# PYROLYTIC SYNTHESIS AND CHARACTERIZATION OF BIOCHAR DERIVED FROM RICE HUSKS FOR REMOVAL OF SELECTED HEAVY METALS FROM WATER

# ALICE WAITHIRA NDEKEI

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# Pyrolytic Synthesis and Characterization of Biochar Derived from Rice Husks for Removal of Selected Heavy Metals from Water

Alice Waithira Ndekei

A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry of the Jomo Kenyatta University of Agriculture and Technology

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### DECLARATION

This thesis is my original work and has not	been presented for a degree in any other
University.	
Signature	Date
Alice Waithira Ndekei	
This thesis has been submitted for examination	with our approval as supervisors
Signature	Date
Dr. Peter Gititia Muigai, PhD	
JKUAT, Kenya	
Signature	Date
Dr. Njagi Njomo, PhD	
UON, Kenya	
Signature	Date
Dr. Damaris Mbui, PhD	
UON, Kenya	

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### **DEDICATION**

This work is dedicated to my husband, Shadrack Kariuki, my children; JoyEmily Nyambura, Victor Njoroge, Hellen Njeri, and Dickson Ndekei, Njoroge and Ndekei`s families.

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## ABBREVIATIONS AND ACRONYMS

AAS	Atomic Adsorption Spectroscopy
AC	Activated Carbon
ATSDR	Agency for Toxic Substance and Disease Registry
BET	Brunauer Emmert Teller
BC	Biochar
BCs	Biochars
FT-IR	Fourier Transform Infra-Red Spectroscopy
GHGs	Greenhouse gases
IARC	International Agency for Research on Cancer
PAC	Percentage Ash Content
n	Adsorption intensity
RO	Reversed Osmosis
RH	Rice Husk
RHB	Rice Husk Biochar
RHBT	Rice Husk Biochar Treated
RHBT500	Rice Husk Biochar Treated pyrolyzed at 500°C
SEM	Scanning Election Microscopy
WHO	World Health Organization

#### ABSTRACT

Accumulation of heavy metals such as lead, copper, and cadmium released by various industries, poses a potential ecological risk of contamination due to their persistent nature and nonbiodegradability. A remedial action was needed to mitigate this risk, adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2</sup> was carried out using eco-friendly and cost-effective activated biochar from rice husk as a potential adsorbent. In order to evaluate the efficiency of rice husk biochar in the removal of lead, copper, and cadmium in aquatic systems. The rice husk (Oryza sativa) biochars were pyrolyzed at different temperatures between 300 - 700 °C in a muffle furnace. The optimal biochar was produced at 500°C, which was later activated chemically using KOH and ZnCl<sub>2</sub>. Characterization of the biochars was achieved by use of Fourier Transform Infrared, Scanning electron microscope for the surface morphology and Brunauer Emmert Teller for the surface area determination. The batch adsorption studies were conducted to determine the best conditions for effective and efficient metal ions uptake. The Infrared spectra of the rice husk biochars were characterized by O-H, -CH, C=C, and C=O functional groups, which played a key role in contributing to the adsorption process. The morphology of chemically activated optimal biochar indicated it was the best adsorbent. The Brunauer Emmert Teller (BET) results revealed that specific surface area increased with pyrolytic temperature, was the highest in RHBT600 and lowest in unpyrolyzed rice husk. The optimal contact time for adsorption for Pb<sup>2+</sup>and Cu<sup>2+</sup> was observed to be 60 minutes while Cd<sup>2+</sup> was 30 minutes at all initial metal ions concentrations of 1, 2, and 4 mg/L. Optimum adsorbent dosage of all three metals was found to be 0.250 g, initial metal ion concentration for  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  was 2 mg/L. The optimal pH for the three metal ions, Pb,  $Cu^{2+}$  and  $Cd^{2+}$  was (7.0) and the optimal adsorption temperature was found to be 35°C for all metal ions. The pseudo second order was found to fit well because it had relatively high linear regression coefficient values for  $Pb^{2+}$  (0.995),  $Cu^{2+}$  (0.7906) and  $Cd^{2+}$ (0.999). The equilibrium fitted the Langmuir equation well, with higher linear regression coefficient values for  $Pb^{2+}(0.98632)$  and  $Cu^{2+}(0.9889)$  indicating monolayer adsorption on a homogeneous material. The Cd<sup>2+</sup> metal ion removal best fitted to the Jovanovich isotherm model on a monolayer adsorption with  $R^2$  value of 0.9994. The Freundlich adsorption process was favorable for  $Cu^{2+}$  and  $Pb^{2+}$  because n>1 that is  $Pb^{2+}$  (2.3229) and  $Cu^{2+}$  (1.82615) indicating a strong bond between rice husk biochar and the two metal ions but, for Cd<sup>2+</sup> was 0.23496 indicating normal adsorption since n < 1 and linear regression coefficient values for  $Pb^{2+}$ (0.9675), Cu<sup>2+</sup> (0.85181) and Cd<sup>2+</sup> (0.39893). This indicated that Pb<sup>2+</sup> and Cu<sup>2+</sup> underwent both monolayer and multilayer adsorption, unlike the  $Cd^{2+}$  ion. The chemically activated rice husk biochar has proved to be a viable low-cost adsorbent with excellent adsorption ability in the removal of heavy metal ions.

#### **CHAPTER ONE**

#### **INTRODUCTION**

#### 1.1 Background of Study

Due to their persistent nature and non-biodegradability, heavy metal accumulation from various industries poses a potential ecological risk of contamination (Cui *et al.*, 2015). This contamination has accelerated the degenerative changes of water quality and environmental problems over the decades. According to Daffalla *et al.* (2020), removing heavy metals from fresh water bodies is an imperative task. As a result, various conventional methods for removing heavy metal ions from wastewater have been used, including membrane filtration, which has been used in industries around the world for wastewater treatment. Membrane filtration, according to Lech *et al.* (2022), is a selective barrier process that separates two different phases, allowing certain components to pass while retaining others. It is a critical technology that is based on a sieving mechanism and the chemical interaction of separated components with a membrane (Zirehpour and Rahimpour, 2016). The disadvantages of membrane filtration include sludge formation and the high operating costs of membrane systems (Schlosser, 2014).

Ion exchange processes, whether using natural or synthetic exchange resin, have been widely used for wastewater treatment. Because of its effectiveness in removing heavy metals from solutions, synthetic resin is the most commonly used (Maingi, 2018). According to Renu *et al.* (2017b), ion exchange has a high treatment capacity, a high removal efficiency, a fast kinetic, and the ability to exchange cations with metals present in wastewater. However, the method is prohibitively expensive in the purification of large amounts of wastewater containing low concentrations of heavy metals (Kurniawan *et al.*, 2006).

Chemical precipitation is a proven technology for the removal of metals, other inorganic and suspended solids. Calcium hydroxide and sodium hydroxide have been used to precipitate copper, lead, and cadmium (Kamau *et al.*, 2020). The chemical precipitation is costly due to the formation of secondary waste such as gypsum and metal hydroxide sludge (Wang *et al.*, 2005). On the other hand, most researchers have put a lot of attention into the adsorption technique, which has stood out as the most effective and efficient technique for the removal of pollutants from water. Researchers have investigated some agricultural biomasses which they have used to produce biochar as adsorbents, for example, Kenaf (Saeed *et al.*, 2021), sugarcane bagasse (Saleh *et al.*, 2020) and the banana peel (Taralgatti, 2016).

