BINDURA UNIVERSITY OF SCIENCE EDUCATION

FACULTY OF SCIENCE EDUCATION

BACHELOR OF SCIENCE EDUCATION HONORS DEGREE

AN INVESTIGATION INTO THE DETERMINATION OF HEAVY METALS IN WATER BY FLAME ATOMIC ABSORPTION SPECTROSCOPY AND THEIR REMOVAL BY PHOSPHORUS-DOPED BIOCHAR

BY

NTULI LIZZY

B225688B

A DISSERTATION SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE BACHELOR OF SCIENCE HONORS DEGREE IN CHEMISTRY EDUCATION

June 2024

RELEASE FORM

Investigation into the determination of heavy metals in water by FAAS and their removal by phosphorus-doped biochar.

1. **To be completed by student**
   I certify that this dissertation is in conformity with the preparation guideline as presented in the Faculty Guide and Instructions for Typing Dissertations.

(Signature)

06 / 06 / 2024
(Date)

2. **To be completed by the Supervisor.**
   This dissertation is suitable for submission to the Faculty. This dissertation should be checked for conformity with Faculty guidelines.

(Signature)

07/10/2024
(Date)

3. **To be completed by the Department**
   I certify to the best of my knowledge that the required procedures have been followed and the preparation criteria have been met for this dissertation.

(Signature)

(Date)

APPROVAL FORM

Name of the Student: Ntuli Lizzy

Registration number: B225688B

Dissertation Title: An investigation into the determination of heavy metals by FAAS and their removal by phosphorus-doped biochar.

Degree Title: HBScEd Chemistry

Year of Completion: 2024

Permission is hereby granted to Bindura University of Science Education to Single copies of this dissertation and to lend or sell such copies for private, school scientific purposes only. The author reserves any publication rights and neither dissertation nor extensive extracts from it be granted or otherwise be reprinted without the author's consent.

06 / 06 / 2024

Signed **Date**

Permanent Address: 2661 Area 14 Dangamvura, Mutare

DEDICATION

This research is dedicated to my loving husband, Mwamuka and our children, Tinodaishe and Makanaka.

ACKNOWLEDGEMENTS

I would like to thank my Supervisor, Dr W. Munzeiwa for his guidance and support. Without his guidance and tireless efforts, this project would not have been a success. My gratitude also goes to the Chemistry laboratory staff at BUSE Astra campus for their guidance through all practical work. Many thanks also to my family and friends for their moral and financial support.

ABBREVIATIONS AND ACRONYMS

FAAS – Flame Atomic Absorption Spectroscopy
FTIR- Fourier Transform Infrared
PBC – Phosphorus-Doped Biochar
TDS- Total Dissolved Solids
TSS- Total Suspended Solids

ABSTRACT

Contamination of water by heavy metals is of great concern as it results in health and environmental risks. The aim of this research was to determine concentrations of heavy metals in water samples using FAAS and find out on the effectiveness of PBC in removing the heavy metals. Water samples were collected, tested for the presence of arsenic, cadmium and lead. FAAS analysis showed the concentration of the heavy metals, and this gave valuable data on the quality of the water. PBC was made and adsorption capacity evaluated. Characterization of the biochar was done using a wide range of techniques to understand its physical and chemical properties. Parameters such as contact time, adsorbent dosage and initial metal concentration were optimized to achieve maximum removal. Adsorption kinetics and isotherms were analyzed to make the underlying mechanisms of the adsorption process clear. The results obtained proved that PBC is a very effective adsorbent of heavy metals in water and therefore can be recommended for use as a cost-effective and environmentally friendly adsorbent for the remediation of heavy metal-contaminated water.

TABLE OF CONTENTS

Contents

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1:

1.0 INTRODUCTION

In this chapter the researcher gives the background to the study, statement of the problem, aims and objectives of the study. Definition of terms, limitations and delimitation of the study will also be looked into.

1.1 BACKGROUND TO THE STUDY

According to Kiflom and Tarekegn (2015), heavy metals are metals that are denser than water and have a tendency to bio accumulate and humans can take them in through consumption of water and fish. The authors also noted that these heavy metals can be harmful even at very low concentrations.

Several studies have shown that water sources are being polluted and one of the pollutants are heavy metals. Some of the sources of heavy metals have been cited by Skipton et al (2006) as agriculture, industry and mining.

With rise in illegal mining activities in Zimbabwe in recent years, there is fear that a lot of heavy metals are being discharged into water bodies, putting aquatic life and humans at risk. This has prompted the author to carry out an investigation to detect heavy metals in drinking water by Flame Atomic Absorption Spectroscopy (FAAS) and assess the efficacy of Phosphorus- doped biochar in their removal. If these methods are found to be cost-effective and eco-friendly, the researcher will recommend their usage in large scale water treatment, ensuring protection of the environment and good health of the general populace.

The techniques that have found relevance in the application of analytical chemistry for the determination of heavy metals, even in trace quantities, are Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Flame Atomic Absorption Spectrometry (FAAS)(Burham,2009).

Of late, various methods (chemical, biological and physical have been used to remove heavy metals in water. However, the variety in nature of pollution levels and the different types of pollution, have posed as very big impediments in the effective removal of the metals by the aforementioned approaches. (Burham ,2009). Several studies have revealed adsorption as a promising technique because, besides being able to remove heavy metals in the environment, it also immobilizes them.

Numerous materials, including biomaterials, nanomaterials, mineral materials and carbon-based materials have obtained attention as potential adsorbents. Biochar has found widespread application in the treatment of both organic and inorganic pollutants because of its characteristics such as high porosity and persistence. Modifying its properties like specific surface area and abundance of surface functional groups, adsorption capacity of biochar of for heavy metals in water can be enhanced. (Vidu et al 2020).

A wide range of techniques can be used to modify biochar such as, physical modification, corrosive modification and doping modification. Of particular interest is the preparation of phosphorus -doped biochar which significantly enhances its conductivity, thermal stability and the number of active surface sites, finding broad applications in electrochemistry, catalysis and adsorption, among other fields. (Rana et al, 2021).

Phosphorus holds significant functional value in biochar. PBC has outstanding properties that make it well suited for use as an adsorbent. The effectiveness of PBC depends, among other factors, on the type of biomass. For example, PBC can be made from plant-derived waste (agricultural or forestry products) or it can be made from animal-based waste such as poultry droppings, livestock dung and animal residues. (Xiang et al, 2020).

There are various ways of making PBC but in this study, conventional pyrolysis was used. This is the dry treatment of biomass in limited oxygen. PBC's adsorption mechanisms of heavy metals include mineral participation, ion exchange, functional group complexation, electrostatic interaction, physical adsorption, cation interaction and redox. (Shikha and Singh, 2021).

1.2 STATEMENT OF THE PROBLEM

Zimbabwe is endowed with various rivers and dams, some of which are perennial, and as such has been proud of its population having enough fresh water. However, in recent years, a lot of illegal mining and uncontrolled agriculture have increased due to the declining economy. This has seen many water bodies getting polluted by various pollutants, including heavy metals such as mercury, lead, chromium, zinc and cadmium. There is fear that people are getting exposed to these metals not only through drinking water but also through the consumption of fish as the metals have a tendency to bio accumulate.

Though traditional methods of water purification can be used to remove heavy metals, they can be expensive and may result in secondary pollutants. As such, there is need that research be done in order to find other ways that are not just cost-effective in removal of heavy metals but also eco-friendly.

1.3 AIMS

1. To investigate the determination of heavy metals in water using FAAS
2. To evaluate the effectiveness of phosphorus-doped biochar in the removal of heavy metals from water.

1.4 OBJECTIVES

1. To determine heavy metals in water by FAAS
2. To remove heavy metals from water by phosphorus -doped biochar
3. To compare the efficiency of phosphorus -doped biochar to other methods of heavy metal removal
4. To assess the potential application of phosphorus -doped biochar in large scale water treatment

1.5 SIGNIFICANCE OF STUDY

The results of this research may help to:

- develop cost-effective and eco-friendly methods for removal of heavy metals from drinking water
- protect the environment and humans by reducing their exposure to heavy metals.

The recommendations can be used by water providers such as ZINWA and water works in towns and cities to provide clean, safe drinking water. This helps to improve people's health using less expensive methods and as such reduce consumers' water bills.

2.0 REVIEW OF RELATED LITERATURE

2.1 Introduction

Fresh water has become a scarce resource in most parts of the world in recent years. According to Parsi (2000), with increasing industrialization, various pollutants are being introduced into the environment and these include heavy metals. Heavy metals like arsenic, lead, cadmium and mercury can gain entry into the human body through drinking water. Where illegal mining activities are common, chances of heavy metal contamination are very high (Diparthy et al 2020).

