly caused by the extraction of colouring material from humus of forests or the deposit of vegetable matter in swamps and low-lying areas. This colouring matter is composed of humus and tannic acid compounds which cause the yellowish-brown tea colour of surface waters (Sach, 2001). The colour is of two types, true colour which is present in water after suspended matter has been removed and apparent colour which is true colour plus any other colour produced by substances in suspension. Removal of colour is a function of water treatment which leads to increased plant efficiency (Sach, 2001). Coloured water can limit the penetration of light. Thus highly coloured body water cannot sustain aquatic life which can lead to long term impairment of ecosystem.

2.7 Water turbidity

Turbidity is a measure of water clarity and how much the material suspended in water decreases the passage of light through the water (Alpha, 1992). Suspended materials include soil particles (clay, silt and sand), algae, plankton, microbes, and other substances. Turbidity can affect the colour of the water (Alpha, 1992). Higher turbidity increases water temperatures because suspended particles absorb more heat. This, in turn, reduces the concentration of dissolved oxygen (DO) because warm water holds less DO than cold (Mitchell and Stapp, 2003).
Higher turbidity also reduces the amount of light penetrating the water, which reduces photosynthesis and the production of DO. Suspended materials can clog fish gills, reducing resistance to disease in fish, lowering growth rates, and affecting egg and larval development. Sources of turbidity include soil erosion, waste discharge, urban run offs and eroding stream banks (TVA, 1995).

2.8 Sorption studies

Adsorption is a separation process in which certain components of the fluid phase are transferred to the surface of the solid adsorbents (Satya et al., 2012). When a solid surface is exposed to a fluid phase, the molecules from the bulk of the fluid phase have tendency to accumulate or concentrate at the surface of a solid (Satya et al., 2012). The phenomenon of the enrichment of chemical substances at the surface of a solid is called ‘adsorption’. All adsorption performance processes are depends on solid-liquid equilibria and on mass transfer rates (Hui et al., 2009). If the mass transfer is in opposite direction then it is called as ‘Desorption’.

Most adsorbents are highly porous materials, and adsorption takes place primarily on the walls of the pores or at the specific sites inside the particle (Cederberg et al., 1985). Separation occurs because differences in molecular weight, shape, or polarity cause some molecules to be held more strongly on the surface than others or because the pores are too small to admit the larger molecules (Cederberg et al., 1985) Adsorption reactions can be described by various models. Empirical models provide descriptions of adsorption data without theoretical basis. Examples are the
distribution coefficient, the Freundlich adsorption isotherm and the Langmuir adsorption isotherm.

2.8.1 Factors affecting adsorption

Adsorption of heavy metals from aqueous solutions depends on several factors. Factors which were investigated in this study were; shaking speed, initial metal ion concentration, adsorbent dose and temperature. These factors are briefly discussed in the following subsections

2.8.1.1 Effect of shaking speed

Adsorption of metal ion is affected by the shaking (agitation) speed, the higher the shaking speed the higher the rate of adsorption. This can be explained by the fact that as the agitation speed is increased, it increases the resistance of mass transfer between the solution and the adsorbent. The percentage removal efficiency of metal ions also increases with increase in shaking speed though at different rate for different metal ions which can be explained by different molecular sizes of metal ions (Singh et al., 1985).

2.8.1.2 Effect of adsorbent dose

Adsorption of metal ions from aqueous solution is also affected by the adsorbent dose in that as the adsorbent dose is increased the rate of adsorption also increases. Increasing the adsorption dosage increases the surface area which makes it possible for more metal ions to be adsorbed.
2.8.1.3 Effect of initial metal ion concentration

Another factor which affects adsorption is initial metal ion concentration, at low concentration of metal ions there is high percentage removal of metal ions by the adsorbent, which can be explained by the fact that, as the concentration increases there is saturation of the adsorbent sites leading to low metal ion uptake (Genson et al., 2012). Therefore increase in concentration leads to decrease in percentage removal of the metal ion from the aqueous solution.

2.8.1.4 Effect of temperature

Temperature is also another factor which affects the adsorption of metal ions. The percentage removal efficiency decreases with increase in temperature. At low temperatures the adsorption capacity is very high which may imply that adsorption of metal ions is a exothermic reaction (Viraraghavan and Kapoor, 1995). In any chemical reaction, increasing the temperature enables equilibrium to be attained within a short time.

2.8.1.5 Effect of contact time

The effect of contact time on the removal of metals to reach equilibrium varies depending on the type of metals. As the time increases, more amounts of metal gets adsorbs onto the surface of the adsorbent and surface area available decreases. The adsorbate, normally, forms a thin one molecule thick layer over the surface. When this monomolecular layer covers the surface, the capacity of the adsorbent is exhausted (Satya et al., 2012).
2.9 Adsorption equilibrium

Adsorption isotherms are probably the best methods to determine the amount of adsorbate that an adsorbent can retain and that remaining in the solution after equilibrium; they also provide information on the capacity of the adsorbent (Goldberg and Sposito, 1989). Adsorption isotherms also help provide basis for the design of adsorption systems and they are characterized by certain constant values which express the surface properties and affinity of the adsorbent for different pollutants (Sposito and Caves, 1988). They can also be used to compare the adsorptive capacities of the adsorbent for different pollutants (Jennings et al., 1982).

2.9.1 Langmuir isotherm

The Langmuir isotherm relates the adsorption of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature (Goldberg and Sposito, 1989). The Langmuir equation is valid for monolayer sorption onto a surface with a finite number of identical sites and is given by the following equation

\[
q_e = \frac{bQ_mC_e}{1 + bC_e}
\]

Equation (1)

where \(b\) and \(Q_m\) are Langmuir parameters related to maximum adsorption capacity and free energy of adsorption, respectively. In the equation \(C_e\) is the equilibrium concentration in the aqueous solution and \(q_e\) is the equilibrium adsorption capacity of adsorbent. A linear form of Equation (1) above will give

\[
\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m}
\]

Equation (2)
And a plot of \( \frac{1}{q_e} \) vs \( \frac{1}{C_e} \) should give a linear plot which will allow b and qm to be determined (Westall, 1982).

**2.9.2 Freundlich isotherm**

The Freundlich adsorption isotherm is used for heterogeneous surface energy system (Westall, 1979). It is used to estimate the adsorption intensity of the sorbent towards the adsorbate and it is given by

\[
q_e = K_f C_e^{1/n}
\]

Equation (3)

Where, \( K_f \) and \( 1/n \) are Freundlich constants related to adsorption capacity and intensity of adsorption respectively (Westall, 1979). The linear form of the Freundlich equation becomes,

\[
\log q_e = \log K_f + \frac{1}{n} \log C_e
\]

Equation (4)

or

\[
\ln q_e = \ln K_f + \frac{1}{n} \ln C_e
\]

Equation (5)

A plot of \( \ln q_e \) vs. \( \ln C_e \) would give the values of the Freundlich constants \( K_f \) and \( 1/n \)

**2.10 Techniques for metal analysis**

**2.10.1 Atomic absorption spectrometry (AAS)**

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements. Atomic absorption is so sensitive that it can measure
down to parts per billion of a gram (μg dm$^{-3}$) in a sample. The technique makes use of the wavelengths of light specifically absorbed by an element. They correspond to the energies needed to promote electrons from one energy level to another higher energy level.