Rice (*Oryza sativa*) is a food grain that forms a staple diet and is one of the most widely consumed staple food throughout the world by the human population (Mohan *et al.*, 2006). Rice farming results in large amounts of rice straws and husks being produced as abundant lignocellulosic waste material. The burning of these residue wastes may cause air pollution problems that could affect human health negatively. As a remedial measure, alternative methods for the disposal of these wastes have been suggested. Rice husk wastes can be used profitably through value addition and for national economic benefit by synthesizing biochar from the rice husks for the removal of heavy metals in aquatic solutions.

Biochar (BC) is a carbon-rich solid product that can be obtained through pyrolysis or carbonization processes. Pyrolysis is the direct thermal decomposition of organic materials or biomass under anaerobic conditions at temperatures below 700°C. Biochar is created in three stages: pre-pyrolysis, main pyrolysis, and the formation of carbonaceous carbon (Lee *et al.*, 2017b). The first stage from ambient temperature to 200°C, according to Tomczyk *et al.* (2020), involves the evaporation of moisture and light volatile matters. Moisture evaporation causes weak bonds to break and the formation of hydroperoxide –COOH and CO groups. The second stage occurs at a temperature of 200 - 500°C, where hemicellulose and cellulose devolatilize and decompose at a high rate. The final stage (above 500°C) is attributed to lignin and other

organic matter with strong chemical bonds degrading. The process yields a combination of solid (biochar), liquid (bio-oil), and gaseous (syngas) products. The pyrolysis temperature has a significant impact on the physiochemical parameters of the biochar such as surface area, pH, and functional groups. Rice husk biochar is a suitable adsorbent due to its advantageous properties such as high specific surface area, porous structure, enriched surface functional groups, and mineral components. These properties increase its affinity to adsorb molecular ions, allowing it to be used in a variety of toxicological remediation strategies. The utilization of rice husks in the production of biochar would reduce solid waste disposal problems and enhance the treatment of water bodies. The biochar reduces the bioavailability and leaching potential of heavy metals in water and soil (Devi and Saroha, 2014). Therefore, conversion of rice husk biomass into biochar as the sorbent is a "win-win" solution for both improving waste management and protecting the environment (Inyang *et al.*, 2012 and Zheng *et al.*, 2010).

#### **1.2** Statement of the Problem

Heavy metals in the environment have become more prevalent in recent years, as a result of industrialization, high input agriculture such as pesticides, herbicides, and fertilizers, surface run-off, and deep percolation of water containing heavy metals from industries and garages, posing a threat to public health and aquatic life. To protect current and future generations, heavy metal-contaminated wastewater must be treated before discharge into the environment. Previous research has found that conventional treatment processes have significant drawbacks, such as high capital and operational costs, incomplete removal, high energy requirements, and the production of toxic sludge, which is more difficult to treat and dispose off. As a result, adsorption has emerged as one of the alternative wastewater treatment methods. Some adsorbents, such as activated carbon, are expensive and unsustainable, particularly in developing countries. Therefore, the search for low-cost adsorbents with high metal-binding capacity is essential. Biosorbents are quite promising in this regard because they are abundant, cost-effective, and play an important role in the removal of metal ions from aquatic systems. The advantages of this technique include biomaterial reusability, low operating costs, improved selectivity for specific metals of interest, efficient removal of heavy metals from effluents, short operation time, and metal recovery and reuse.

#### **1.2.1** Production of Rice in Mwea Irrigation Scheme

About 95% rice production in Kenya is grown under irrigation in paddy schemes managed by the National Irrigation Board (NIB). The rice in Kenya is mainly produced by small-scale farmers in Central (Mwea), Western (Bunyala), Coast (Tana delta, Msambweni) and Nyanza provinces (Ahero, West Kano, Migori and Kuria). Mwea irrigation scheme accounts for 80 percent of Kenya's rice, playing a major role in the nationwide supply of grain. The total annual rice production in the scheme is estimated at 113,000 metric tons, with a potential for enhanced production.

#### 1.3 Justification

The toxicity, long biological half-life, bioaccumulation in the food chain, and nonbiodegradability of heavy metals such as lead, cadmium, copper, and zinc in drinking water at concentrations above allowable levels have negative effects on the environment, human health, and animals (Çeribasi and Yetis, 2001). Hossain *et al.* (2012b), reported that reactive free oxygen generated by excess copper in the blood system damages vital substances in the body such as protein, lipids, and Deoxy-ribonucleic Acid (DNA). Lead exposure also causes developmental neurotoxicity, reproductive dysfunction, and kidney, blood, and endocrine system toxicity (Sanborn *et al.*, 2002). The abovementioned heavy metals and their metalloids target the liver, kidneys, lungs, brain, and bones once absorbed through various path ways (Assi *et al.*, 2016). Therefore, there is a need to remove these pollutants from aquatic systems, preferably using a non-hazardous, cost-effective adsorbent with high adsorptive capacity, and one that is highly efficient like the rice husk biochar. Recent studies have shown that biochar in collaboration with chemical activation has high adsorption and absorption abilities, which play a great role in the removal of contaminants from effluents (Ameloot *et al.*, 2013). This study will provide knowledge on how to use rice husks' biochar as an adsorbent for the removal of some heavy metals. The findings on the adsorption capacity of heavy metal by chemically activated rice husk biochar will provide reference material for future researchers in developing remedial action on water treatment by using agricultural waste as an adsorbent.

#### 1.4 Null Hypothesis

The biochar derived from rice husk does not have high efficiency and adsorptive capacity for removal of lead, copper, and cadmium metal ions from contaminated water.

#### **1.5** Objectives of the Study

#### **1.5.1 General Objective**

To evaluate the efficiency of rice husk biochar in the removal of lead, copper, and cadmium in aquatic systems.

#### 1.5.2 Specific Objectives

- To synthesize and characterize of the biochar derived from rice husk using Fourier Transform Infrared spectroscopy, Scanning electron microscope and Brunauer Emmert Teller.
- ii. To determine the efficiency of biochar derived from rice husk in the removal of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  from water through optimization of adsorption conditions.
- iii. To determine adsorption kinetics and adsorption isotherm models of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$ , adsorbed by chemically activated rice husk biochar.

#### 1.6 Scope of Study

The study dealt with pyrolytic synthesis and characterization of the biochar derived from rice husk for removal of heavy metals from aqueous phase its efficiency, adsorptive capacity, and biosorption mechanisms.

#### 1.7 Limitation of Study

The present research did not deal with the removal of other contaminants such as organic and inorganic substances, pesticides, and pharmaceutic effluent waste from wastewater systems. The rice husk biochar was used for removal of heavy metal ions in synthetic pollutant not in real water samples. The biochar for adsorption of heavy metals was derived only from rice husk biomass, not from rice straws or any other biomass. The regeneration study of formulated rice husk biochar was not done. The batch adsorption mode process was used and not the continuous adsorption mode therefore, there is a need for comparison for the two models. The effect of variation of agitation speed on adsorption was also not done.

#### **CHAPTER TWO**

#### LITERATURE REVIEW

#### 2.1 Removal of Heavy Metals From Aqueous Solution

Researchers have developed various methods, which are cost-effective and efficient for the removal of heavy metals wastewater (Kurniawan *et al.*, 2006). The most common methods used to remove heavy metals from wastewater around the globe are ion exchange, electrolysis, chemical precipitation, membrane filtration, solvent extraction, reverse osmosis (RO), coagulation-flocculation, resin, nanotube, silica gel and activated carbon (Okoya *et al.*, 2020). These methods have their advantages and limitations. These processes also demonstrate some significant disadvantages such as high operation costs, high energy requirement, toxic sludge production and they differ in their effectiveness especially when metals are at very low concentrations in solutions (Juang and Shiau, 2000).