2.2 Effects of heavy metals on human health

2.2.1 Lead (Pb)

The world health organization (WHO)'s acceptable levels of lead in drinking water is 0.01ppm. Lead can enter the human body through ingestion of food and water contaminated with the metal. It can enter drinking water through industrial activities and plumbing (old water pipes eventually release lead into water). The effects of lead toxicity include: inhibition of haemoglobin synthesis, kidney failure, and damage to the joints, reproductive system cardiovascular system and the central nervous system. (Rashmi and Pratima 2013).

2.2.2 Cadmium (Cd)

According to Gupta (2010), the WHO acceptable levels of cadmium in drinking water is 0.003ppm and it is very toxic metal even in extremely low levels. It usually finds its way into water sources through mining and smelting of minerals (Kazi et al 2009). Long time exposure to cadmium can cause renal, lung disease (cadmium pneumonitis), bone defects such as osteomalacia and osteoporosis, increased blood pressure and heart disease and increased risk of cancers (Gupta 2010).

2.2.3 Mercury (Hg)

The WHO acceptable level of mercury in water is 0.001ppm. Mercury can gain access into water bodies mainly through run-off from mineral refineries amongst other sources. It is also used in artisanal and small-scale gold mining. It affects negatively the brain, lungs, kidneys, liver, cardiovascular system, endocrine and reproductive system. (Rashmi and Pratima 2013), mercury, in whatever form, has nothing positive to contribute to the human body, it is always toxic. (Abrahim and Parker 2008). Organic mercury can cause neurological and developmental effects. Inorganic mercury can damage kidneys and the central nervous system.

2.2.4 Arsenic (As)

This metal can be released into the environment through mining, smelting and combustion of fossil fuels. It can then contaminate ground and surface water. The WHO acceptable levels of arsenic in drinking water is 0.01ppm. (Abrahim and Parker 2008). Exposure to arsenic can adversely affect the skin, lungs, brain, kidneys, cardiovascular system and endocrine system, amongst many other body organs and systems. (Rashmi and Pratima 2013).

2.3 Methods of determining heavy metals in water

There are a wide range of methods at the exposure of researchers that can be used to remove heavy metals from water before it can be released into the environment. Heavy metal contamination has detrimental effects on both humans the ecosystem since these metals have a tendency to bioaccumulate. Choice of method of heavy metal removal depends on such factors as flexibility of the method, its precision and accuracy of the method and cost.

2.3.1 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

An inductively coupled plasma is used to ionize the sample and the mass spectrometer separates and detects the ions. This helps to identify and quantify the heavy metals. According to Kanwal et al (2019), this method is extremely sensitive, it can detect heavy metals in

extremely low quantities(ppt) and it can be used to analyze many elements at once. However, this method is very expensive. (Antony et al 2019).

2.3.2 X-ray Fluorescence (XRF) Spectroscopy

This method uses x-rays to excite the atoms in a sample, causing the atoms to emit characteristic x-rays that can be used to identify and measure the concentration of heavy metals. (Abrahim et al 2008). The main advantages of this method are that, it is a simple and fast analysis, and it can provide information on the chemical form of the heavy metals. However, this method is less sensitive compared to AAS and ICP-MS, it requires a relatively large sample size and may not be able to detect very low concentrations of heavy metals. (Kazi et al 2009).

2.3.3 Anodic Stripping Voltammetry (ASV)

ASV concentrates the heavy metal ions on an electrode and when the ions are stripped off, current generated is measured. This allows for sensitive detection of the heavy metals. It is a highly sensitive method, and relatively simple and not expensive. However, it is prone to interferences and only be used with a few heavy metals that can be electrochemically deposited and stripped. (Majumdar et al 2018)

2.3.4 Flame Atomic Absorption Spectroscopy (FAAS)

This method uses the absorption of light by atoms in gaseous state to quantify the concentration of specific heavy metal ions in a sample. According to Skoog et al (2017), FAAS is a method that has been used by several researchers to analyze and determine concentrations of heavy metals in water samples because this technique is highly sensitive (can detect even very small concentrations of the metals) and it is less demanding in preparation when compared to other methods. Studies by Daliparthy et al (2020) showed very high success of FAAS in determining heavy metals such as lead, cadmium, copper and zinc. However, Welz and Sperling (1999) were quick to point out that this method's performance can be affected by interferences and other factors, and as such, care must be taken to consider the factors during development and validation.

2.4 Methods of removing heavy metals in water

2.4.1 Ion exchange

Undesirable heavy metal ions in water are replaced with more desirable ones using ion exchange resins or membranes. This method is very much effective in removing heavy metals, even those in very low concentrations. Besides, the resins can be regenerated and reused (Dhote and Mahendra 2010). However, studies by Wang et al 2019 showed that the resins used may be susceptible to failing and this method requires careful control of pH and other water parameters.

2.4.2 Membrane Filtration

This method involves techniques like reverse osmosis, nanofiltration and ultrafiltration (Dhote and Mahendra 2010).

- **Reverse Osmosis (RO**) –with this technique, water is forced through a semi-permeable membrane. The water molecules pass through but the contaminants (heavy metals, organic compounds and microorganisms) are trapped, producing high quality drinking water (Drioli and Giorno 2009).
- **Nano filtration** – used to soften water, getting rid of odour and colour. The technique is similar to RO but makes use of a membrane that has larger pores and uses a lower operating pressure. The method does not remove essential minerals from the water (Gryta Karakulski 2018).
- **Ultrafiltration** – this technique is usually used for removing suspended solids and macromolecules during water treatment. It is similar to nanofiltration but the membrane has larger pores which enable it to remove larger particles. It is energy-saving and suitable for a wide range of water treatment applications such as desalination and wastewater reuse (Baker 2004).

  The merits of this method include: its capacity to remove a wide range of heavy metals, it is very effective in treating water and is very easy to operate (Dhote and Mahendra 2010). However, it is very expensive as it consumes a lot of energy, membranes can get damaged by some water characteristics and generates a concentrated waste stream that needs disposal (Gupta et al 2010).

2.4.3 Chemical Precipitation

A chemical reagent like calcium hydroxide is added to the water and the mixture is stirred to ensure maximum contact between the reagent and water. The reagent then reacts with the metal ions forming insoluble precipitates which settle at the bottom of the water as sludge. The water is separated from the sludge by filtration. Chemical precipitation is usually used in water treatment plants and industries to remove heavy metals effectively from water sources. This method is simple and cost-effective and suitable for removing heavy metals that are in high concentrations in water. It can also remove a wide range of heavy metals simultaneously. However, it requires proper disposal of the sludge produced and it is not effective when the heavy metals are in low concentrations (Wang and Chen 2009).

2.4.4 Bioremediation

This method uses living organisms such as bacteria, fungi and algae to remove heavy metals from water through mechanisms such as biosorption, bioaccumulation and biotransformation.

- **Biosorption** – microorganisms absorb the heavy metals and they adsorb onto the external surfaces of the microorganisms. These metals will then be removed from the environment by harvesting and disposing the biomass. (Ahluwalia and Goyal 2007).
- **Bioaccumulation –** this involves living organisms take up and store contaminants within their cells or tissues, thus, removing them from the environment. The organisms can then detoxify the pollutants.
- **Biotransformation –** microorganisms change contaminants into less toxic or harmless substances through metabolism. This way, very complex contaminants are broken down into less harmful compounds. As such, biotransformation can be a very powerful mechanism in bioremediation by facilitating complete detoxification of contaminants in the environment (Mohan et al 2001).

Bioremediation is environmentally friendly, it is cost-effective and some organisms target certain metals (offering selective removal) and it requires less energy compared to other methods (Rathore and Kumar 2016). However, it is time-consuming since it is a slow process, it needs constant monitoring and optimization to make sure the process is effective, and the technique may be restricted to certain types of heavy metals or specific environmental conditions (Bose et al 2010).

2.4.5 Adsorption

Activated carbon, biochar, zeolites, clay minerals can be used to remove heavy metals from water. The metals adsorb to the surface of the material used for the removal

Adsorption is the most widely used process due to its removal efficiency, low energy demand, less chemical investment, simplicity of operation and low implementation costs when compared with other treatment methods (Harman et al., 2016). Adsorption is a surface accumulation of pollutants on adsorbent. It occurs when a solution containing absorbable solute comes into contact with a solid with a highly porous surface structure causing some of the solute molecules from the solution to be concentrated or deposited at the solid phase by liquid-solid intermolecular forces of attraction (Rashed, 2013). The absorbate is the solute retained on the surface while the solid onto which it is retained is called the adsorbent. In the absorbent, all the bonding of the constituent atoms of the material are filled by other atoms of the material (Zhang, 2019). However, atoms on the surface of the adsorbent are not wholly surrounded by other adsorbent atoms and therefore can attract adsorbates. The adsorption process is generally classified as physisorption (characteristic of weak Van Der Waals forces) or chemisorption (characteristic of covalent bonding). It may occur due to electrostatic attraction.