Atoms of different elements absorb characteristic wavelengths of light. Analysing a sample to see if it contains a particular element means using light from that element. For example with lead, a lamp containing lead emits light from excited lead atoms that produce the right mix of wavelengths to be absorbed by any lead atoms from the sample. In AAS, the sample is atomised, meaning it is converted into ground state free atoms in the vapour state – and a beam of electromagnetic radiation emitted from excited lead atoms is passed through the vaporised sample. Some of the radiation is absorbed by the lead atoms in the sample. The greater the number of atoms there is in the vapour, the more radiation is absorbed.

The amount of light absorbed is proportional to the number of lead atoms. A calibration curve is constructed by running several samples of known lead concentration under the same conditions as the unknown. The amount the standard absorbs is compared with the calibration curve and this enables the calculation of the lead concentration in the unknown sample. Consequently an atomic absorption spectrometer needs the following three components: a light source; a sample cell to produce gaseous atoms; and a means of measuring the specific light absorbed.
2.10.2 Turbidimeter

A turbidity meter consists of a light source that illuminates a water sample and a photoelectric cell that measures the intensity of light scattered at a 90 angle by the particles in the sample. It measures turbidity in nephelometric turbidity units or NTUs. Meters can measure turbidity over a wide range from 0 to 1000 NTUs.
2.10.3 Uv-visible spectrometer

Ultraviolet (UV) and visible radiation comprise only a small part of the electromagnetic spectrum, which includes such other forms of radiation as radio, infrared (IR), cosmic, and X rays. The absorption of radiations involves transfer of energy to medium and this is specific phenomenon related to the characteristic molecular structure. For a given excitation process, molecules absorb discrete amount of energy corresponding to only one frequency which should give rise to absorption line.
CHAPTER THREE

MATERIALS AND METHODS

3.1 Apparatus and reagents

3.1.1 Instrumentation

The analysis of lead (II) and cadmium (II) ions in water samples was done using flame atomic absorption spectrometer (AAS) model: AA-6300 Shimadzu whose detection limit was \( \leq 0.0100 \) mg/L, absorbance \( \geq 0.02300 \) Abs, base line drift \( \leq 0.0060 \) Abs/30 min and wavelength accuracy of \( \leq \pm 0.70 \) nm. The AAS was set at operating conditions at wavelength of 283.3 nm for lead and 228.9 nm for cadmium. Turbidimeter (model 2100P HACH) was used to determine the turbidity of water. Ultra violet spectrometer, (model C=2041), 2000 series at wavelength 601.0 nm was used to determine the colour of water.

3.1.2 Reagents

All the solutions used were prepared from analytical grade chemicals obtained from Unilab chemicals. Stock solution of lead of 1000 mg/L was prepared by dissolving 1.5990 g of lead nitrate in distilled water in 1000 mL volumetric flask and adding water up to the mark. Working solution of 10 mg/L was prepared by placing 10 mL of the stock solution in 1000 mL volumetric flask and adding distilled water up to the mark. Lead (II) ions standards were prepared by placing 10 mL of the stock solution in 100 mL volumetric flask and adding distilled water up to the mark, standards of 2, 4, 6, 8 and 10 mg/L were then prepared by placing 2, 4, 6, 8 and 10 mL of the solution in 100 mL volumetric flask and adding distilled water up to the
mark. Stock solution of cadmium of 1000 mg/L was prepared by dissolving 2.7440 g of cadmium nitrate in distilled water in 1000 mL volumetric flask and adding water up to the mark.

Working solutions of 10 mg/L were prepared by placing 10 mL of the stock solution in 1000 mL volumetric flask and adding distilled water up to the mark. Cadmium (II) ions standards were prepared by placing 10 mL of the stock solution in 100ml volumetric flask and adding distilled water up to the mark, standards of 2, 4, 6, 8 and 10 mg/L were then prepared by placing 2, 4, 6, 8 and 10 mL of the solution in 100 mL volumetric flask and adding distilled water up to the mark. All the experiments were carried out in triplicates and average values used in calculations.

3.1.3 Optimization of contact time
To determine equilibrium time for both lead (II) and cadmium (II) ions batch experiments for both were carried out using the three adsorbents, maize cob charcoal, activated charcoal and ash. 0.2g of each adsorbent was mixed with 50 mL solution of both lead and cadmium ions at initial concentration of 10 mg/L. The mixture was then shaken constantly at time intervals of 30 minutes for 150 minutes. In order to get maximum adsorption a mixture of 0.2 g of the adsorbent and 100 mL of both lead and cadmium was shaken at constant speed for 1440 minutes. After completion of each batch experiment the mixture was centrifuged at a speed of 3800rpm for 20 minutes and then decanted. Absorbance’s of lead (II) and cadmium (II) ions in the remaining solutions was determined using FAAS.
3.1.4 Optimization of initial metal ion concentration

The initial metal ion concentration for both lead (II) and cadmium (II) ions was varied from 5 to 200 mg/L i.e. 5, 10, 15, 20, 30, 50, 100, 150 and 200 mg/L. 0.2g of the adsorbent was added to 50 mL of the solution at different concentrations as stated above, the mixture was then shaken at a constant speed for two hours after which it was centrifuged for 20 minutes at 3800rpm and filtered. The filtrate was analysed for the remaining metal ion concentration using AAS.

3.1.5 Optimization of temperature

0.2g of the adsorbents were added to 10 mg/L of 50 mL of both lead (II) and cadmium (II) ions solution, the mixture was then shaken at a constant speed for two hours at different temperatures of 25, 50, 75 and 100°C after which it was centrifuged for 20 minutes at 3800rpm and then filtered. The filtrate was analysed for the remaining metal ions concentrations using FAAS.

3.1.6 Optimization of adsorbent dose

Effect of adsorbent dose on adsorption of metal ions was achieved by varying the adsorbent dose from 0.1 to 0.5 g for all the adsorbents. 10 mg/L of 50 mL solution was used for both metal ions. The mixture was shaken at a constant shaking speed for two hours after which it was centrifuged and filtered, the filtrate was analysed for the remaining metal ions concentrations using AAS.

3.1.7 Optimization of shaking speed

An adsorbent dose of 0.2 g was placed in conical flask containing 50 mL of 10 mg/L of lead (II) and cadmium (II) ions, the mixture was then shaken at different
shaking speeds starting from 0 rpm (without shaking) to 360rpm. The mixture was then centrifuged and filtered. The filtrate was analysed for the remaining metal ion concentrations using AAS.