Lately, the adsorption technique has proven to be the most appropriate and co-friendly method for the removal of heavy metals, inorganic pollutants, organic pollutants, and other pollutants from aqueous solutions (Duwiejuah *et al.*, 2017). This is due to the specific characteristics of biochar and activated charcoal including, large specific surface area, porous structure, enriched surface functional groups such as hydroxyl, amides, thioester, phenolic hydroxyl, carbonyl groups, and mineral components. These properties increase its affinity to adsorb molecular ions thus making it possible to be used for various toxicological remediation strategies. Biochar as an adsorbent has a porous structure similar to activated carbon (AC). Activated carbon is the most commonly employed and efficient sorbent for the removal of a wide variety of pollutants from water throughout the world (Lelario *et al.*, 2017). Biochar compared with AC is a low-cost, and effective adsorbent even at low heavy metal concentrations, consumes less energy, shorter process time, less generation of toxic sludge, availability of a wide range of absorbents, and most importantly high removal efficiency (Hameed, 2006 and

Kurniawan *et al.*, 2006). The cost involved in the use of adsorption technology can be reduced because the adsorbent is cheap (Zafar *et al.*, 2020).

#### 2.2 Biochar

Biochar (BC) is a stable carbon-rich solid product obtained via pyrolysis or carbonization processes. The biochar is made from a range of biomass that have different chemical and physical properties. The diverse range of biochar applications depends on its physiochemical properties, which are governed by the pyrolysis conditions (heating temperature and duration) and the origin of feedstock (Enders *et al.,* 2012). Several agro-based materials have been widely investigated as adsorbents in water pollution control. Some of the biomass that has been previously used as adsorbents are outlined in this the next section.

The water hyacinth (*Eichhornia crassipes*) is a noxious weed that has attracted worldwide attention due to the rate of its spread and its congested growth, which leads to serious problems in navigation, irrigation, and power generation. Attempts to control the weed have proved to be costly with minimum results (Mahamadi, 2012). Water Hyacinth has demonstrated an amazing ability as an environmentally friendly, potential bio adsorbent, suitable and efficient material for adsorption of toxic heavy metals from the aquatic environment due to its poly-functional groups such as carboxyl and amine functional groups (Mahmood *et al.*, 2010). It was found to effectively remove zinc and chromium from industrial waste waters (Gakwavu *et al.*, 2007). The equilibrium bio sorption isotherms showed that water hyacinth possesses high affinity and sorption capacity for  $Cu^{2+}$  and  $Zn^{2+}$  ions, with sorption capacities of 99.42 mg  $Cu^{2+}$  and 83.01 mg  $Zn^{2+}$  per 1 g biomass, respectively. Therefore, the water hyacinth biochar is an alternative low-cost bio sorbent for the removal of heavy metal ions from aqueous media (Buasri *et al.*, 2012).

Sawdust has also been found to be a potentially, cheap and useful adsorbent for the removal of heavy metals from an aqueous solution. Sawdust was observed to contain

lignin and cellulose which easily trap impurities present in waste water and was found to efficiently remove  $Zn^{2+}$  ions from water (Sumint *et al.*, 2015). The main adsorption sites in sawdust biochar are carbonyl, hydroxyl, amine, and halide compounds which complex with metal ions in an aqueous solution. The active sites were found to effectively bind with  $Cr^{3+}$  ions either through electrostatic attraction or complexation mechanisms (Gunatilake, 2016). The adsorption of Pb<sup>2+</sup>, Cu<sup>2+,</sup> and Cd<sup>2+</sup> ions was found to agree with the order of electronegativity of the atoms, which are 2.33, 1.9, and 1.65 for Pb<sup>2+</sup>, Cu<sup>2+,</sup> Cd<sup>2+</sup> respectively. The adsorption of the metal ions with larger ionic radii was greater than those with smaller ionic radii.

Banana peels as discarded waste material are readily available and abundant in the local market and have been used to produce bio adsorbents through easy and environmentally friendly processes. Banana peel biochar (BPB) was found to contain very high specific surface, potential binding sites, and functional groups such as carboxylic acids. Hossain *et al.*, (2012a) revealed that BPB was used to remove  $Cu^{2+}$  ions from water and waste waters and was regenerated and reused seven times without reducing efficiency. The BPB was found to remove  $Co^{2+}$  and Ni<sup>2+</sup> from an aqueous solution (Abbasi *et al.*, 2013). The results were evaluated by the Langmuir isotherm, and indicated that the adsorption constant of  $Co^{2+}$  was 9.02 mg/g and for Ni<sup>2+</sup> it was 8.91 mg/g respectively. The study by Padilha *et al.* (2011), revealed that the kinetics of copper and lead uptake reached equilibrium in 10 minutes and extraction was successful above pH 3. Studies by Taralgatti (2016) found out that the removal of  $Cu^{2+}$  was removed at the lowest experimental solution concentration (2 mg/g) while 57.6% was removed at a higher concentration of the solution.

Rice husks are the by-products of rice, a major food crop in most developing countries including Kenya, and are an agricultural 'waste' material available in plenty in rice-producing regions. The Rice husk (RH) is abundant in lignocellulosic biomass and this

makes it suitable for biochar production. Lignocellulosic biomasses include those from agricultural residues (corn stover, crop straws, and bagasse), herbaceous crops, woody plants, forestry residue, waste paper, and other municipal green wastes that are mainly composed of cellulose, hemicellulose, and lignin (Mohan et al., 2006). Feedstock with high lignin content generally produces the highest biochar yields when pyrolyzed at moderate temperatures of 500°C (Demirbas et al., 2008). The rice husk is a versatile material with good adsorption properties and mainly consist of crude protein (3%), ash (including silica (17%), lignin (20%), hemicellulose (25%), and cellulose (35%) rendering it suitable for metal cation fixation (Krishnani et al., 2008). Rice husk biochar (RHB) has high porosity and an extensive surface area. Rice husk biochar has similar aspects as activated carbon and plays an important role in controlling contaminants in the environment. According to Yakout et al., (2016) 90% of toluene from pharmaceutical water waste was removed by rice husk biochar after a contact time of two hours. Akhtar et al. (2010), reported that activated rice husk biochar is very effective for removal of Pb, Cd, Zn, and Cu from aqueous solution over pH range (1-10) via batch adsorption techniques. According to Wong et al. (2003), rice husks modified with tartaric acid showed the highest binding capacities for copper and lead as indicated from Langmuir isotherm with the maximum sorption capacities of 29 and 27 mg/g at 27°C for copper and lead respectively. The study by Wong et al. (2003), investigated the removal of copper and lead by tartaric acid modified rice husk the adsorption capacity increased when pH was raised from 2 to 3. The results also indicated that adsorption was dependent on contact time, concentration, temperature, adsorbent dosage and agitation speed.

The feedstock properties such as particle size, ash content, silica content, can limit the practicality of its use in biochar production. These challenges are overcome by eliminating silica from the "char" before pyrolysis. However, under controlled decomposition conditions, amorphous silica with high reactivity, ultra-fine size, and large surface area is produced (Chandrasekhar *et al.*, 2003). The findings of Tan *et al.* 

(2015b), indicated that adsorption efficiency of biochar for removal of contaminants in aqueous systems tends to be influenced by certain characteristics such as ash removal treatment, pH, adsorbent loading, surface area/porosity, Cation Exchange Capacity (CEC) and temperature.