- **Activated carbon** – is a highly effective method for removing heavy metals from water. Activated carbon is a porous material with a large surface area that can attract and trap heavy metal ions present in water. The heavy metal ions bind to the activated carbon surface (Sarici-ozdemir et al, 2018). Traditional systems that aim at the removal of organic contaminants from water, including some pharmaceuticals, still revolve around the use of activated carbons but it is known that their capacity and selectivity greatly decrease due to competition from the many species involved in the water matrix (Cabrera-lafaurie et al, 2012).

- **biochar** – is a highly porous carbon material produced by pyrolysis of biomass. It can remove heavy metals from water through both physical and chemical processes such as adsorption and ion exchange. It also has a very large surface area and functional groups (carboxylic and phenolic) that can chemically bind with heavy metals, effectively immobilizing them. (Uchimiya et al ,2010)
- **Zeolites** – these are crystalline aluminosilicate minerals with a three-dimensional structure made up of pores and channels. The surfaces of zeolites are negatively charged surfaces and they attract the positively charged metal ions. The ions are then captured and retained within the zeolite, thus removing them from the water (Li et al, 2016).
- **Clay minerals** – examples are montmorillonite, bentonite and kaolinite with a high surface area and strong adsorption properties. These minerals have negatively charged surfaces which attract the metal cations, effectively immobilizing them (Zhao and Zhang, 2020).
- **Removal of heavy metals by phosphorus -doped biochar (PBC)**

Biochar is a product of the pyrolysis of biomass such as sawdust. Inyang et al (2016) in their study, noted that, biochar has a very high potential to remove heavy metals from water effectively. Further studies by Dai et al (2018) revealed that, doping the biochar with phosphorus increased its adsorption capacity as the phosphorus formed complexes with the heavy metals. According to Shen et al (2020), phosphorus -doped biochar proved to be effective in removing such heavy metals as lead, cadmium, copper and nickel from water.

The phosphorus -doped biochar removes the heavy metals through ion exchange, surface complexation and precipitation but these mechanisms are affected by pH of the sample, adsorbent dosage, contact time and initial concentration of the metal (Wang et al 2016).

2.4 Integrating FAAS and PBC

Iqbal et al (2021) noted that, combining FAAS and PBC in determining and removing heavy metals respectively, can produce tremendous results in addressing water pollution issues because the two are not only effective but are cost-effective and eco-friendly too.

2.5 Conclusion

Plucking a leaf from the literature compiled from related studies, the researcher observed with keen interest, the great potential that FAAS has in determining heavy metals in water and the probable efficiency of PBC in removing the heavy metals from water. As such, carrying out a study with the two techniques combined might produce a synergy that could resoundingly address heavy metal pollution in water sources

CHAPTER 3: RESEARCH METHODOLOGY

3.0 INTRODUCTION

This chapter provides the step-by-step literature on the experimental procedures that were taken in satisfying the objectives and aim of this research. The chemical reagents and instruments used are mentioned in this chapter. The chapter reports all investigations of the project, all of which were carried out at the ASTRA laboratories.

3.1 Instruments and Chemicals

3.1.1 Instruments and apparatus

a) atomic absorption spectroscopy - for measuring the concentration of specific elements in a sample by analyzing the absorption of light by free metallic ions in gaseous state.

b) flame atomizer- converts the sample into gaseous state for analysis

c) sample introduction system - for placing the sample into the flame atomizer

d) calibration standards - for the accurate quantification of heavy metals in water. Results can be used to plot a graph of light absorption against concentration of the metal

e) gas supplies - acetylene and air supplied to the flame atomizer to generate the flame

f) pyrolysis equipment (kiln)- used to convert the precursor materials into phosphorus -doped biochar

g) adsorption testing equipment - used to evaluate the effectiveness of the phosphorus-doped biochar in removing heavy metals from water.

h) safety equipment - to include: gas leak detectors, fire extinguishers, lab coat, safety goggles, gloves, fume hood.

3.1.2 Reagents and chemicals

a) standard metal solutions - for creating calibration curves and quantifying the concentration of heavy metals in water samples using FAAS

b) acids such as HCl and HNO3- used to ensure that the metals are converted into a form suitable for FAAS analysis

c) magnesium - used to improve the sensitivity and accuracy of FAAS analysis, as it reduces interference by other chemicals not under study.

d) deionized water - for preparing solutions and rinsing the biochar

e) phosphoric acid - where the saw dust is soaked before pyrolysis, for doping the biochar with phosphorus.

e) sawdust - heated in the absence of oxygen to produce biochar

f) regeneration reagents - for desorption of the absorbed metals, separating them from the biochar.

3.2 Sample Collection and Synthetic water preparation.

Raw water samples were collected from various sources where heavy metal contamination was most likely. The water was filtered to remove suspended solids and stored in clean containers.1000 ppm concentrations of Pb2+, Cd2+, As+ and Hg+ solutions were prepared in conical flasks from the respective inorganic salts. The stock solution was then used in preparation of solutions with lower concentrations. The blank was a flask filled with distilled water only.

3.3 Biochar preparation and activation

Saw dust was collected from untreated wood and dried thoroughly. The saw dust was then soaked in a solution of 0.2M phosphoric acid. It was then heated in a kiln at 500^{o}C, in the absence of oxygen. After activation the pyrolyzed sample was cooled to room temperature. The sample was washed several times with distilled water then allowed to dry overnight at 110°C.Characterization of the biochar was done to confirm presence of phosphorus and to determine the biochar's physical and chemical properties and its effectiveness in heavy metal removal.

3.4 Characterization of adsorbent

The prepared biochar was characterized for ash content, moisture content and fixed carbon. The surface functional groups of sawdust biochar were examined by Fourier transform infrared (FTIR) spectrometer (Thermo Scientific, Nicolet iS5 iD7 ATR).

3.4.1 Ash content

0.5g of biochar was weighed into a dried crucible. The contents of the crucible were heated in a muffle furnace at 500oC for a period of two hours. The crucible was left to cool and the ash content was determined as;

Ash content= (weight of ash/ sample weight) x100………………Equation 3.1

3.4.2 Moisture content

0.5g of biochar was weighed into a dried crucible. The contents of the crucible were heated in a muffle furnace at 310oC for a period of one hour. The crucible was left to cool and the moisture content was determined as;

Moisture content= [(a-b)/b] x100…………………. Equation 3.2

Where a= initial weight of biochar

b= weight of biochar after heating

3.4.3 Fixed carbon

Pure bonded carbon = 100%-(A+B) ……………. Equation 3.3

Where A = ash content

B= moisture content

3.5 Characterization of process parameters

3.5.1 Effect of contact time

50ml of 10ppm of synthetic aqueous solution was separately added to 0.2g of the adsorbent. The aliquot was stirred using a shaker at 240rpm and withdrawn at different time intervals in the range 5-90 minutes and filtered. The residual concentration was quantified using AAS.

3.5.2 Effect of initial concentration

0.2g of the adsorbent was added to 50ml of synthetic water within the concentration range of 2-50 pm. The mixture was stirred for 70 minutes using a shaker at 240 rpm and filtered through Whatman filter paper and the residual concentration of ions was quantified.

3.5.3 Effect of dosage

Varying masses the adsorbent in the range 0.05g to 0.25g with 0.05g increase per run were added to 50ml of water containing 10 ppm synthetic water and the mixtures were stirred for 90 minutes at 240rpm. The mixture was filtered using a Buchner funnel through Whatmann filter paper and the metal ion concentrations of the filtrate were determined using AAS.

3.6 Batch adsorption studies

A portion of 0.2g of the adsorbent was weighed into 250ml beaker to which 50ml of the water sample with a concentration of 10 ppm of each heavy metal was added. The samples were shaken at a constant speed for 70 minutes. The suspensions were filtered and the filtrates were collected in separate, clean bottles and the exact initial and final metal ion content was determined using AAS. Adsorption capacity was calculated using the equation;

$qe(mg/g) = ([Ci - Ce] \times V)/M$ …………………………. Equation 3.4

Where Ci is initial concentration in ppm

Ce is the concentration at equilibrium

V is the volume of the water sample

M is mass of the adsorbent

The percent adsorbed was calculated using the equation below;

%Adsorption = (Ci-Cf) x 100/Ci …………………. Equation 3.5

where Ci and Cf are the initial and final concentrations of the metal ions in solution respectively.