3.1.8 Optimization of pH
The effects of pH on percentage of lead and cadmium ions adsorbed were done at pH 7. Adsorption of lead (II) and cadmium (II) ions is best at pH value between 6 and 9 (Mbugua et al., 2014). To adjust the pH of the solution a calibrated pH meter (Calibrated using buffer 4, 7 and 9) was used and concentrated solution of nitric (V) acid and sodium hydroxide.

3.2 Collection of raw materials and preparation of activated charcoal
Maize cobs samples were collected from a local farmer in Ruiru Sub County in Kiambu County. The maize cobs were transported to the laboratory where they were washed with distilled water and sun dried. The dry maize cobs were heated in furnace in absence of air at a temperature of 400°C for eight hours. The charcoal obtained was cooled in air and crushed to finer particles using motor and pestle. 200g of the charcoal obtained was then activated using 1M sulphuric acid, the charcoal powder and the acid were mixed in the ratio of 1:2 respectively (Based on mass). The mixture was then heated in the furnace at a temperature of 350°C for six hours after which it was cooled in air stored in stoppered beaker ready for use. Ash from maize cobs was made by heating dry maize cobs in furnace at a temperature of 400°C in presence of air. The chemical composition of the ash obtained was determined.
3.3 Removal of colour

To investigate removal of colour by the three adsorbents, methylene blue was used. 1g of methylene blue was dissolved in one litre of distilled water to make 1000 mg/L of solution from which working solutions of 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L and 25 mg/L were prepared by dilution. To 50 mL of the solution 0.2g of the adsorbent was added. The mixture was shaken for two hours at constant shaking speed after which it was centrifuged and filtered. The intensity of methylene blue colour remaining in solution was measured using uv visible spectroscopy (Model C≡2041, 2000 series at wavelength 601.0 nm).

3.4 Removal of suspended particles

To investigate removal of suspended particles from water, 20g of red soil was added to 1000 mL of distilled water, stirred for about 10 minutes and allowed to settle. The mixture was then filtered and turbidity of the water measured using turbidity meter (model 2100P HACH). Five water samples of 50 mL each were put in different bottles. Different adsorbent dose of 0.1, 0.2, 0.3, 0.4 and 0.5g was added to water samples, they were then shaken at constant speed for two hours. The mixture was filtered and water samples measured using turbidity metre. This was done for all the three adsorbents.
CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Carbonization and ashing

Carbonization and ashing of 420 g of dry maize cobs afforded 200 g of charcoal. Figures 4.1 and 4.2 show plates of maize cob charcoal and activated charcoal obtained from maize cobs respectively. The photos show different surfaces of maize cob charcoal and activated maize cob charcoal. After activation the surface was crystalline.

![Figure 4.1 Plate showing maize cob charcoal](image1)

![Figure 4.2: Plate showing activated maize cob charcoal](image2)

4.2 Elemental Composition of Ash

The percentage composition of major elements in maize cob ash was analysed by use of X-ray fluorescence (XRF). Table 4.1 shows percentage elemental composition of ash.
Table 4.1: Elemental composition of ash

<table>
<thead>
<tr>
<th>Compound</th>
<th>SiO₂</th>
<th>P₂O₅</th>
<th>SO₃</th>
<th>Cl</th>
<th>K₂O</th>
<th>CaO</th>
<th>TiO₂</th>
<th>MnO</th>
<th>Fe₂O₃</th>
<th>ZnO</th>
<th>PbO</th>
</tr>
</thead>
<tbody>
<tr>
<td>% oxide</td>
<td>15.0</td>
<td>2.3</td>
<td>4.8</td>
<td>6.1</td>
<td>67.1</td>
<td>3.1</td>
<td>0.07</td>
<td>0.1</td>
<td>1.0</td>
<td>0.49</td>
<td>0.08</td>
</tr>
</tbody>
</table>

The percentage of lead was 0.08% while cadmium was not present or could not be detected in maize cob ash. Since cadmium ions were not detected and lead levels were very low (lead detected could be due to limitation of the XRF instrument used which loses precision at low concentrations), then the products from maize cobs could be used in water remediation. The ash obtained also contained 15% silica which has been reported as one the components in zeolitic material used as an adsorbent for lead (II) and cadmium (II) ions (Mbugua et al., 2014). Iron (III) oxide and calcium oxide which were present in ash produced are important components of coagulants used to remove turbidity in water.

4.3 Batch adsorption experiments

The effects of various parameters (adsorbent dose, contact time, initial concentration, shaking speed and temperature) on the percentage of Cd²⁺ and Pb²⁺ ions adsorbed were investigated by varying one parameter while keeping all the others constant. Concentration of metal ion remaining in solution was then determined. All the experiments were done at pH 7. As reported earlier in section 3.1.8 adsorption of lead (II) and cadmium (II) is best at a pH value between 6 and 9. At very low pH the ions tend to compete with hydrogen ions and at pH value above 10 there is precipitation taking place due to high concentration of hydroxyl ions.
4.3.1 Effect of initial metal ion concentration

The percentages of Pb\(^{2+}\) ions adsorbed by ash, charcoal and activated charcoal from maize cobs was influenced by the initial concentrations of Pb\(^{2+}\) ions in aqueous solutions. The initial concentrations of Pb\(^{2+}\) were varied from 5 to 200 mg/L while maintaining the adsorbent dosage at 0.2 g. Figure 4.3 and appendix 21 shows the effect of initial concentration on percentage removal of Pb\(^{2+}\) ions. The percentage removal of Pb\(^{2+}\) decreased from 100 % for 5 mg/L to 67 % for 200mg/L at a contact time of 2 hrs and adsorption temperature of 25 °C when 0.2 g of maize cobs charcoal, (MC) was used. Decrease in percentage removal using MC adsorbent suggested that amount of Pb\(^{2+}\) ions surpassed the fixed number of available active sites.