The ash content in rice husks biochar is more than 50% and creates a problem for pores development compromising its structure thus lowering biochar stability (Kimetu and Lehmann, 2010). The porosity of rice husk biochar can increase with time when the ash is dissolved and removed from the pores. According to Ahiduzzaman and Sadrul Islam (2016), the chemical activation of char by the use of zinc chloride assists in developing more pores on the surface area and porosity of biochar which improves its adsorption capacity and porosity.

The pH affects not only the adsorbent surface charge but also the degree of ionization and the speciation of adsorbent (Kołodyńska *et al.*, 2017 and Li *et al.*, 2013b). According to Abdel-Fattah *et al.*, (2015) and Oh *et al.* (2012), at low pH most of the functional groups present in biochar are protonated and are present in a positively charged form and they favor adsorption of anions. Lower adsorption is observed at low pH because of electrostatic repulsion, which occurs between cation contaminants and the positively charged biochar surface. Adsorption is enhanced at higher pH values as a result of competition among metal ions and protons for binding sites.

The dosage of the adsorbent has a great influence on the efficiency of adsorption Liu *et al.* (2020), reported that adsorption efficiency increases with an increase in the mass of biochar. The number of adsorption sites increases in line with the increase in adsorbent dosage. The higher the dosage of adsorbent the higher the adsorption because more surface and functional groups, which interact with the metals, are available on the adsorbent (Onyeji and Aboje, 2011). Yakout *et al.* (2016), observed that with chemical treatment, the biochar ash content and volatile matter decreases, while the surface area and micro porosity of the biochar increases. Tsai and Chen (2013), reported that the

adsorption of contaminants is an endothermic process and adsorption capacity increases with increasing pyrolytic temperatures from 500 - 700°C.

The rice husk biochar has been recognized as a multifunctional material that has shown good performance in various agricultural and environmental applications. Some advantages of rice husks biochar (RHB) as indicated in Figure 2.1, include: used as an effective adsorbent for waste water treatment, as a soil amendment to improve soil productivity, used in biofuels production, climate change mitigation, for carbon storage, and filtration of percolating soil water and waste management (Manyà, 2012). Several investigators have reported that the application of biochar as an adsorbent in wastewater treatment showed promising results for adsorption of nearly 45% of heavy metals, 40% of organic pollutants, 13% of nitrogen and phosphorous contaminants, and 2% of other pollutants (Patra *et al.*, 2017).



Figure 2.1: Applications of biochar (Lim et al., 2008)

The use of biochar in soil improvement is not a luxury but a necessity in many regions of the world. Biochar makes nutrients more readily available for crops hence, increasing productivity, stimulating the growth of soil micro-organisms, and reducing the
requirement of synthetic fertilizers, for example, the nitrogenous-based which released nitrous oxide in the atmosphere (Xu *et al.*, 2013). Adding biochar into the soil improves the structure and properties of the soil such as the organic matter content, pH value, water holding capacity, CEC, formation of aggregate in soil, and due to its large negative surface charge, it retains positively charged nutrients and reduces nutrients' leaching (Lim *et al.*, 2008 and Manyà, 2012). The incorporation of biochar within the soil has been proven to diminish the emission of methane (CH<sub>4</sub>) and nitrous oxide (N<sub>2</sub>O) which are the two main contributors of Greenhouse gases (GHGs).

Biochar is one of the few strategies used for the removal of carbon dioxide (CO<sub>2</sub>) from the atmosphere. Photosynthesis stores CO<sub>2</sub> from the atmosphere as organic carbon in the plant biomass. When the plant biomass dies or decays, they release GHGs like CO<sub>2</sub> and CH<sub>4</sub> which are contributors to radiative climate thus global warming. Through the pyrolysis process, the carbon present in the biomass can be fixed and stored in the soil for hundreds of thousands of years. This prevents the carbon from degrading and returning to the atmosphere (Sohi, 2012). The biochar can sequester approximately 50 -80% of carbon which is available in the biomass (Liang *et al.*, 2008). Carbon sequestration is a process by which CO<sub>2</sub> present in the atmosphere is removed and stored in a most stable pool and has been cited as one of the most potent strategies for the removal of GHGs which are present in the atmosphere.

The burning and natural decomposition of biomass of particular agricultural waste add a large amount of  $CO_2$  to the atmosphere. The biochar is highly resistant to degradation due to its chemical and biological stability. It may be utilized as a carbon sink in soils for thousands of years thus reducing the growth of GHGs levels in the atmosphere (Lehmann, 2007). Temperatures above 700°C favors the yield of the liquid and gas fuel components of biomass. The bioenergy produced during the pyrolysis process provides a potential substitute for fossil fuel (carbon neutral) (Lehmann, 2007). The feedstock for biochar production such as rice husks is readily available and at a low cost (Jindo *et al.*,

2014). Rice husk contains 20% silica, which is present in its hydrated amorphous form. During the pyrolysis procedure, the silica is converted to crystobalite, which is its crystalline form.

# 2.3 Heavy Metals and their Effects

The concentrations of heavy metals released into the environment have greatly increased as a result of natural activities, for example, rocks and volatiles from volcanic origins and anthropogenic activities such as population explosion, industrialization, high-input agriculture (fertilizer, pesticides, and herbicides), surface run-off and percolation of water containing heavy metals from industries and garages. These heavy metals have posed negative effects on the environment, human health, and animals due to their toxicity, long biological half-life, bioaccumulation in the food chain, and non-biodegradability making them accumulate in the environment Çeribasi and Yetis, 2001). Daba and Ezeronye (2005), found that metallic effluents especially essential metals bio-accumulate in water bodies and lead to eutrophication, which can progressively lead to oxygen deficiency, algal bloom, and death of aquatic life. According to Volesky and Holan (2003), the presence of heavy metals even in trace amounts is toxic and negatively affects an organism's survival, activity, growth, metabolism, and reproduction.

Accumulated lead is toxic in most of its chemical forms, whether it is inhaled or ingested in water or feed. It affects all biological systems (Assi *et al.*, 2016). Acute and chronic lead poisoning interferes with enzyme activities and the formation of red blood cells. Other fatal consequences include cardiovascular illnesses and hypertension (Navas-Acien *et al.*, 2007). Exposure to low levels of lead may cause hypertension in both humans and animals (Agency for Toxic Substance and Diseases Registry 2012). Exposure to lead also causes developmental neurotoxicity, reproductive dysfunction, and toxicity to the kidneys, blood, and endocrine system. In fish, lead bio-concentrates in the skin, bones, kidneys, and liver rather than in muscle and does not bio magnify up the food chain. However, Wright and Welbourn (2002), reported that people and wildlife who eat the whole fish can potentially be exposed to high concentrations of lead.

Cadmium is a by-product of zinc production and enters the environment from a variety of natural and anthropogenic sources (Mahvi *et al.*, 2005). Cadmium is non-degradable and once released to the environment, stays in circulation and new releases added to the already existing deposits of cadmium in the environment. Cigarette smoking is one of the most significant sources of human cadmium exposure. This is because, the tobacco plant like other plants for example rice accumulates cadmium from the soil because, its compounds are relatively water-soluble and more mobile (Nordic Council of Ministers, 2003). Cadmium can cause serious effects on renal function, bones and the pulmonary system (Bernhoft, 2013), bio accumulates in the kidney, lung and liver of vertebrates and invertebrates (Mahurpawar, 2015), disruption of several biological systems (Bernard, 2008). Cadmium is classified by the International Agency for Research on Cancer (IARC) as a Group 1 known human carcinogen for lungs through inhalation based on human evidence and animal studies. It has also been implicated as a possible contributor to cancers (kidney, bladder, pancreas, and hormone-influenced cancers such as breast, and uterine (WHO, 2010).