3.7 Data presentation

Sorption kinetics was represented in the form of graphs. Line graphs were used because they clearly show the relationship of the data and show the changes in the data over time.

3.8 Adsorption isotherm model fitting procedure

Langmuir adsorption isotherm

Langmuir expression is given by Equation:

1/qe = (1/qmKaCe) + 1/ qm ………………. Equation 3.6

Where: qe is the amount of metal adsorbed per specific amount of adsorbent (mg/g)

qm is the maximum adsorption capacity

Ce is the equilibrium concentration of solution (mg/L)

Ka is the enthalpy of biosorption (L/mg) independent of temperature, and the values of Ka and qm are obtained from the intercept and slope respectively, from the straight-line plot of Ce/qe against Ce.

Freundlich absorption isotherm

The Freundlich absorption isotherm is presented as:

log qe = logKf + (logCe ×1/n) ....Equation 3.7

Kf is the adsorption capacity and 1/n is the adsorption intensity, both of which are Freundlich equilibrium coefficients.

A plot of log qe against log Ce gave a straight line with a slope.

3.9 Kinetic studies

In order to control the kinetic mechanism which controls the processes, Pseudo first and second order models were tested and the validity of the models were verified by linear equations.

Pseudo First order

Equation below represents the pseudo first order:

log(qe-qt) = logqe - (k1/2.303) t …………Equation 3.8

Where qt is the amount of adsorbate at time t

Qe is the quantity adsorbed at equilibrium

k1 is the constant speed of adsorption of the pseudo model

The plot of log (qe -qt) as a function of t provided the k1 and qe values.

Pseudo second order

Pseudo second order kinetics is represented as:

t/qt = (k/ k2qe^2) + 1/qe ……………Equation 3.9

Where k2 is the constant speed of adsorption of the model pseudo second order(g.mg-1.min-1).

If the equation is checked by tracing t/qt according to t, a line of slope 1/qe should be obtained and the coordinate in the beginning equal to 1/ (k2qe2).

From the slope and intercept of the graph as a function of t, k2 and qe were obtained.

CHAPTER 4: RESULTS AND DATA ANALYSIS

4.1 INTRODUCTION

This chapter shows the results and presents data obtained from the analysis done in the previous chapter.

4.2 PHYSIO-CHEMICAL PROPERTIES OF ADSORBENTS

Ash %	**Moisture content**	**Fixed carbon**
0.79	9.46	89.45

4.3 OPTIMIZATION OF PROCESS PARAMETERS

Figure 4a: FTIR Spectra of sawdust

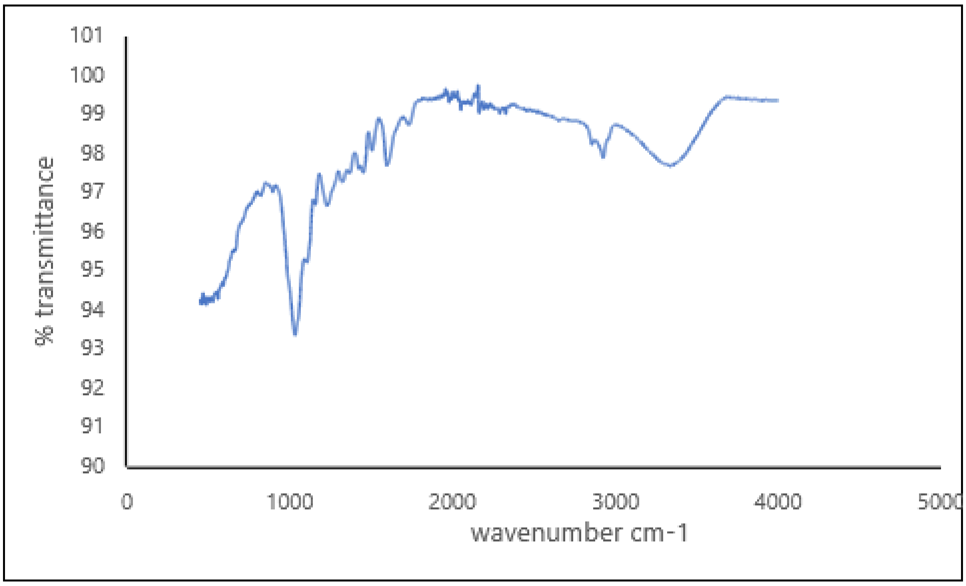
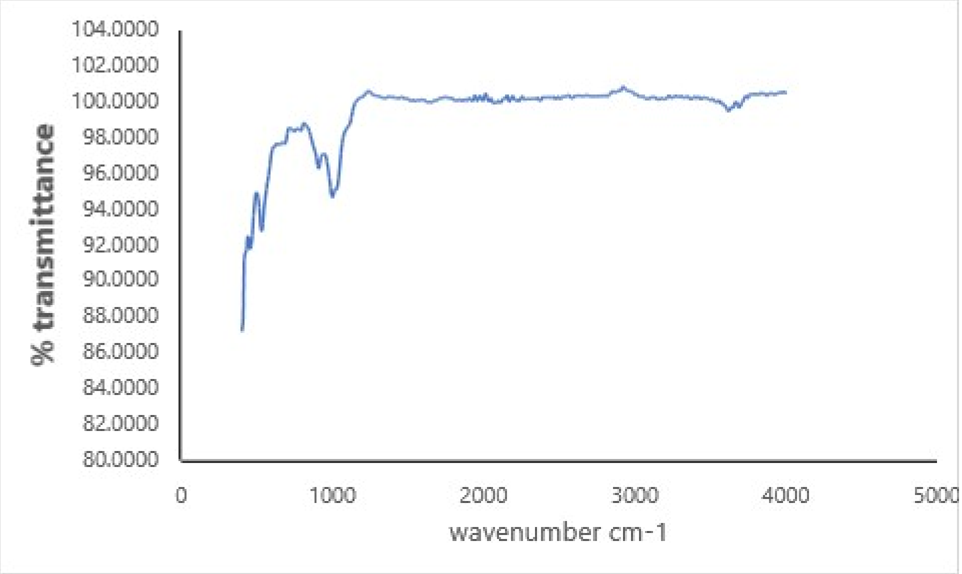


Figure 4b: FTIR Spectra of Biochar



4.3.1 Optimizing for effect of dosage

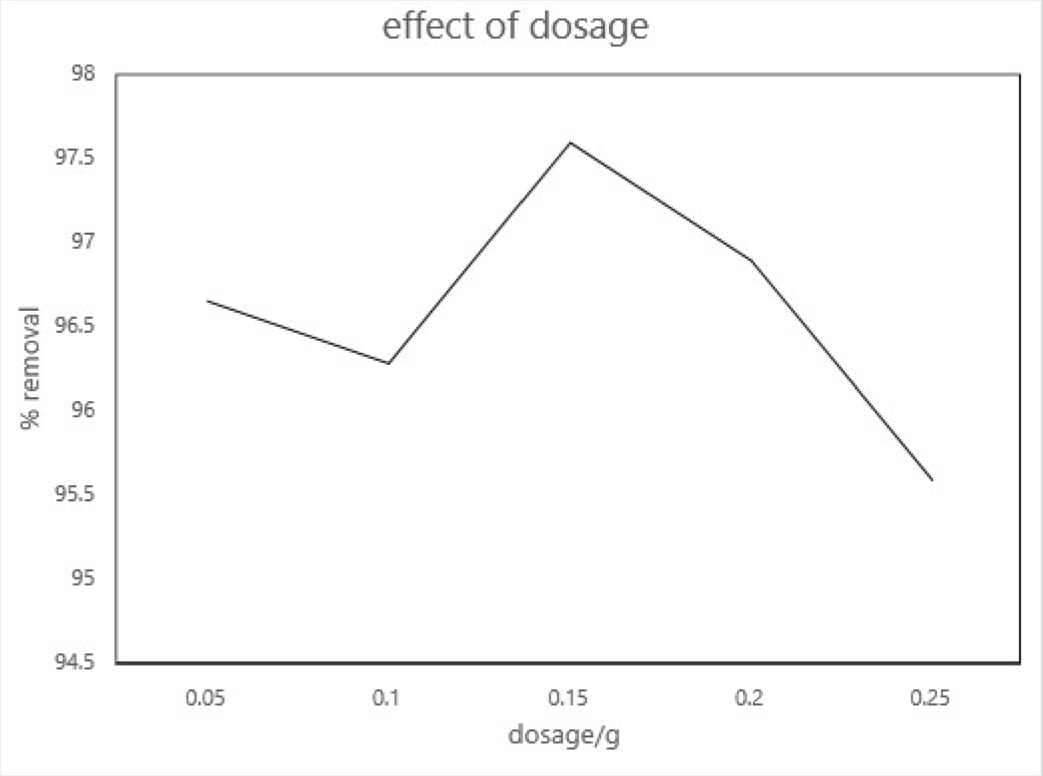


Figure 4. 1: Effect of adsorbent dosage in removing Pb (II) ions.