The trend was different for activated charcoal (AMC) and ash since the percentage removal increased with increase in concentration then followed by decrease. At 5 mg/L the percentage removal was 40 percent which increased to 98 % at 25 mg/L. This may be explained by a progressive increase in electrostatic mutual interaction between sites that have lower affinity for metal ions as the population of occupied sites decreases (Al-Asheh et al., 1997). The percentage removal then decreased to 21 % at 200 mg/L. This was caused by saturation of the pores at high concentrations. The percentage removal by ash increased from 12 % at 5 mg/L to 65 % at 20 mg/L then decreased to 30% at 200 mg/L.
Figure 4.3: Effect of initial metal concentration on percentage removal of lead (II) ions (0.2 g, 25°C, 2 hrs, 240 rpm and pH 7)

The effects of percentage removal of Cd$^{2+}$ ions at various initial concentrations are presented in figure 4.4 and appendix 22. Both AMC and Ash adsorbents showed a similar trend of increase in percentage removal as initial concentrations were increased followed by decrease, while MC showed decrease in percentage removal decrease as the initial concentration was increased. The percentage removal efficiencies of ash and activated maize cobs increased from 4 to 91 %, and 23 to 91 % respectively as initial concentration was varied from 5 to 200 mg/L while for maize cob charcoal the percentage removal decreased from 100 to 78%. The percentage removal was 100 % at 5 mg/L for MC after which it started to decrease, suggesting saturation of the finite active sites on adsorbent surface with the metal ions (Mureithi et al., 2012). Similar results were reported by Mbugua et al. (2014).
Figure 4.4: Effect of initial metal ion concentration on percentage removal of cadmium (II) ions (0.2 g, 25°C, 2 hrs, 240 rpm and pH 7)

4.3.2 Effect of contact time

Experiments were conducted by varying contact time from 1 to 1440 minutes while maintaining all other experimental conditions constant (0.2 g of the adsorbent, 10 mg/L of Pb$^{2+}$ and Cd$^{2+}$, temperature of 25°C, shaking speed 240 rpm and pH 7). The data obtained are shown in Figure 4.5 and appendix 23. As shown the three adsorbents gave the similar trend. The percentage removal of Pb$^{2+}$ ions increased as contact time was increased until a plateau was reached at 150 minutes for all adsorbents. One sample in each case was shaken to 1440 minutes in order to get maximum adsorption capacity for the adsorbents. Activated maize cob charcoal gave the highest percentage removal after 150 minutes compared to the other adsorbents. The percentage removal efficiency for AMC at equilibrium time (150 min) was
79.5 % while that of ash was 77.6 % and MC was 74 % at the same shaking speed and constant adsorbent dose of 0.2 g. At equilibrium the rates of adsorption are equal to the rate of desorption. Similar results were obtained by Mureithi et al., 2012 using water hyacinth.

![Graph showing the effect of contact time on the percentage removal of lead (II) ions](image)

**Figure 4.5: Effect of contact time on the percentage removal of lead (II) ions (0.2 g, 25°C, 10 mg/L, 240 rpm and pH 7)**

Variation of contact time on percentage of adsorbed cadmium (II) ions showed a similar trend for the three adsorbents as shown in Figure 4.6 and appendix 24. The percentage removal increased with increase in contact time. Ash gave the highest percentage removal for cadmium ions at the equilibrium time followed by AMC which gave 70% and MC gave 61.5 %. The trend observed for both cadmium and
lead is in agreement with findings of Ho and McKay (1998). The nature of the adsorbent and its available sorption sites affected the time needed to reach equilibrium. This may be explained by the fact that initially a large number of vacant sites were available and as the adsorption process continued, much of the available sites were used up which slowed the process down later due to exhaustion of remaining surface sites and repulsive forces developed between solute molecules and bulk phase.

![Graph](image)

**Fig 4.6:** Effect of contact time on percentage removal of cadmium (II) ions (0.2g, 25°C, 10 mg/L, 240 rpm and pH 7)

### 4.3.3 Effect of dosage on percentage removal of metal ions

Experiments were conducted with the adsorbent dose of 0.1, 0.2, 0.3, 0.4 and 0.5 g per 50 mL of test solution (10 mg/L). When the adsorbent dose increased, the percentage removal of metal ions also increased as shown in Figure 4.7 and appendix 25. The percentage of adsorption of lead ions increased due to increase in
number of binding sites as the adsorbent dose increased as reported by Mbugua et al. (2014). Ash recorded the highest percentage removal of 62 % at a dose of 0.4 g followed by AMC which gave 52 % at a dose of 0.4 g while MC gave its highest percentage of 46.5 % at a dose of 0.4 g.

![Figure 4.7: Effect of adsorbent dose on percentage removal of lead (II) ions (25°C, 10 mg/L, 2Hrs, 240 rpm and pH 7)](image)

Figure 4.7: Effect of adsorbent dose on percentage removal of lead (II) ions (25°C, 10 mg/L, 2Hrs, 240 rpm and pH 7)

Figure 4.8 and appendix 26 show variations in the percentage removal of cadmium (II) ions as the adsorbent doses were increased. The highest percentage removal by maize cob charcoal (MC) was 91 % at a dose of 0.3 g followed by ash which gave 90.6 % at a dose of 0.5 g while activated maize cob charcoal (AMC) gave 90 % at 0.4 g. MC plateaued at 0.3 g and AMC at 0.4 g. Increase in percentage removal is due to increase in adsorbent surface area as well as the active sites available as the adsorbent dose is increased. Between 0.4 g and 0.5 g percentage removal was minimal this could have been so due to saturation of adsorption sites as reported by Mureithi et al. (2012) using water hyacinth as the adsorbent.
4.3.4 Effect of shaking speed

Effect of shaking speed on percentage removal of lead (II) ion was investigated for three adsorbents only AMC and MC were affected by shaking speed using 50mL of solution whose metal ion concentration was 10 mg/L. The results in figure 4.9 and appendix 27 show that as the shaking speed is increased the percentage removal of the metal ion also increased. The maximum percentage removal for AMC was 59% at 120rpm and 81% for MC at 360rpm. Ghodbane et al. (2008) suggested that when increasing the agitation speed, the diffusion rate of metal ions from the bulk liquid to the liquid boundary layer surrounding sorbent particles become higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer. Good diffusion of ions towards the sorbent particles is also ensured.
For cadmium (II) ions, percentage removal increased with increase in shaking speed, for AMC the percentage removal increased from 51 to 82 % at 240rpm and for MC the percentage removal increased from 66 to 79 % at 240rpm. For both adsorbents the maximum percentage removal was attained at a shaking speed of 240 revolutions per minute as shown in figure 4.10 and appendix 28. This is due to increased diffusion rate of metal ions from the bulk liquid to the liquid boundary layer surrounding sorbent particles as the agitation speed is increased. Low et al. (1997) suggested that increasing the agitation rate increases the external film mass transfer coefficient hence the rate of uptake due to reduction of the film boundary layer surrounding the sorbent particles. Similar results were reported by Genson et al. (2012) who investigated kinetic and equilibrium study for sorption of lead (II) ions from aqueous phase using water hyacinth.
Figure 4.10: Effect of shaking speed on percentage removal of cadmium (II) ions (0.2 g, 25°C, 10 mg/L, 2 hrs and pH7)

4.3.5 Effect of temperature

The effect of temperature on the percentage removal of lead (II) ions is shown in figure 4.11 and appendix 29. From the figure it is clear that the percentage removal efficiency decreased with increase in temperature for both activated maize cob charcoal and ash. The maximum percentage removal occurred at low temperatures. Ash recorded the highest percentage removal for lead (II) ions of 80 % at 25°C which decreased to 74 % at 100°C followed by activated maize cob charcoal which showed a decrease from 53 % at 25°C to 50 % at 100°C while for maize cob charcoal the percentage removal was almost constant at all temperatures. Increasing the temperature increases the kinetic energy of metal ions which
overcomes the binding energy making the particles not to bind on the surface of the adsorbent (Mbugua et al., 2014)