Copper is a trace element that is essential for the function of specific protein enzymes. However, at high concentrations, it is toxic to the living organism. Human beings are exposed to copper via inhalation of particulate copper, drinking copper-contaminated water, and eating copper-contaminated food. The increasing industrial activities and the use of copper sulphate (CuSO<sub>4</sub>) as a fungicide in agricultural practices as well as in the control of algae and pathogens in fish culture ponds have increased copper concentrations in aquatic systems. Vital substances in the body such as protein, lipids, and DNA get damaged by reactive free oxygen generated by excess copper in the blood system (Hossain *et al.*, 2012b). Copper is present in normal human serum (the liquid part of the blood) at concentrations of 120-140  $\mu$ g/L Signs of toxicity will be seen if the

copper concentration rises significantly above this range (Wright and Welbourn, 2002). The study by Brewer (2010), on copper toxicity in diseases of aging revealed that excess copper in the body causes atherosclerosis and Alzheimer's diseases. Results also indicated that excess copper compounds in the body cau cause mental illness and affect plants in which the leaves change to dark green then turn white since chlorophyll fails to enable effective photosynthesis. Roots of plants get damaged by excess copper causing slow growth of the plant and the plant wilts or dries up as a result (Qu *et al.*, 2015).

### 2.4 Methods of Analysis

### 2.4.1 Atomic absorption spectrophotometry

The Atomic absorption spectrophotometer is an analytical tool used for determination of the concentration of a particular metal element within the sample. The sample atoms absorb the light energy at a specific, unique wavelength because, each element has a hollow cathode lamp. The atoms absorb the energy and electronic excitation takes place and metal atoms jump to higher energy levels and returns to ground level by emitting radiations. The radiation from a hollow cathode lamp for that specific element passes through the monochromator lens by selecting the frequency that reach to the detector at a given time. The signal from the detector then passes to the recorder and gives the readout. The quantity of metal ions is attained by the comparison of standards concentration with the sample concentration Kamau *et al.*, (2020).

# 2.4.2 Characterization Techniques

Fourier Transform Infra-Red spectroscopy (FTIR) is technique used as a tool to identify the various functional groups present in both the pyrolyzed biochar and unpyrolyzed rice husk before chemical activation. According to Jellali *et al.*, (2021) and Zhang *et al.*, (2020), the enrichment of surface functional groups in the biochar plays a vital role in the adsorption of the metal ions. The functional groups detected could be allocated in the catalog of FTIR equipment or the library of functional groups already present in some instrument (Khan *et al.*, 2017).

Scanning Electron Microscope (SEM) is a versatile and powerful tool for material characterization that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. Morphological and structural characterization of rice husk biochar samples was investigated using SEM. The advantages of SEM are that, it produces detailed three-dimensional and topographic images, and it is easy to operate when equipped with training and user-friendly software. According to Phuong *et al.*, (2016), imaging occurs by scanning the sample with a high-energy beam of electrons. When these electrons interact with the sample, they create secondary electrons, characteristic x-rays, and backscattered electrons. One or more detectors collect these signals and form images that can be seen on a computer screen and give information about surface topography and composition of the samples.

The Brunauer Emmert Teller is an analytical tool used for the determination of the specific surface area by indicating the adsorption and desorption of the sample. The specific surface area is the means by which a solid interacts with its surrounding be it liquid, gas, or other solid, and as the particles size decreases the surface area per unit mass increases (Sakr, 2014). The Barrett- Joyner-Halenda (BJH) method using the absorption branch to determine the distribution of pore volume and pore size. The t-plot methods are used to obtain the volume, surface area, and external surface area.

# 2.5 The Adsorption Process

Adsorption is the capability of substances (adsorbate or sorbate) accumulating on the surface of a solid (adsorbent or sorbent) and is exothermic in nature because the particles on adsorbent are unstable and when adsorbate is adsorbed on the surface, the energy of the adsorbent decreases leading to heat evolution. Adsorption is used for evaluating the

physical and chemical properties that are critical for process. Adsorption arises because; the surface particles on the adsorbent are not in the same environment as particles inside the bulk.

# 2.5.1 Sorption

Sorption is a physical and chemical process by which one substance is attached to another (Ugwu *et al.*, 2020). The reverse of adsorption is desorption which involves releasing atomic or molecular species onto the surface. Metal ions can bind to adsorbents through sorption, electrostatic interaction, and metal ion and co-ligand complexation mechanisms (Öztürk *et al.*, 2009).

### 2.5.2 Electrostatic Interaction

This process takes place in the absence of ligands in the aqueous system. Metal ions attach onto the carboxylic group of cellulose as the hydrogen ions leave.

# 2.5.3 Metal Ion and Co-Ligand Complexation

In the presence of cellulose, which acts as a ligand, competition for the metal ion occurs between the ligand and co-ligand. When the stability of the metal ion co-ligand complex is sufficiently weak, cellulose complexes with the metal ions and the co-ligands are released. Studies by Mckay (1984) and Murithi *et al.*, (2012), reported that an adsorption process takes place in four steps which are dependent on each other. They include; metal ion transfers from the aqueous solution to adsorbent material, metal ion (adsorbate) interactions with functional groups of the adsorbent, metal ion transfers from the surface of an adsorbent material into the intra-particle active sites in the adsorbent structure and the interaction of the metal ion with available functional groups on the internal surface of the adsorbent.

The adsorption process depends on the nature of the metal ion and the properties of the adsorbent material used. Therefore, any of the four steps determines the overall rate of the adsorption process. The adsorption can either follow pseudo-first order or pseudo-

second order models (Amuda *et al.*, 2009). According to Kołodyńska *et al.* (2012), adsorption mechanisms are influenced by adsorption kinetics when they are involved in mass transport and chemical reaction processes.

# 2.6 Adsorption Kinetics

Adsorption kinetics are used to establish the relationship between the solute uptake rate of the adsorption and the adsorption time or physical and chemical characteristics of the adsorbent (Duwiejuah *et al.*, 2017). Different kinetic models have been used to test the adsorption behavior of heavy metals on the adsorbent materials. Kinetic equations are used to find the overall rate of the adsorption process and they are Lagergren's pseudo-first order, pseudo-second order, and Elovich kinetic models among others.

### 2.6.1 Pseudo-First Order Kinetic Model

The pseudo-first order model is based on the assumption that the rate of solute uptake with time is directly proportional to difference in saturation concentration and amount of solid uptake (Lin and Wang, 2009). The model of pseudo-first order is given by equation 2.1.

$$\ln(q_e - q_t) = \ln q_e - K_1 t \quad \dots \quad 2.1$$

Where  $q_t (mg/g)$  is the equilibrium adsorption capacity at time t (minutes) respectively

 $q_e$  is the equilibrium adsorption capacity of the heavy metal adsorbed

 $K_1$  (min<sup>-1</sup>) is the pseudo-first order rate constant of adsorption.

The linear plot of  $\ln(q_e - q_t)$  versus  $q_{e_1}$  gives the intercept as  $K_1$ .

### 2.6.2 Pseudo-Second Order Kinetics

The pseudo-second order kinetics model is based on the assumption that the rate-limiting step is chemical sorption and predicts the behavior over the whole range of adsorption. Chemisorption occurs due to the exchange of electrons among adsorbent and adsorbate (Mckay, 1984). The integrated linear equation of the pseudo-second order kinetic model is given by equation 2.2.

$$\frac{t}{q_t} = \frac{1}{K^2 q_e^2} + \frac{1}{q_t} t \dots 2.2$$

Where  $q_e^2$  and  $q_t$  (mg/g) are the adsorption capacities at equilibrium and at time t (mins) respectively. The plot of  $\frac{t}{q_t}$  versus *t* gives the intercept as  $K^2$ .