4.3.2 Optimizing for effect of initial concentration

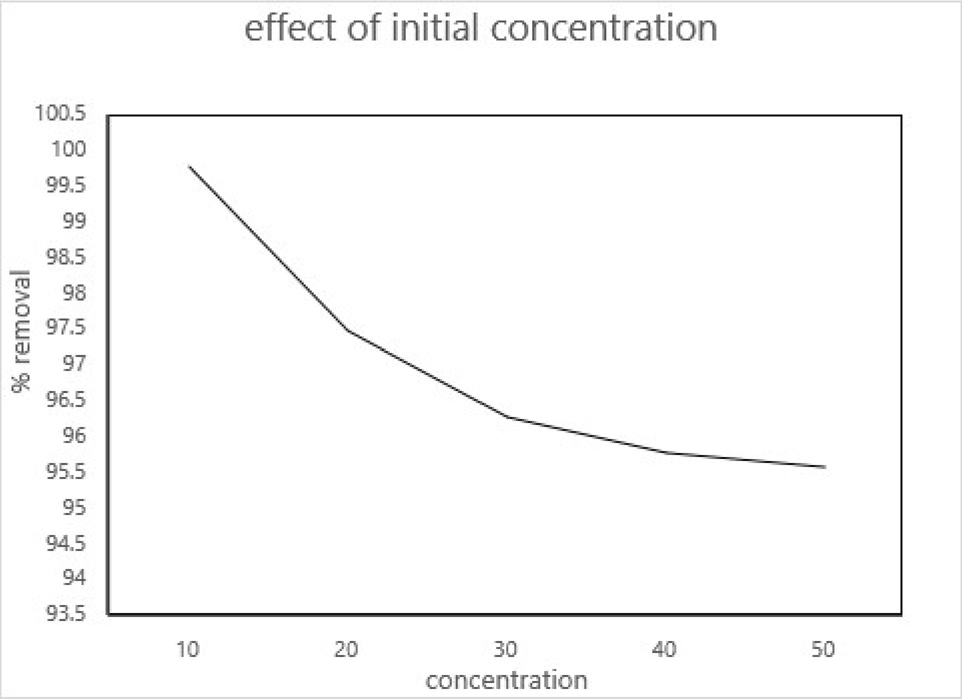


Figure 4. 2: Effect of initial concentration in removing Pb (II) ions

4.3.3 Optimizing for effect of pH

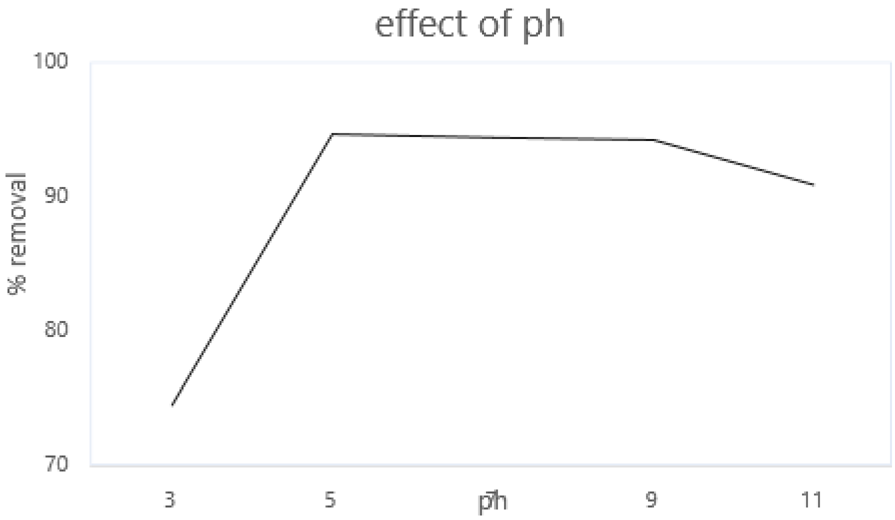


Figure 4. 3: Effect of pH in removing Pb (II) ions

4.3.4 Optimizing for effect of contact time

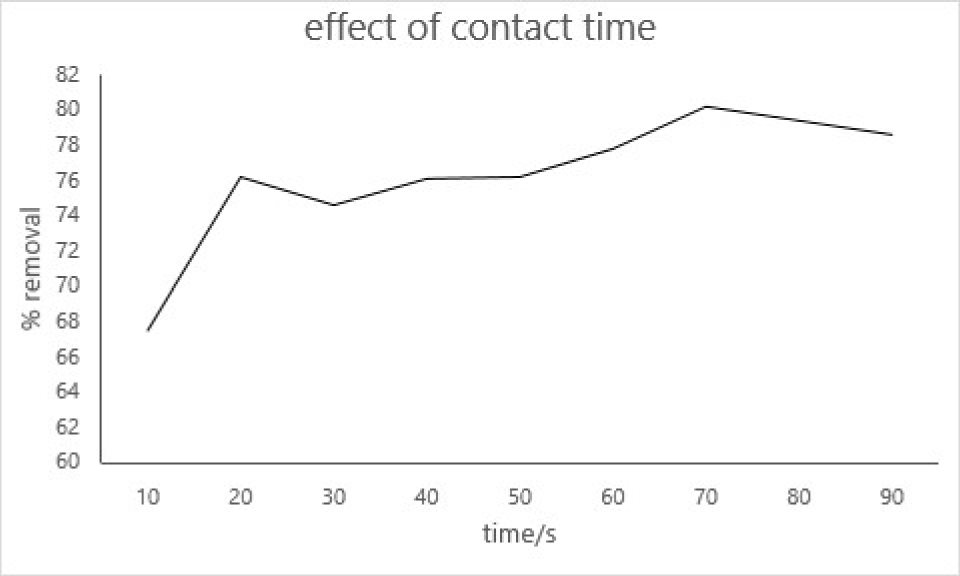


Figure 4. 4: Effect of contact time in removing Pb (II) ions

4.4 KINETIC STUDIES

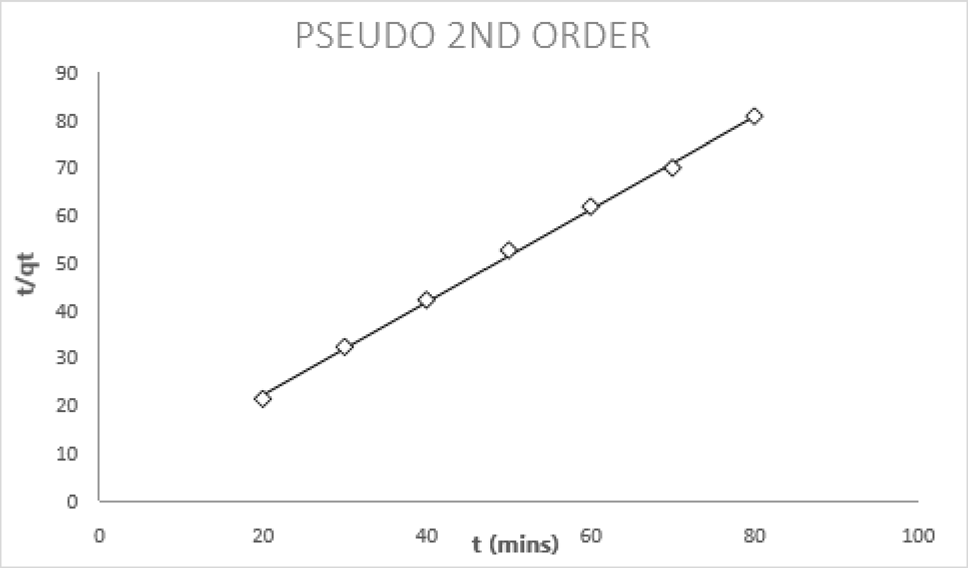


Figure 4.5: Pseudo second order kinetics

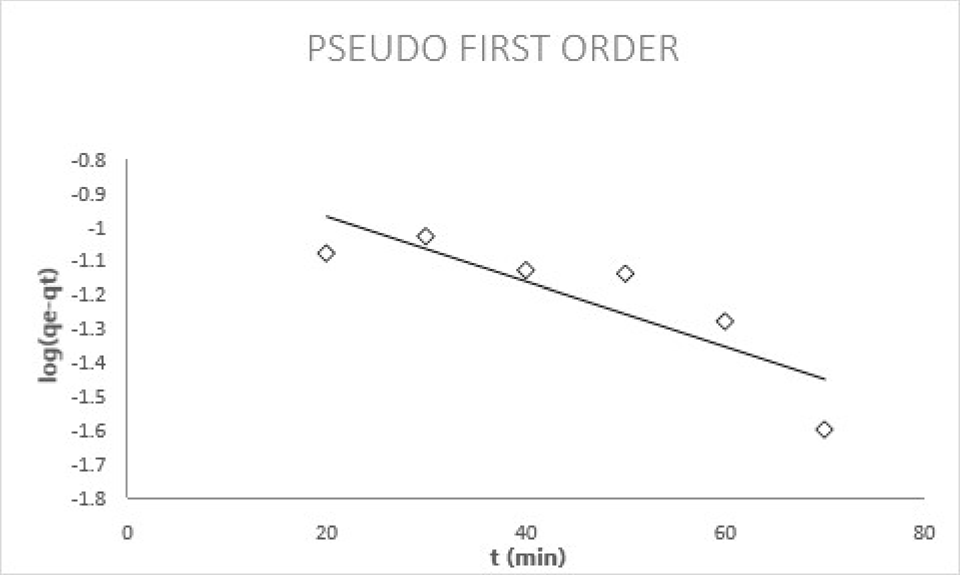


Figure 4.6: Pseudo first order kinetics

4.5 ADSORPTION STUDIES

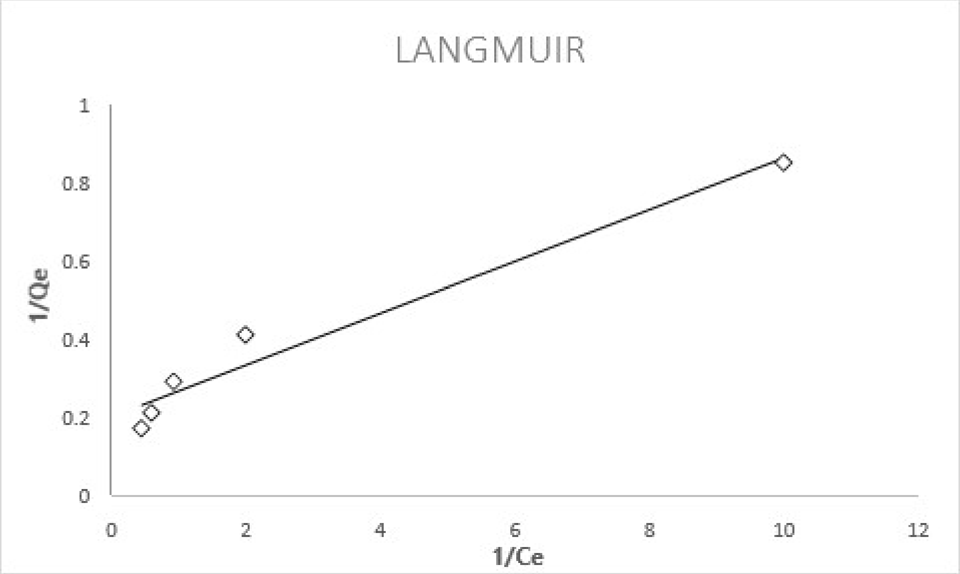


Figure 4.7: Langmuir adsorption isotherm

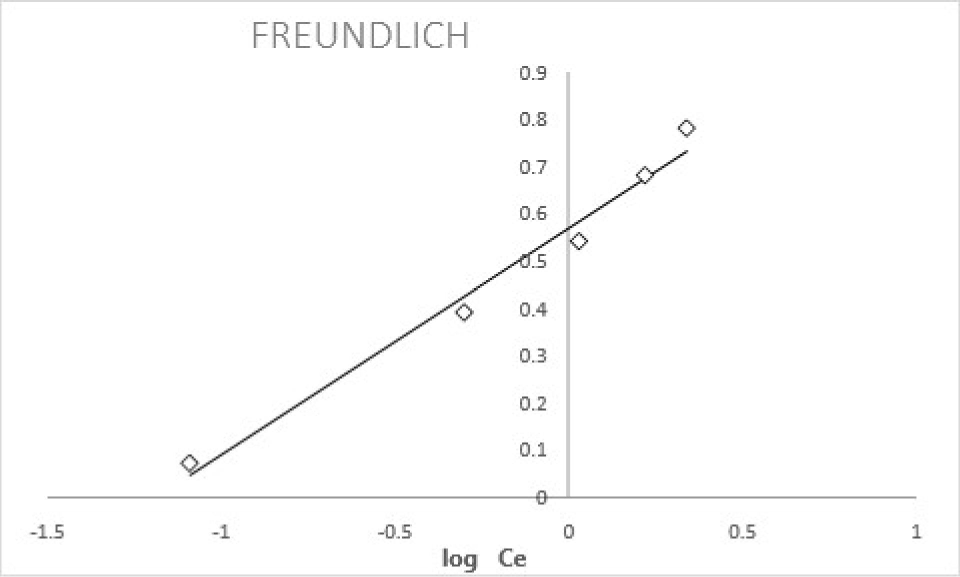


Figure 4.8: Freundlich adsorption isotherm

4.6 PARAMETERS FOR KINETIC AND BATCH ADSORPTION STUDY MODELS

Langmuir	q_m (mg/g)	4.9826
	K_a (L/mg)	0.0133
	R^2	0.9622
Freundlich	1/n	0.4801
	K_f	3.7051
	n	2.0829
	R^2	0.9806

Pseudo first order	qe	0.1667
	K_1	0.0221
	R^2	0.7412
Pseudo second order	qe	1.0252
	K_2	0.3566
	R^2	0.9986

4.7 RESULTS FOR SAMPLE TREATMENT

Parameter	Before treatment	After treatment		
		Biochar Adsorbent	Commercial Adsorbent	WHO*/SAZ Standards
pH	8.55	6.50	7.33	6-9
TSS	39.43	12.80	13.07	<50
TDS	466	442	295	<1500
Pb	0.1702	0.0010	ND	0.1
Cd	0.0944	0.0034	ND	0.003*
As	0.1121	ND	ND	<4

CHAPTER 5: DISCUSSION

5.1 Introduction

This chapter focuses on discussing the results that are tabulated in the previous chapter relating the observations and the trends to theory and findings from other studies that have used similar adsorbents.

5.2 Characterization of physical properties

The spectrum from figure 4a shows several peaks ranging from 1042 cm^{-1} to 3640 cm^{-1}; which could define an overlapping between –OH and –NH stretching, and C–O and N–H vibrations, hence proving the presence of hydroxyl groups and amine groups on the surface of the sawdust. The hydroxyl groups are an indispensable component of sawdust, thus emphasizing the importance of biochar in attracting heavy metal ions. Figure 4b which is an FTIR spectra of biochar showed a combination of peaks corresponding to various functional groups such as hydroxyl (-OH) groups at around 3400-3500cm-1, and carboxyl (-COOH) groups