![Figure 4.11: Effect of temperature on percentage removal of lead (II) ions (0.2 g, 10 mg/L, 2 hrs 240 rpm and pH 7)](image)

For cadmium (II) ions, the percentage removal decreased with increase in temperature with the highest percentage removal of 73 %, 51 % and 90 % for AMC, MC and ash respectively been recorded at 25°C. Just as for lead (II) ions ash recorded the highest percentage removal of 90 % at 25°C which decreased to 88 % at 100°C, the percentage removal for AMC increased from 73 % at 25°C to 78 % at 50°C then decreased to 50 % at 100°C suggesting that maximum adsorption occurred at 50°C and the binding energy at that 50°C was overcome by kinetic energy leading to decrease in percentage removal. For MC the percentage removal remained almost constant for all temperatures as shown in figure 4.12 and appendix 30 this could have been caused by saturation of adsorption sites at 25°C. Adsorption of metal ions is an exothermic reaction hence it is favoured at low temperatures.
Similar results were reported by Benhima et al. (2008) using orange peels as adsorbent.

![Figure 4.12: Effect of temperature on percentage removal of cadmium (II) ion (0.2 g, 10 mg/L, 2 hrs, 240 rpm and pH 7)](image)

### 4.4 Removal of methylene blue

Figure 4.13 and appendix 31 shows the effect of varying initial concentration on percentage removal of methylene blue from water. The percentage removal increased as initial concentration of the solution was increased. For activated charcoal, percentage removal increased as the initial concentration was increased then followed by a slight decrease. Increased concentration led to increased binding sites hence high percentage removal. Among the three adsorbents, MC gave the highest percentage removal of methylene blue of 86% from water at 25 mg/L. Similar results were previously reported by Alzaydien (2009) who investigated adsorption of methylene blue from aqueous onto a low cost natural Joranian Tripoli.
Figure 4.13: Effect of concentration on percentage removal of methylene blue (0.2 g, 25°C, 2 hrs, 240 rpm and pH 7)

4.5 Removal of suspended particles

Figure 4.14 and appendix 32 shows the effect of adsorbent dose on removal of turbidity from water using ash. The graph shows that the percentage removal of turbidity from water increases with increase in adsorbent dose because as the adsorbent dose is increased more surfaces are available for adsorption. After a dosage of 0.2g the percentage removal was almost constant. The highest percentage removal was 60 % at dosage of 0.5g. AMC and MC were found to increase turbidity rather than reducing it.
Figure 4.14: Effect of adsorbent dose on turbidity removal using ash from maize cobs (25°C, 10 mg/L, 2 hrs, 240 rpm and pH 7)

The graphs given in figure 4.15 and 4.16 are examples of adsorption isotherm adsorption of cadmium (II) ions using maize cob charcoal (MC). For Langmuir isotherm, plot of Ce/qe against Ce gave nonlinear relationship with $R^2 = 0.8335$. For Freundlich isotherm, plot of log qe against log Ce gave linear relationship with $R^2 = 0.9972$ explaining why the data fitted in Freundlich isotherm and not Langmuir.

Figure 4.15 Langmuir isotherm for Cd$^{2+}$ using MC
4.6 Adsorption isotherms

The data obtained for adsorption of both lead (II) and cadmium (II) ions were fitted into linearized equations of Langmuir and Freundlich models. The thermodynamic constants obtained for maize cob charcoal, activated maize cob charcoal and ash are summarized in table 4.2-4.4 and appendix 2.

The results obtained for lead using the three adsorbents were fitted in both Langmuir and Freundlich isotherm and the constants obtained are summarised in table 4.2. As shown in the table 4.2, AMC and MC best fitted into the Langmuir model based on $R^2$ values of 0.934 and 0.925 respectively compared with Freundlich values of 0.540 and 0.052. Similar studies by Nale et al. (2012) on kinetic and equilibrium studies of the adsorption of lead (II) and nickel (II) ions from aqueous solutions on activated carbon prepared from maize cobs indicated that lead adsorption best fitted in to the langmuir model.
The adsorption capacities, $q_{\text{max}}$, of AMC and MC for lead were found to be 13.0 and 2.91 mg/g respectively. The adsorption coefficient, $b$, which is related to the apparent energy of adsorption for Pb$^{2+}$ on MC (2.804 L/mg) was greater than on AMC (0.173L/mg). This shows that the energy of adsorption is more favourable in AMC than MC. Ash gave best fit in Freundlich isotherm with $r^2$ value of 0.953 and adsorption capacity of 2.59 mg/g. This shows that AMC had the highest adsorption capacity as a result of activation increasing the binding sites of the adsorbent.

### Table 4.2: Langmuir and Freundlich constants for removal of lead

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$q_{\text{max}}$</th>
<th>$B$</th>
<th>$r^2$</th>
<th>$K_r$</th>
<th>$1/n$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMC</td>
<td>13.0</td>
<td>0.173</td>
<td>0.934</td>
<td>3.026</td>
<td>0.313</td>
<td>0.540</td>
</tr>
<tr>
<td>MC</td>
<td>2.91</td>
<td>2.804</td>
<td>0.925</td>
<td>6.89</td>
<td>0.302</td>
<td>0.052</td>
</tr>
<tr>
<td>ASH</td>
<td>256.4</td>
<td>8.49</td>
<td>0.001</td>
<td>2.59</td>
<td>0.902</td>
<td>0.953</td>
</tr>
</tbody>
</table>

Table 4.3 shows thermodynamic adsorption constants for Langmuir and Freundlich isotherms towards cadmium (II) ions in solution. All the three adsorbents gave best fit in Freundlich isotherms with $r^2$ values of 0.988, 0.997 and 0.997 for AMC, MC and Ash respectively as shown in appendices 4, 6 and 8. MC gave the highest adsorption capacity towards Cd$^{2+}$ of 24.3 mg/L compared to 16.06 mg/L for Ash and 15.61mg/L for AMC. $1/n$ is a function of the strength of adsorption in the adsorption process (Voudria et al., 2002). 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 (Mohan and Karthikeyan, 1997) the smaller $1/n$, the greater the expected heterogeneity.