## 2.6.3 Elovich Diffusion Model

Elovich model is a rate equation based on kinetic principles, which involve multilayer adsorption capacities  $q_t (mg/g)$ (Pakade *et al.*, 2017). Elovich equation describes the kinetics of chemisorption of a sorbent onto a solid. The Elovich model is represented in equation 2.3.

$$q_t = B \ln(AB) + B(\ln t) \dots 2.3$$

Where, B (mg/g) is the number of available sites for adsorption, A is the initial sorption rate constant (mg/g min),  $q_t \text{ (mg/g)}$  is amount of solute adsorbed at time t. The Elovich constant A is evaluated from the slope and intercept of the plot of  $q_t$  versus lnt.

# 2.7 Adsorption Isotherms

Adsorption isotherms refer to the relationship between metal ions adsorbed on the surface of the adsorbent at a constant temperature while varying the concentration of the solution at equilibrium. According to Ahiduzzaman and Sadrul Islam (2016), isotherms are useful for estimating the amount of adsorbent needed to remove a required amount of adsorbate from a bulk solution. In addition, it is used to determine the possibility of reaching a desired purity level with the adsorbent. Adsorption isotherms are based on the heterogeneity and homogeneity nature of adsorbent and distribution of adsorbate species among liquid and adsorbed phases. Adsorption isotherms explain the equilibrium relationship established between the amount of adsorbate adsorbed and the amount of adsorbate in solution with its pressure if gas and concentration if liquid (Foo and

Hameed, 2009). The adsorption isotherm is essential in optimizing the use of adsorbents because it describes how adsorbates interact with adsorbents (Goh *et al.*, 2008). Langmuir, Jovanovic, Freundlich, and Tempkin isotherms are the most commonly used isotherms for the application of activated carbon in water and wastewater treatment.

### 2.7.1 Langmuir Isotherm

The Langmuir adsorption model is the most common model used to quantify the amount of adsorbate on an adsorbent as a function of partial pressure or concentration at a given temperature.

The Langmuir model is based on the following hypotheses (Onyeji and Aboje, 2011).

- 1) Biosorption is a monolayer process.
- 2) All bio sorbent sites are similar
- 3) No interaction takes place between the molecules on different sites.
- 4) The capacity of the sites to be occupied by the sorbate is independent of the nature of the occupancy of sites in its vicinity.

A monolayer is formed on the adsorbent at maximum adsorption that is, molecules of adsorbate do not trans-migrate on already adsorbed adsorbate species on the plane of the adsorbent surface due to uniform adsorption energy (Nworie *et al.*, 2019 and Yahaya *et al.*, 2011). According to Foo and Hameed (2009) and Wang *et al.* (2010), the adsorbent surface is composed of a fixed number of adsorption sites of equal energy therefore there is no steric effect or lateral interaction. The Langmuir isotherm is given by equation 2.4.

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{1}{q_{max}}.....2.4$$

Where  $C_e$  is the concentrations of adsorbate solution (mg/L) after adsorption.

 $q_e$  is concentration capacity of sample (mg/g) of heavy metal adsorbed on adsorbent

 $K_L$  (L/mg) is the Langmuir constant

q<sub>max</sub> maximum monolayer coverage capacity (mg/g).

The Langmuir constants  $q_{max}$  and  $K_L$  can be calculated from  $C_e/q_e$  versus  $C_e$ .

The adsorption data were also used to calculate the separation factor or equilibrium parameter using equation (2.5)

$$R_L = \frac{1}{1 + K_l C_o} \dots 2.5$$

Where  $C_o$  is the highest initial metal ions concentration

 $K_L$  (L/mg<sup>-1</sup>) is the Langmuir constant.

 $R_L$  equilibrium parameter which usually indicates adsorption system is either; unfavorable ( $R_L$ >1) linear ( $R_L$ =1), favorable (0< $R_L$ >1) and irreversible  $R_L$ =0.

#### 2.7.2 Jovanovic Isotherm

The Jovanovic isotherm is a monolayer isotherm based on the homogenous nature of the adsorbent. Adsorption in all adsorbates is supposed to be ranked from low energies to high energies ( Lee *et al.*, 2017a). The linearized Jovanovic model is formulated as equation 2.6

$$\ln q_e = (q_{max} - K_J C_e).....2.6$$

Where  $q_{max}$  is concentration capacity of sample (mg/g) of heavy metal adsorbed.

 $q_e$  is the equilibrium adsorption capacity,  $C_e$  is the concentrations of adsorbate solution (mg/L) and  $K_J$  is Jovanovic constant (energy of adsorption). A plot of  $\ln q_e$  versus  $C_e$  gives the slope and intercept as  $K_J$  and  $q_{max}$  respectively.

# 2.7.3 Freundlich Isotherm

The Freundlich adsorption isotherm is an empirical relation between the concentration of a solute on the surface of an adsorbent and the concentration of the solute in the liquid with which it is in contact. It applies to adsorption that occurs on a heterogeneous surface by multilayer sorption and the amount of adsorbate adsorbed increases infinitely with increasing concentration (Adeyemo and Adebowale, 2014, Duwiejuah *et al.*, 2017 and Yahaya *et al.*, 2011). The Freundlich adsorption isotherm is mathematically expressed as equation 2.7

$$Log q_e = Log Kf + \frac{1}{n} Log C_e....2.7$$

Where  $C_e$  is the equilibrium concentration of adsorbate in solution in mg/L, *Kf* is the Freundlich constant or binding affinity which gives the extent of adsorption,  $q_e$  is the amount adsorbed at equilibrium (mg/g), and 1/n is the heterogeneity factor which is related to the capacity and adsorption intensity. The values of *Kf* and 1/n can be obtained from the slope and intercept of the plot of log  $q_e$  against log  $C_e$ .

### 2.7.4 Temkin Isotherm

The Temkin isotherm is a heterogeneous surface energy system that takes into account the interaction between the adsorbent and the metal ions to be adsorbed. The adsorption is characterized by a uniform distribution of binding energies up to the maximum binding energy (Padmesh *et al.*, 2006 and Zheng *et al.*, 2010). The linearized Tempkin model is formulated as equation 2.8.

$$q_e = \frac{RT}{b_T} (ln A_T C_e) \dots 2.8$$

Equation (2.7) can be expressed in its linear form as:

$$q_e = BlnA_T + BlnC_e....2.9$$

The adsorption data can be analyzed according to Equation (2.9).

Where,  $A_T$  is the equilibrium binding constant corresponding to the maximum binding energy,  $b_T$  is the Tempkin isotherm constant related to the heat of adsorption, T is the

temperature (K) and R is the ideal gas constant (8.315 J/mol/K). A plot of  $q_e$  versus ln  $C_e$  gives an intercept as  $A_T$  (equilibrium constant) and B as the slope and y-intercept enable.