at around 1600 cm-1. The presence of these functional groups enhances the biochar's cation exchange capacity and ability to absorb positively charged ions. Table 4.1 shows the various physical properties of the prepared biochar, i.e. ash content, fixed carbon, and moisture content. Calculated ash content for the biochar was found to be relatively low at 0.79%. Ash content has an influential role in affecting the quality of biochar produced. Very high ash content can lead to clogging of the pores on the biochar such that the surface area of the biochar becomes reduced (Scroder E et al, 2006). Fixed carbon content is highly affected by the amount of cellulose and lignin content that can be converted to carbon. The adsorbent had a high amount of fixed carbon, which enhances the sorption capacity of the adsorbent (Ingole et al,2016). Moisture content is dependent on the concentration of the activator. The moisture content of biochar was fairly high at a concentration of 0.2M KOH used. This is due to the process of residual pyrolysis and organic minerals on the surface of the adsorbent which gets better with high activator concentrations. The high activator concentration increases the amount and volume of pores, thus increasing the surface area, resulting in an increase in the performance of adsorbent to absorb water from the air (Maulina S, Iriansyah M 2017). The values presented in Table 4.1 show that the prepared biochar meet the requirements of the National Industrial Standards 06-3730-1995.

5.3 Characterization of process parameters

5.3.1 Effect of contact time

The effect of contact time on the removal of Pb (II) on the adsorbent was studied from an initial concentration of 10ppm and 0.2g of the adsorbent. The results were presented in fig 4.4. The removal of Pb (II) rises rapidly at first due to the availability of more surface sites. The nature of adsorbent and its available sorption sites affects the time needed to reach equilibrium. For biochar this time is 70mins. The study was continued up to 90mins with a noticeable exponential decrease in removal efficiency after 70mins. This is due to the diffusion of the metal ions into the inner part of the adsorbent. As a result, active sites available for adsorption are removed and the removal efficiency is reduced.