**Table 4.3: Langmuir and Freundlich constants for removal of cadmium**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$Q_{\text{max}}$</th>
<th>B</th>
<th>$r^2$</th>
<th>$K_r$</th>
<th>$1/n$</th>
<th>$r^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMC</td>
<td>1.10</td>
<td>0.056</td>
<td>0.671</td>
<td>15.61</td>
<td>1.338</td>
<td>0.988</td>
</tr>
<tr>
<td>MC</td>
<td>2.14</td>
<td>0.038</td>
<td>0.834</td>
<td>24.3</td>
<td>1.183</td>
<td>0.997</td>
</tr>
<tr>
<td>ASH</td>
<td>0.807</td>
<td>0.053</td>
<td>0.247</td>
<td>16.06</td>
<td>1.159</td>
<td>0.997</td>
</tr>
</tbody>
</table>

Table 4.4 shows adsorption isotherm constants for removal of methylene blue using the three adsorbents. From the table, AMC gave best fit in Langmuir model with $r^2=0.977$ compared to Freundlich which gave $r^2=0.765$. 
Table 4.4: Langmuir and Freundlich constants for removal of methylene blue

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Q_{\text{max}}</th>
<th>b</th>
<th>r^2</th>
<th>K_r</th>
<th>1/n</th>
<th>r^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>AMC</td>
<td>12.18</td>
<td>0.102</td>
<td>0.977</td>
<td>1.520</td>
<td>1.248</td>
<td>0.765</td>
</tr>
<tr>
<td>MC</td>
<td>0.805</td>
<td>0.292</td>
<td>0.476</td>
<td>75.73</td>
<td>5.715</td>
<td>0.965</td>
</tr>
<tr>
<td>ASH</td>
<td>0.301</td>
<td>0.257</td>
<td>0.992</td>
<td>378.2</td>
<td>5.680</td>
<td>0.848</td>
</tr>
</tbody>
</table>

The maximum adsorption capacity was 12.18mg/g. The data for adsorption of MC best fitted in Freundlich isotherm with $r^2=0.965$ compared with Langmuir isotherm which gave $r^2=0.476$. The $1/n$ value of 5.72 is indicative of cooperative adsorption. These cooperative effects usually involve fluid-fluid interactions, fluid-solid interactions with suitably located site or sites which are bridged with clusters of water molecules resulting to enhanced adsorption. This point to a likelihood of intermolecular interactions of methylene blue molecules resulting to a second adsorption layer (Zhang et al., 2002). The adsorption capacity of methylene on MC was 75.73mg/g. Ash gave best fit in Langmuir isotherm with $r^2=0.992$ compared with Freundlich which had $r^2=0.848$. The values of $r^2$ were obtained from appendices 15to 20 for both Langmuir and freundlich isotherms.
CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSION
Findings herein show that MC, AMC and ash obtained from maize cobs are effective in removing lead ions, cadmium ions and methylene blue from contaminated water. The efficiency of the three adsorbents to remove $\text{Cd}^{2+}$ and $\text{Pb}^{2+}$ and methylene blue from water is affected by initial metal ion concentration, temperature, contact time, adsorbent dose and shaking speed. AMC and MC were found to increase water turbidity while on the other hand ash was able to reduce water turbidity.

The sorption studies for cadmium ions using AMC, MC and Ash showed that the isotherms fitted in Freundlich model with adsorption capacities of 15.61, 24.3 and 16.06 mg/g respectively. Based on adsorption capacities MC was found to be the best adsorbent for cadmium ions.

The sorption studies for lead ions using AMC and MC gave best fit in Langmuir model with adsorption capacities of 13.0 mg/g and 2.91 mg/g respectively. Ash fitted in Freundlich model with adsorption capacity of 2.59 mg/g. AMC was found to be the best adsorbent for lead ions based on adsorption capacities which is 13.0 mg/g.

For removal of methylene blue from water, MC was found to be the best adsorbent with adsorption capacity of 75.73 mg/g as compared to 12.18 mg/g for AMC and 0.301 mg/g for ASH.
5.2 Recommendations

For further studies the following are recommended.

1. Sulphuric acid was used as an activating agent and other activating agents be used and their effects on adsorption of metal ions be investigated.

2. The optimized temperature for production of the adsorbents was not established thus optimization is recommended.

3. Studies on adsorption of other heavy metals using products derived from maize cobs should be carried out.
REFERENCES


APPENDICES

Appendix 1: Calibration curve for Pb$^{2+}$ ions

Appendix 2: Calibration curve for Cd$^{2+}$ ions
Appendix 3: Ash Langmuir isotherm model for Cd\(^{2+}\) ions

\[
y = -1.2388x + 23.222 \\
R^2 = 0.2465
\]

Appendix 4: Ash Freundlich isotherm model for Cd\(^{2+}\) ions

\[
y = -1.1593x + 1.2057 \\
R^2 = 0.9973
\]
Appendix 5: AMC Langmuir isotherm model for Cd$^{2+}$ ions

Appendix 6: AMC freundlich isotherm model for Cd$^{2+}$ ions

Appendix 7: MC Langmuir isotherm model for Cd$^{2+}$ ions
Appendix 8: MC Freundlich isotherm model for Cd\(^{2+}\) ions

\[ y = -1.338x + 1.3853 \]
\[ R^2 = 0.9972 \]

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{freundlich_cdm_mc.png}
\caption{Freundlich Cd MC}
\end{figure}

Appendix 9: AMC Langmuir isotherm model for Pb\(^{2+}\) ions

\[ y = 0.0769x + 0.444 \]
\[ R^2 = 0.9335 \]

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{langmuir_pbm_amc.png}
\caption{Langmuir Pb AMC}
\end{figure}

\[ y = 0.3127x + 0.481 \]
\[ R^2 = 0.54 \]

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{freundlich_pbm_amc.png}
\caption{Freundlich Pb AMC}
\end{figure}
Appendix 10: AMC Freundilich isotherm model for Pb $^{2+}$ ions

\[ y = 0.3436x + 0.1225 \]
\[ R^2 = 0.9247 \]

Appendix 11: MC Langmuir isotherm model for Pb $^{2+}$ ions

\[ y = -0.3024x + 0.8385 \]
\[ R^2 = 0.0522 \]

Appendix 12: MC Freundlich isotherm model for Pb$^{2+}$ ions
Appendix 13: Ash Langmuir isotherm model for Pb$^{2+}$ ions

\[ y = -0.0039x + 4.5919 \]
\[ R^2 = 0.001 \]

\begin{align*}
\text{Ce}/q_e & = 0.9022x - 0.4136 \\
R^2 & = 0.9526
\end{align*}
Appendix 15: Langmuir adsorption isotherm for colour removal using MC

Appendix 16: Langmuir adsorption model for colour removal using AMC
Appendix 17: Langmuir adsorption isotherm for colour removal using ash

\[ y = 3.322x + 12.927 \]
\[ R^2 \text{ Linear} = 0.992 \]

Appendix 18: Freundlich adsorption model for colour removal using MC

\[ y = 5.715x + 1.879 \]
\[ R^2 \text{ Linear} = 0.765 \]
Appendix 19: Freundlich adsorption isotherm for removal of colour using AMC

\[ y = 1.248x + 0.1818 \]
\[ R^2 \text{ Linear} = 0.856 \]