The adsorption kinetic was used to achieve the objectives of the study by establish the relationship uptake rate of metal ions by the rice husk biochar, physical and chemical characteristics of adsorbent and adsorption mechanism between biochar and metal ions. The adsorption isotherm helped to estimate the amount of adsorbent needed to remove the required amount of adsorbate from a bulk solution and helped to determine the possibility of reaching a desired purity level with the adsorbent through the removal of heavy metal ion from waste solution

# **CHAPTER THREE**

# **MATERIALS AND METHODS**

# 3.1 Sampling Site

The rice husk biomasses were collected from Nice Rice Millers Ltd located at 0`39`0`S and 37'210`E (Figure 3.1) in Mwea, Kirinyaga county in Kenya. The rice in Nice Millers Ltd is usually obtained from farmers located in all sub-county schemes, that is Tembere, Nguka (Mwea), Thiba, Wamumu, and Karaba. Approximately 50 Kg of rice husks were put in the sacks and then transported to the University of Nairobi Chemistry Department laboratory for storage.



Figure 3.1: Sampling site in Mwea Irrigation Scheme

# 3.2 Apparatus and Instruments

The apparatus and instruments used in this research include desiccators, stirrer, Mammert oven, Dalhan Scientific muffle furnace. Volumetric flasks, beakers, conical flasks, pipettes, Magnetic Follower, Shimadzu analytical balance, Pye-unican pH- Meter, G24 New Brunswick Scientific Orbital Shaker, AA-6300 Shimadzu Atomic Absorption Spectrophotometer (AAS), IRAffinity-1S Fourier Transform Infra-Red (FTIR) Spectrometer (Shimadzu Corp., 03191), Scanning Electron Microscopy (SEM) and Brunauer Emmert Teller (BET) model was Nova-1000 gas sorption analyzer Quanta Chrome Co.

### **3.3** Cleaning of Glassware and Apparatus

Glassware and apparatus were soaked overnight in Aqua Regia reagent. They were then, washed with soap and rinsed repeatedly with distilled water. Finally, they were oven dried at 105°C.

### 3.4 Sample Preparation

The 20 kg of rice husks were washed thoroughly with tap water to remove mud and other water-soluble impurities. They were then air-dried under a shade for 36 hours and then oven-dried at 105°C for 24 hours. The dried rice husks were ground and placed into a ceramic crucible each covered with a fitting lid for the pyrolysis process.

### 3.5 Chemical and Reagents

The following analytical grade chemicals all from Fisher's Chemical were used in this project: cadmium nitrate, lead nitrate, hydrated copper nitrate, sodium hydroxide, zinc chloride, Hydrochloric acid, and Nitric acid.

### **3.5.1** Preparation of Solutions of Synthetic Pollutants

Stock solutions of 1000 mg/L of copper, cadmium, and lead were prepared in distilled water, which was later serially diluted to the required working standard solutions. They were obtained from  $Cu(NO_3)_2.3H_2O$ , anhydrous  $Pb(NO_3)_2$ , and anhydrous  $Cd(NO_3)_2$ . Nitrate salts were selected because of the low chelating capacity of nitrate concerning metal ions (Inyang *et al.*, 2012). The synthetic pollutant solutions were prepared by dissolving appropriate masses of metal salt in distilled water as indicated in Table 3.1 and transferred in one litre volumetric flask.

Salt Name	Relative	molecular	Salt was dissolved in	Volumetric	flask
	Mass (g)		1000 mg/L of distilled	(L) Used	
			water (g)		
$Cu(NO_3)_2.3H_2C$	) 241		3.8402	1000	
Pb(NO3) <sub>2</sub>	331		1.6470	1000	
$Cd(NO3)_2$	208		1.8759	1 000	

**Table 3.1: Preparation of solution of synthetic pollutant** 

The working standards were prepared by pipetting 10mL of each of the above stock solutions and transferring to 100mL volumetric flask and diluted to the mark with distilled water. This gave 100mg/L of the working standards. The calibration standard solutions were made by serially diluting as indicated in table 3.2 from 100mg/L of each salt of synthetic solution pollutant by pipetting 0.1, 0.5, 2. 4, 8, and 10mL using the formula given in equation 3.1.

Where  $C_1$  and  $C_2$  is the concentration of the stock solution and working standard respectively (mg/L),  $V_1$  and  $V_2$  is the volume (mL) of the stock and working solution to be withdrawn for dilution.

Table 3.2: Preparation of standard solutions of synthetic pollutant

Stock Solution	Volume of Stock	Concentration of	Volume of
Concentration (C <sub>1</sub> )	Solution Taken	Working Standard	Working Solution

mg/L	(V <sub>1</sub> ) mL	$(C_2)$ mg/L	(V <sub>2</sub> ) mL
1000	100	100	1000
100	100	10	1000
100	8	8	100
100	4	4	100
100	2	2	100
100	1	1	100

### 3.6 Production of Rice Husk Biochar

Rice husk biochar was prepared by weighing 10g of ground rice husks and temperatures, ranging from 300, 400, 500, 600, and 700°C for 2 hours for each. The rice husk was first heated from ambient temperature to 200°C in automated muffle furnace, the temperature and time (2h) were set and after pyrolysis was over the muffle Furnanc was allowed to cool gradually and the same procedure was repeated at the temperature of 300 - 700°C. The biochar samples were obtained at different temperatures to assist in the identification of the optimal temperature for producing quality and efficient activated carbon. The synthesized biochar samples were stored in plastic containers ready for further analysis.

### 3.6.1 Rice Husk Biochar Chemical Activation

According to Prapagdee *et al.*, (2016), Shrestha *et al.*, (2019) and Wong *et al.* (2003), adsorption efficiency increased by treating the biochar using various agents like tartaric acid, KOH, HNO<sub>3</sub>, HCl, H<sub>2</sub>SO<sub>4</sub>, and NaOH solution. Since ash content in rice husk biochar (RHB) retards its porosity, NaOH solution was the most preferred activating chemical in this project since it can leach ash from RHB (Rajapaksha *et al.*, 2019).

After the removal of ash, the RHB was dried in an oven at 105°C and kept in desiccators. Following the procedure by Ahiduzzaman and Sadrul Islam (2016), with some modification, the treated rice husk biochar's were further activated using 0.5 M ZnCl<sub>2</sub> solution. The biochar with ZnCl<sub>2</sub> solution was mixed to form a paste/slurry at the ratio of 2:1 for 24 hours. This was to enhance the generation of more interfaces between carbon layers, which would lead to surface modification by increasing the micro porosity of the biochar and the surface area. The mixture was then washed with dilute hydrochloric acid (0.1 M) to dissolve all the carbonates after which it was thoroughly washed with distilled water until a pH of 7.0 was attained. This was to remove any traces of ZnCl<sub>2</sub> and HCl. The Rice husk biochar samples were dried in the oven at 105°C for 24 hours. The dried samples were preserved in desiccators to avoid further absorption of moisture. The modified biochar was notated as RHBT that is, rice husk biochar treated.

## **3.7** Determination of Physical Parameters

# 3.7.1 Determination of pH of Untreated Biochars

Determination of pH was carried out as described by (Rajkovich *et al.*, 2012) with some modifications. The pH of the untreated rice husk biochars and the raw rice husk was determined by first preparing a suspension of 2 g of the sample in 50 mL distilled water and stirring for 30 minutes with a magnetic stirrer to ensure sufficient equilibrium between the surface of the biochar and the solution. The suspension was allowed to settle and the pH of the solutions was determined using a Pye-unican pH meter. The same procedure was repeated with raw rice husks and with the various biochars; RHB300, 400, 500, 600, and 700.

### 3.7.2 Determination of Percentage Ash Content of the Biochars

It was, therefore, necessary to determine the percentage ash content (PAC) of unpyrolyzed rice husk because of presence of silica, untreated and the treated biochar. 0.5 g of sample (A) was placed in the porcelain crucibles and accurately weighed with a Shimadzu analytical balance. The weighed samples were put in a digital Dalhan Scientific Muffle furnace and heated for 4 hours at 800°C. The sample was cooled in a desiccator and then the weight (B) was taken. The PAC was determined using equation 3.2.