5.3.2 Effect of adsorbent dosage

The dependence of varying adsorbent dose on the adsorption of Pb (II) was studied at a dose range of 0.05 to 0.25g of biochar. The percentage removal of Pb (II) increased from 96.66 to 97.6% when the adsorbent dosage was increased from 0.05 to 0.2g. This is a result of the additional active sites that were introduced due to an increase in the surface area of the adsorbent. However, there was a sharp decrease afterward in the percentage amount of Pb (II) that was adsorbed when the adsorbent dosage was increased to 0.25g. This suggests that a dosage of 0.2g can produce enough active sites sufficient for Pb (II) removal. Also, further increase in dosage may perhaps result in an increase in adsorption density which causes an aggregation of adsorption sites hence limiting the capacity for effective adsorption (Mangale, 2013).

5.3.3 Effect of initial concentration

The efficiency of Pb (II) removal is affected by the initial metal ion concentration, with decreasing removal percentages as concentration increases from 10 to 50 mg/l. An adsorbent dosage of 0.2g was maintained for all the adsorbents considered for this study. This effect can be explained as follows: at low metal ion/adsorbent ratios, metal ion adsorption involves higher energy sites. As the metal ion/adsorbent ratio increases, the higher energy sites are saturated and adsorption begins on lower energy sites, resulting in a decrease in the adsorption capacity (Kardivelu and Namasivayam,2003).

5.3.4 Effect of pH

Adsorption is a pH-dependent process and the effect of pH on the removal of Pb (II) was investigated at a range of 3-11. Maximum adsorption was observed at pH 5. At low pH values, there is a large availability of H^+ ions and these compete with the Pb (II) for active sites on the adsorbent thus consequently causing lower adsorption. Additionally, due to high positive charge density on the surface sites, electrostatic repulsion will be high during the uptake of metal ions resulting in lower removal efficiency. As the pH increases, the concentration of H^+ ions decreases progressively and the surface charge of the adsorbent becomes negative favouring the uptake of the positively charged metal specie. It has also been observed that at pH above neutral pH, adsorption is not the only process responsible for the removal of the Pb (II) ions as precipitation occurs and hydroxides like $Pb(OH)^+$, $Pb(OH)_2$, $Pb2(OH)_2^{2+}$ and $Pb(OH)^-{}_3$ are produced (Ben-Ali et al, 2017).

5.4 Portable water treatment

5.4.1 pH

From Table 4.3, the pH of the water was 8.55 before treatment and it was reduced to 6.50 after treatment with biochar. After treatment with a commercial adsorbent, the pH of the water was reduced to 7.33. Water treatment with all biochar as adsorbent gave a pH that falls within the recommended acceptable range for portable water (6-9) according to SAZ guidelines. The results show a similar trend as the findings by Aarti Sownya et al 2018 on the use of a carbon-based waste material as an adsorbent for water treatment.

5.4.2 TDS and TSS

From the study conducted it was observed that the initial TDS was 466 mg/l. After water treatment with biochar, the TDS was reduced to 442mg/l. The TDS of the water before and after water treatment was found to be within the SAZ permissible limit for portable water as shown in Table 4.3. The SAZ set a standard of <50mg/l for total suspended solids. Although the TSS of the water was below the set standard before treatment, the TSS value was however reduced to 12.80mg/l after water treatment using the biochar adsorbent. The observed decrease in the TSS and TDS values indicate improvement in the water quality.

5.4.4 Metal ion adsorption

Adsorption was done on the water to quantify the extent of adsorption capacity of the prepared adsorbent on other metal ions, i.e., Cd and As. A great adsorption capacity was observed on As which initially was found to have a concentration of 0.1121mg/l.

After treatment with the adsorbent, no arsenic ions were detected. Treatment with a commercial adsorbent also resulted in notable removal of cadmium and lead ions. The initial concentration of lead ions was above the required SAZ limits at 0.1702mg/l but was reduced to 0.0010mg/l after treatment with the biochar. Generally, sawdust biochar showed a considerably great behaviour in increasing the quality of the portable water.

5.5 Adsorption studies

The adsorption isotherms express the relation between the amount of adsorbed metal ion per unit mass of adsorbent and the metal ion concentration in the solution (Babalola et al, 2012). The models are used to describe the interactive behaviour between the adsorbate and adsorbent and also for investigating the mechanisms of adsorption. The equilibrium data of the adsorption process for this study was described by fitting the data with different isotherm models. The assigning of the isotherms was based on the highest R^2 value.

The results of the study were tested using Freundlich and Langmuir isotherm models and are presented in Figures 4.7 and 4.8. According to the correlation (R^2) values, lead adsorption using the sawdust biochar fitted best the Freundlich isotherm. Freundlich equation predicts that the Pb (II) concentration on the adsorbent will increase as long as there is an increase in the Pb (II) concentration; this is compatible with the experimental results. The Freundlich isotherm model assumes neither homogeneous site energies nor minimal levels of sorption. It has been shown to be consistent with the exponential distribution of active centers, which is characteristic of heterogeneous surfaces (Ho ;2005). A dimensionless separation factor RF defines the important element of the Freundlich isotherm (1/n). This is indicative of the isotherm shape, which predicts whether an adsorption system is favorable or unfavorable (Mohammad et al, 2000). The magnitude of 1/n indicates the nature of the adsorption where; 1/n =0 (irreversible), 0<1/n<1 (favourable) and 1/n >o (unfavourable). The value of 1/n for the adsorption of Pb (II) with the Composite was obtained as 0.4801. It can therefore be deduced that the adsorption of Pb (II) on biochar was favourable since $0<\frac{1}{n}<1$.

5.6 Kinetic Studies

From the experiments that varied contact time, it can be deduced that, for the adsorbent, adsorption reached equilibrium after approximately 50-70 minutes. After 70 minutes it was observed that there was negligible change in the removal percentage and therefore the reaction was taken as having reached a steady state at that point. After 60 minutes there was a slightly greater increase in the removal percentage. This was a result of the release of Pb (II) ions from adsorption sites and into the solution as the interactions between the biochar and the metal ions might have been weaker.

The correlation coefficient of the linear regression of pseudo first order equation to the data was 0.7412 for adsorption of Pb (II) the biochar. When the data points were fitted with the second order linear regression, the trend line gave an R^2 value of 0.9986. This value indicates a better fit in pseudo second order than in the other kinetic model. From the regression analysis, the value of pseudo second order rate constant was calculated to be 0.3566g/mg.min. The conformance of the adsorption data to the pseudo second order linear regression meant that the adsorption process was based on the assumption that the rate limiting step may have been chemisorption involving forces through the sharing or exchange of electrons between adsorbent and adsorbate (Chang and Tsai, 2003). The implication of this is that the surface of the adsorbent likely contains heterogeneous and homogeneous active sites (Azizian, 2004

CHAPTER 6

6.1 CONCLUSION

The potential use of biochar as an adsorbent for water treatment was studied. The main objectives were to evaluate its effectiveness in water treatment and check efficiency using adsorption studies. After water treatment, the water sample was analysed for parameters like As, Cd, and Pb and all were found to be greatly reduced. The adsorption characteristics have been examined at different contact times, initial Pb (II) ion concentrations, initial adsorbent dosage, and pH. The increase in Pb (II) concentration results in a decrease of percent removal of Pb (II). The equilibrium time for the adsorption process was 60 minutes. The percent removal of lead increased with an increase in the adsorbent dosage up to 0.2g of powder per 50ml of solution. The data for the adsorption fit well with the Freundlich isotherm model. The kinetics of the Pb-sorption rate was best explained by the pseudo-second-order kinetic equation. Overall, sawdust effectively reduces metal ions in water and its proper utilization has the potential as an adsorbent, even, for wastewater treatment at domestic and industrial applications.

6.2 RECOMMENDATIONS

The present study can be further done to assess the effectiveness of using this adsorbent in microbiological treatments. Furthermore, adsorption of burgeoning and prevalent water pollutants such as mercury, cyanide, and chemical chiral pollutants can be studied. Necessary is also research to extend the reuse of the adsorbent over several cycles and recovery procedures for utilization or valotization of spent adsorbent.

REFERENCES

Abrahim.G.M and Parker.R.J (2008) Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand.Environmental Monitoring and Assessment. 136(1-3), 227- 238.

Ahluwalia , S.S and Goyal, D. (2007). Microbialand Plant derived biomass for removal of heavy metals from wastewater. Bio resource Technology, 98(12), 2243 – 2251.