Appendix 20: Freundlich adsorption isotherm for removal of colour using ash

\[ y = 5.680x + 2.577 \]
\[ R^2 \text{ Linear} = 0.848 \]
<table>
<thead>
<tr>
<th>Concentration(mg/L)</th>
<th>ASH Mean % removal± SE</th>
<th>AMC Mean % removal± SE</th>
<th>MC Mean % removal± SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>12.00±0.12</td>
<td>39.47±0.74</td>
<td>100.00±0.00</td>
</tr>
<tr>
<td>10</td>
<td>53.20±0.20</td>
<td>70.00±0.58</td>
<td>96.47±0.03</td>
</tr>
<tr>
<td>15</td>
<td>54.80±0.73</td>
<td>92.60±0.73</td>
<td>95.36±0.02</td>
</tr>
<tr>
<td>20</td>
<td>65.00±0.95</td>
<td>96.10±0.55</td>
<td>93.63±0.02</td>
</tr>
<tr>
<td>25</td>
<td>61.33±0.77</td>
<td>98.68±0.00</td>
<td>90.12±0.14</td>
</tr>
<tr>
<td>30</td>
<td>60.00±0.38</td>
<td>96.00±0.02</td>
<td>83.23±0.12</td>
</tr>
<tr>
<td>50</td>
<td>58.71±0.05</td>
<td>94.22±0.22</td>
<td>73.20±0.12</td>
</tr>
<tr>
<td>100</td>
<td>58.00±0.12</td>
<td>54.00±0.01</td>
<td>66.97±0.03</td>
</tr>
<tr>
<td>150</td>
<td>39.04±0.20</td>
<td>33.22±0.06</td>
<td>67.31±0.02</td>
</tr>
<tr>
<td>200</td>
<td>29.98±0.04</td>
<td>21.67±0.26</td>
<td>67.28±0.29</td>
</tr>
</tbody>
</table>

Appendix 21: Effect of initial metal concentration on percentage removal of lead (II) ions (0.2 g, 25°C, 2Hrs, 240 rpm and pH 7)

<table>
<thead>
<tr>
<th>Concentration(mg/L)</th>
<th>ASH Mean % removal± SE</th>
<th>AMC Mean % removal± SE</th>
<th>MC Mean % removal± SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>4.23±0.02</td>
<td>22.96±0.74</td>
<td>100.00±0.00</td>
</tr>
<tr>
<td>10</td>
<td>5.19±1.85</td>
<td>34.07±0.74</td>
<td>100.00±0.00</td>
</tr>
<tr>
<td>15</td>
<td>26.17±0.25</td>
<td>37.09±0.12</td>
<td>100.00±0.00</td>
</tr>
<tr>
<td>20</td>
<td>37.59±0.19</td>
<td>48.89±1.28</td>
<td>95.35±0.35</td>
</tr>
<tr>
<td>25</td>
<td>43.26±0.15</td>
<td>49.87±0.35</td>
<td>93.84±0.08</td>
</tr>
<tr>
<td>30</td>
<td>46.05±0.12</td>
<td>54.20±0.12</td>
<td>93.12±0.05</td>
</tr>
<tr>
<td>50</td>
<td>67.48±0.07</td>
<td>67.33±0.13</td>
<td>90.27±0.48</td>
</tr>
<tr>
<td>100</td>
<td>82.56±0.00</td>
<td>82.07±0.04</td>
<td>81.96±0.01</td>
</tr>
<tr>
<td>150</td>
<td>87.48±0.00</td>
<td>88.10±0.02</td>
<td>78.09±0.09</td>
</tr>
<tr>
<td>200</td>
<td>90.81±0.02</td>
<td>90.52±0.02</td>
<td>78.05±0.03</td>
</tr>
</tbody>
</table>

Appendix 22: Effect of initial metal ion concentration on percentage removal of cadmium (II) ions (0.2 g, 25°C, 2 Hrs, 240 rpm and pH 7)
### Appendix 23: Effect of contact time on the percentage removal of lead (II) ions (0.2 g, 25°C, 10 mg/L, 240 rpm and pH 7)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>AMC</th>
<th>MC</th>
<th>ASH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(mins)</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
</tr>
<tr>
<td>30</td>
<td>55.95±0.01</td>
<td>43.20±0.00</td>
<td>67.26±0.67</td>
</tr>
<tr>
<td>60</td>
<td>70.83±0.06</td>
<td>62.60±0.00</td>
<td>71.06±1.33</td>
</tr>
<tr>
<td>90</td>
<td>75.61±0.00</td>
<td>69.09±0.02</td>
<td>73.21±1.33</td>
</tr>
<tr>
<td>120</td>
<td>78.07±0.00</td>
<td>72.31±0.00</td>
<td>75.95±0.33</td>
</tr>
<tr>
<td>150</td>
<td>79.52±0.01</td>
<td>74.24±0.07</td>
<td>77.60±0.67</td>
</tr>
<tr>
<td>1440</td>
<td>79.71±0.11</td>
<td>74.36±0.04</td>
<td>77.91±1.20</td>
</tr>
</tbody>
</table>

### Appendix 24: Effect of contact time on percentage removal of cadmium (II) ions (0.2 g, 25°C, 10 mg/L, 240 rpm and pH)

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>AMC</th>
<th>MC</th>
<th>ASH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(mins)</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
</tr>
<tr>
<td>30</td>
<td>58.68±1.66</td>
<td>60.01±0.22</td>
<td>84.31±0.53</td>
</tr>
<tr>
<td>60</td>
<td>63.07±1.78</td>
<td>60.54±0.23</td>
<td>86.25±0.54</td>
</tr>
<tr>
<td>90</td>
<td>64.30±1.82</td>
<td>60.68±0.21</td>
<td>86.91±0.55</td>
</tr>
<tr>
<td>120</td>
<td>66.34±1.88</td>
<td>60.93±0.23</td>
<td>87.24±0.55</td>
</tr>
<tr>
<td>150</td>
<td>70.43±1.99</td>
<td>61.41±0.22</td>
<td>87.44±0.55</td>
</tr>
<tr>
<td>1440</td>
<td>70.42±1.99</td>
<td>61.52±0.23</td>
<td>88.15±0.55</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>AMC</td>
<td>MC</td>
<td>ASH</td>
</tr>
<tr>
<td>-----------</td>
<td>-----------</td>
<td>----------</td>
<td>-----------</td>
</tr>
<tr>
<td>Dose (g)</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
</tr>
<tr>
<td>0.1</td>
<td>47.30±0.92</td>
<td>44.65±0.40</td>
<td>42.20±2.91</td>
</tr>
<tr>
<td>0.2</td>
<td>48.68±0.95</td>
<td>44.88±0.40</td>
<td>50.20±3.46</td>
</tr>
<tr>
<td>0.3</td>
<td>50.00±0.97</td>
<td>46.10±0.41</td>
<td>60.00±3.92</td>
</tr>
<tr>
<td>0.4</td>
<td>52.24±1.02</td>
<td>46.50±0.42</td>
<td>61.80±4.26</td>
</tr>
<tr>
<td>0.5</td>
<td>52.25±1.02</td>
<td>46.60±0.42</td>
<td>61.90±4.27</td>
</tr>
</tbody>
</table>

**Appendix 25: Effect of adsorbent dose on percentage removal of lead (II) ions (25°C, 10 mg/L, 2Hrs, 240 rpm and pH 7)**

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>AMC</th>
<th>MC</th>
<th>ASH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dose (g)</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
</tr>
<tr>
<td>0.1</td>
<td>88.20±0.33</td>
<td>90.83±0.04</td>
<td>89.65±0.17</td>
</tr>
<tr>
<td>0.2</td>
<td>89.12±0.34</td>
<td>90.96±0.03</td>
<td>90.15±0.18</td>
</tr>
<tr>
<td>0.3</td>
<td>89.56±0.33</td>
<td>91.03±0.04</td>
<td>90.46±0.18</td>
</tr>
<tr>
<td>0.4</td>
<td>90.01±0.34</td>
<td>91.06±0.04</td>
<td>90.54±0.17</td>
</tr>
<tr>
<td>0.5</td>
<td>90.05±0.32</td>
<td>91.07±0.05</td>
<td>90.64±0.16</td>
</tr>
</tbody>
</table>

**Appendix 26: Effect of adsorbent dose on percentage removal of cadmium (II) ions (25°C, 10 mg/L, 2Hrs, 240 rpm and pH 7)**
### Appendix 27: Effect of shaking speed on percentage removal of lead (II) ions (0.2 g, 25°C, 10 mg/L, 2 Hrs and pH 7)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>AMC</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed(rpm)</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
</tr>
<tr>
<td>0</td>
<td>58.33±0.03</td>
<td>46.53±0.03</td>
</tr>
<tr>
<td>120</td>
<td>58.73±0.03</td>
<td>51.80±0.00</td>
</tr>
<tr>
<td>240</td>
<td>57.90±0.00</td>
<td>61.47±0.03</td>
</tr>
<tr>
<td>360</td>
<td>57.57±0.03</td>
<td>81.90±0.00</td>
</tr>
</tbody>
</table>

### Appendix 28: Effect of shaking speed on percentage removal of cadmium (II) ions (0.2 g, 25°C, 10 mg/L, 2 Hrs and pH 7)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>AMC</th>
<th>MC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Speed(rpm)</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
</tr>
<tr>
<td>0</td>
<td>51.27±0.55</td>
<td>65.55±0.33</td>
</tr>
<tr>
<td>120</td>
<td>63.23±0.68</td>
<td>67.97±0.34</td>
</tr>
<tr>
<td>240</td>
<td>81.23±0.87</td>
<td>79.45±0.40</td>
</tr>
<tr>
<td>360</td>
<td>81.93±0.88</td>
<td>79.37±0.40</td>
</tr>
</tbody>
</table>
### Appendix 29: Effect of temperature on percentage removal of lead (II) ions
(0.2 g, 10 mg/L, 2 Hrs 240 rpm and pH 7)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>AMC</th>
<th>MC</th>
<th>ASH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp(K)</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
</tr>
<tr>
<td>298</td>
<td>52.92±0.01</td>
<td>52.06±0.00</td>
<td>79.70±1.26</td>
</tr>
<tr>
<td>323</td>
<td>52.19±0.01</td>
<td>51.96±0.00</td>
<td>79.23±1.25</td>
</tr>
<tr>
<td>348</td>
<td>51.24±0.01</td>
<td>51.86±0.01</td>
<td>77.43±1.22</td>
</tr>
<tr>
<td>373</td>
<td>50.06±0.00</td>
<td>51.79±0.01</td>
<td>74.30±1.17</td>
</tr>
</tbody>
</table>

### Appendix 30: Effect of temperature on percentage removal of cadmium (II) ion
(0.2 g, 10 mg/L, 2 Hrs 240 rpm and pH 7)

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>AMC</th>
<th>MC</th>
<th>ASH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp(K)</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
<td>Mean % removal± SE</td>
</tr>
<tr>
<td>298</td>
<td>73.04±0.00</td>
<td>51.17±0.01</td>
<td>89.84±0.33</td>
</tr>
<tr>
<td>323</td>
<td>78.46±0.00</td>
<td>50.00±0.00</td>
<td>88.61±0.33</td>
</tr>
<tr>
<td>348</td>
<td>67.62±0.00</td>
<td>50.03±0.00</td>
<td>88.55±0.33</td>
</tr>
<tr>
<td>373</td>
<td>50.00±0.00</td>
<td>50.00±0.00</td>
<td>88.41±0.33</td>
</tr>
<tr>
<td>Adsorbent</td>
<td>AMC</td>
<td>MC</td>
<td>ASH</td>
</tr>
<tr>
<td>-----------</td>
<td>-----</td>
<td>----</td>
<td>-----</td>
</tr>
<tr>
<td><strong>Concentration (mg/L)</strong></td>
<td><strong>Mean % removal± SE</strong></td>
<td><strong>Mean % removal± SE</strong></td>
<td><strong>Mean % removal± SE</strong></td>
</tr>
<tr>
<td>5</td>
<td>74.17±1.39</td>
<td>50.83±0.44</td>
<td>40.00±0.45</td>
</tr>
<tr>
<td>10</td>
<td>81.46±1.53</td>
<td>74.38±0.64</td>
<td>64.58±0.73</td>
</tr>
<tr>
<td>15</td>
<td>82.11±1.54</td>
<td>81.81±0.71</td>
<td>75.56±0.86</td>
</tr>
<tr>
<td>20</td>
<td>80.94±1.52</td>
<td>85.00±0.74</td>
<td>81.04±0.92</td>
</tr>
<tr>
<td>25</td>
<td>82.00±1.54</td>
<td>86.42±0.75</td>
<td>81.75±0.93</td>
</tr>
</tbody>
</table>

Appendix 31: Effect of concentration on percentage removal of methylene blue (0.2 g, 25°C, 2 Hrs, 240 rpm and pH 7)

<table>
<thead>
<tr>
<th>DOSE(g)</th>
<th>Mean % removal± SE</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>16.09±0.60</td>
</tr>
<tr>
<td>0.2</td>
<td>51.72±1.94</td>
</tr>
<tr>
<td>0.3</td>
<td>55.17±2.07</td>
</tr>
<tr>
<td>0.4</td>
<td>56.32±2.12</td>
</tr>
<tr>
<td>0.5</td>
<td>59.77±2.25</td>
</tr>
</tbody>
</table>

Appendix 32: Effect of adsorbent dose on turbidity removal using ash from maize cobs (25°C, 10 mg/L, 2 Hrs, 240 rpm and pH 7)