Antony.R.S, Nikhil.G.N and Murali Krishman.K (2019) Determination of heavy metals in water samples using inductively coupled plasma mass spectrometry (ICP-MS). Environmental Monitoring and assessment. 191(8), 498 https: //doi.org

Azizian S. (2004), Kinetic models of sorption: A theoretical analysis, Journal of colloid and interface science, 276: 2331-2338.

Babalola J.O, Omorogie M.O, Unuabonah E.I, Song W and Gong J.R. (2012), Efficient chromium abstraction from aqeous solution using a low cost biosorbent: Nauclea diderrichii seed waste in press, available at http://dx.doi.org/10.1016/j.jscs.2012.09.2017.

Baker, R. W (2004) Membrane Technology and applications. John Wiley and sons https:// www.amazon.com.

Ben-Ali S, Jaouali I, Souissi-Najar S and Ouederni A. (2017), Characterisation and adsorpiotn capacity of raw Pomegranate peel adsorbent for Copper removal, Journal of Cleaner Production,142: 3809-3821.

Bose, P. and Bose, M.A(2010). Control of chromium environmental contamination by adsorption. Indian Journal for Environmental Protection, 30(5), 431 – 437.

Burham, N. (2009). Determination of heavy metals in water samples From Nile River, Egypt International Journal of Environmental Science and Technology, 6(4), 651-662.

Cabrera – Lafaurire, W.A., Roman, F.R. and Hernandez – Maldonado, A.J. (2012). Removal of salicyclic acid and carbamazepine from aqueous solution with y – zeolites : Equilibrium, Kinetics and breakthrough studies for drug operation. Journal of Environmental Chemical Engineering, 2(3), 1561 – 1570.

Chang C.Y. and Tsai W.T. (2003), Adsorption of naphthalene on zeolite from aqeous solution, Journal of colloid and interface science, 260: 273-279.

Dai, Y. Zhang, N., Xing ,C., Cui, Q. and Sun, Q.(2018). The adsorption, regeneration and engineering applications of biochar for removal of heavy metals from wastewater. Water science and Technology, 78(9), 1844 – 1859.

Dhote,J. and Matiendra , M.(2010). Heavy metal removal from wastewater using water hyacinth.Journal of Environmental Research and Development 5(2), 363 – 370.

Diparthy, S., Veloga, N. and Datla, R. (2020). Removal of heavy metals from industrial wastewater using adsorption technique. Environmental Technology and Innovation, 18, 100642

Drioli, E and Giorno, L. (2009) Membrane Engineering for the Treatment of gases: Volume 1 Gas – Separation Problems with membranes. El sevier. https:// www.amazon.com.

Gryta, M and Karakulski ,K.(2018) Nanofiltration principles and applications CRC Press

Gupta P.K (2010) Elements of Biotechnology. Rastogi Publications: Meenit

Ho Y.S. (2005), Effect of pH on lead removal from water using tree fern as the sorbent, Bioresour. Technol. 96: 1292–1296

https://doi.org /10.1039/c9ra05646g

Ingole R.S et al, (2016), Adsorption of phenol onto banana peels activated carbon,00(0):1-11

Kanwal. F, Imran. M, Mahmood. Q, Hayat. Y and Waseem. A (2019). Analytical techniques for the determination of heavy metals in water. Principles and applications.Environmental Monitoring and Assessment 191(8), 510. https: //doliary/10.1007/5/066/019-7594.Z

Kazi.T.G , Arain. M.B, Jamali. M.K, Jalbani.N, Afridi.H.I and Sarfrac.R.A (2009). Assessment of water quality of polluted lake using multivariate statistical techniques: A case study. Ecotoxicology and Environmental Safety 72(2), 301 – 309

Kiflom, G. and Tarekegn, B. (2018). Determination of some selected heavy metals in fish and water samples from Hawassa and Ziway lakes. Science Journal of Analytical Chemistry, 3(1).

Labal,J.,Wattoo, F.N., Wattoo,M.H.S., Malik,R. , Tirmizi, S.A, Imran, M. and Haq,Z.(2021).Removal of heavy metals from aqueous solution using Zea mays as biosorbent.Arabian Journal of Chemistry 14(1), 102843.

Li.Y, Du.Q, Liu.T, Sun.J and Wang, X(2016). Adsorption behaviour of heavy metal ions by mesoporous materials prepared using cetyltrimethylammonium bromide as template. Microporous and Mesoporous materials, 226, 43-49

Majumdar. S, Saha. S, Datta.J.K and Mondal.N.K(2018) Anodic stripping voltammetric determination of heavy metals in water samples: A case study from Burdwan west Bengal, India. Environmental monitoring and assessment 190(3), 138 https:// doi.org

Mangale S.M, Chonde S.G, and Raut P.D. (2012), Use of Moringa Oleifera (Drumstick) seed as a natural adsorbent and an antimicrobial agent for ground water treatment, Research Journal of Recent Sciences, 1(3): 31-40.

Maulina S, Iransyah M. (2017), Characteristics of AC resulted from pyrolysis of the oil palm fronds powder

Mohammad A, Rifaqat A.K.R., Rais A and Jameel A. (2000), Adsorption studies on citrus reticulata (fruit peel of orange): Removal and recovery of Ni(II) from electroplating wastewater, Journal of Hazardous Material, 79: 117–131.

Mohan, D. and Pittman , C.U. (2001). Heavy metal removal from aqueous solutions using activated carbons derived from agricultural waste biomass. Bioresource Technology, 76(1), 33-42.

Parsi, Z. (2020) Heavy metal removal from aqueous solutions using agricultural waste – based adsorbents. Journal of Environmental Management 253, 109741.Welz, B. and Spring, M. (1999) Atomic Absorption Spectrometry (3rd Edition Willey – VCH.

Rana. A, Sindhu.M, Kumar. A, Dhaka.R Chabar.M, Singh. S and Nain.L(2021) Restoration of heavy metal – contaminated soil and water through biosorbents: A review of current understanding and future challenges.physiol.Plan CrossRef: Pubmed.

Rashed, MIN (2013). Adsorption Technique for the removal of organic pollutants from water and wastewater.

Rashmi V and Pratima D Heavy metal water pollution – A case study – RRST : Bilaspur

Rathore , D. and Kumar, V. (2016). Removal of heavy metals from wastewater using low- cost adsorbents Environmental Science and Pollution Research, 23(19) , 19376 - 19390

S. Kipton, S.O.., Bruce. I.O, Wayne, W and Steve, D. (2006). Drinking water: lead, University of Nebraska – Lincoln Extension, Institute of Agriculture and Natural Resources.

Sarici – ozdermir, C.(2018). Removal of heavy metals from aqueous solutions by biorsorption on olive tree(Olea europaea L.) leaves. International Journal of environmental Science and Technology, 15(6), 1271 – 1284

Scroder E et al (2006) Experiment on the generation of activated carbon from biomass Institute for nuclear and energy technologies for schungs karlsrube germany, 106-111.

Shen, Z., Jin, F., Wang, F., McMIllan, O. and Al – Tabbaa, A. (2020). Soil washing with novel biobased washing agents for heavy metal extraction. Journal of Environmental Management, 261, 110266

Shikha, D and Singh.P (2021) Insitu phytoremediation of heavy metal- contaminated soil and groundwater: A green inventive approach. Environ sci. Pollut. Res

Uchimiya, M., Lima, .M and Thomas, K. W (2010). Phosphorus adsorption by biochars: potential mechanisms. Journal of Environmental Quality, 39(4).

Vidu.R, Matei.E, Predescu.A.M, Alhalaili.B, Pantiliman. C, Tarcea. C and Predescu.C. Removal of heavy metals from wastewaters: A challenge from current treatment methods to nanotechnology Applications. Toxics, 8,101

Wang, S. and Chen, J.P.(2009). Biosorption of Leavy metals by saccharomyces cerevisiae: A review Biotechnology and Advances , 27(2), 195 – 226.

Wang,S. , GaO,B. , Zimmerman, A.R, Li, Y., Ma, L. , Harris, W.G and Migliccio, K.W .(2016).Removal of arsenic by magnetic biochar prepared from pinewood and natural haematic. Bioresource Technology, 216, 836 – 843.

Wang. J and Wang. S (2019) Preparation, modification and environmental application of biochar: A review: J Clean Prod.

Xiang, M., Li, Y., Yang, J., Li, F., Hu, B and CaO.Y(2020). Assessment of heavy metal pollution in soil and classification of pollution Risk management and control zones in the industry developed city. Environ.Manag

Zhang, C. (2019) Adsorption performance of antimony by modified. 31645 – 31653

Zhao, Y and Zhang, X. (2020) The role of clay minerals in the fate and transport of heavy metals in soil environments: current pollution reports, 6(3).