Percentage Ash Concent (PAC) = 
$$\frac{B}{A}x100....3.2$$

Where PAC is the percentage ash content, A is the initial weight of untreated or treated biochar, and B is the final weight of biochar after cooling.

# 3.8 Determination of Metal Ions Concentration by Atomic Absorption Spectrophotometer

The working standards of metal ions were prepared and then serially diluted as given in Table 3.2. The working standards were used to plot calibration curves as indicate in appendices XIX to XXVII. The analyze solutions after absorption of metal ions were sprayed as droplets into the flame through a capillary tube to the nebulizer each at a time. The heat of the flame (fuel and oxidant which serves as carrier to the flame) atomizes the liquid samples into free atoms and the absorption radiation increases the energy of the molecule. The electronic excitation takes place and electrons jump to higher energy levels and returns back to a lower energy level by emitting radiation. The radiation from a hollow cathode lamp for a specific element passes through the grating lens by selecting the frequency and reaching the detector at a given time. The signal from the detector then passes to the recorder and gives the readout. The AA-6300 Shimadzu AAS was used to determine the concentration of metal the ions.

### **3.9** Characterization of the Rice Husk Biochar

### 3.9.1 Fourier Transform Infra-Red Spectroscopy Characterization

The IRAffinity-1S Fourier Transform Infra-Red (FTIR) Spectroscopy (Shimadzu Corp., 03191) equipped with an Attenuated total reflectance (ATR). The ATR is a popular sampling technique used in FT-IR. This is quick, non-destructive and can analyze both solid and liquid. The unpyrolyzed rice husk, chemically inactivated biochar samples, and

chemically activated biochar were ground into fine powder and pressed against a high reflective index prism and Infra- Red beam was totally internally reflected in the prism. When the beam came into contact with samples changes occurs which was detected by FTIR detector as spectrum, characterization was done before and after adsorption. The instrument was set up to perform a total of 20 scans with a 4 cm<sup>-1</sup> spectral resolution and the scan range between 4000 - 400 cm<sup>-1</sup> (Jindo *et al.*, 2014).

### 3.9.2 Scanning Electron Microscopy Analysis

In the SEM analysis of RHB, a thin layer of carbon glue was spread on the stub and a small quantity of samples was spread on the thin layer of the glue. The RHB samples are non-conducting therefore, the stub was coated with carbon to make the samples conductive (Batagarawa and Ajibola, 2019). The beam of electrons from electron gun was focused on the surface of the RHB samples and the electrons were accelerated by the applied voltage of 100kV. The magnetic lenses converged the stream of electrons into the focused beam which hits the sample surface. The interaction between the electron beam and atoms of the rice husk biochar samples enhanced, the scanning of surface to produce various signal that contained surface morphology of the samples. The magnification of X200 was used.

### 3.9.3 Brunauer Emmert Teller Analysis

The specific surface area of the biochar was characterized by nitrogen adsorptiondesorption isotherm and were measured using the Nova-1000 gas sorption analyzer Quanta Chrome Cop. The samples were placed in an oven at 105°C, placed into a glass sample holder and degassed first in a vacuum system at 150°C for 120 minutes, before gas adsorption. This was to remove water and air from the sample porosity to enable the fixation of nitrogen gas. The samples were cooled in a bath of liquid nitrogen at a temperature of 77 K to avoid gas condensation with increasing temperature. The powder of different biochar samples was accurately weighed and transferred to measurement ports. The Barrett- Joyner-Halenda (BJH) method using the absorption branch was used to determine the distribution of pore volume and pore size. The t-plot methods were used to obtain the volume, surface area, and external surface area.

# 3.10 Optimization of Conditions for Adsorption

### 3.10.1 Optimization of pyrolytic temperature Biochar

0.1250 g of the chemically activated biochar synthesized at different temperatures labeled RHT0, RHBT300, RHBT400, RHBT500, RHBT600 and RHBT700 were accurately weighed and put in 100 mL conical flasks. A volume of 20 mL of 1 mg/L of  $Cu^{2+}$  solution was added into the flask. The samples were agitated at a speed of 200 rpm in an orbital shaker at room temperature and a pH of 7.0 for 30 minutes. The suspensions were filtered and the filtrates were transferred into plastic reagent bottles and then the concentration of a metal ion in the solution was determined using AAS. From the initial metal ion concentration and metal ion concentration after adsorption, the percent metal ion adsorbed was calculated. The procedure was repeated with different metal ion concentrations, namely 2 and 4 mg/L and the percent metal ion adsorbed was then obtained. This was also done using biochars synthesized at various temperatures, that is 300, 400, 500, 600 and 700°C respectively. The percent metal ion adsorbed was then obtained. The biochar which gave the maximum adsorption was considered to be the best (optimal) biochar. The above procedure was repeated for the other two metal ions  $(Cd^{2+} and Pb^{2+})$  and the optimum rice husk biochar sample was produced at pyrolytic temperature of 500°C.

### 3.10.2 Determination of Optimum Contact Time

The contact time plays a significant role in the adsorption process. The optimal rice husk biochar samples (obtained from 3.10.1) was mixed with the metal ion solutions and the suspensions filtered at predefined time. The procedure was repeated at 3.75, 7.5, 15, 30, 60 and 120 minutes through doubling the time to identify whether time cause any effect in efficiency removal. The 0.1250 g of optimum biochar was accurately weighed and

placed in 100 mL conical flasks. The 20 mL of 1, 2 and 4 mg/L of Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> of synthetic pollutants solution which had been maintained at pH 7.0 were each added at a time to the biochar. The samples solutions were agitated at a contact speed of 200 rpm in a magnetic stirrer and were withdrawn at predefined time intervals. When the required time was attained, the suspensions were filtered immediately and filtrates were transferred into plastic reagent bottles. The filtrates' metal ion content was determined using AAS. The contact time which gave the maximum efficiency removal for each metal ion was considered to be optimal that 60 minutes for copper and lead and 30 minutes for cadmium.

### 3.10.3 Determination of Optimum Adsorbent Dosage

According to Chen *et al.* (2011), the ideal dosage of biochar is chosen carefully for effective and efficient removal of contaminants because adsorption is usually influenced by the dosage of adsorbent. The effect of dosage was studied using metal concentrations of 1 mg/L using the optimal biochar (obtained from 3.10.1) and the optimal contact times (obtained from 3.10.2) for each synthetic pollutant solution. The dosage amount was varied from 0.1250, 0.250, 0.50 to 1 g through doubling the weight. The other parameters namely, agitating speed, temperature, and synthetic pollutant pH were held constant. After agitation of suspensions, filtration was done and the concentration of heavy metal ions in the filtrate was determined using AAS. The biochar dosage which adsorbed the maximum metal ions was considered to be the optimal dosage and was 0.250 g for all the metal ions.

### 3.10.4 Determination of Optimum Concentration of Synthetic Pollutant Solutions

In the determination of the optimum concentrations of synthetic pollutant solutions, concentrations of 1, 2, 4, to 8 mg/L for the three metal ions were prepared as given in Table 3.2 and placed into plastic containers. The optimum dosage of adsorbent (obtained from 3.10.3) was placed into 1, 2, 4, and 8 mg/L the different concentrations of synthetic pollutant at pH 7. They were then, agitated at a speed of 200 rpm at the optimum

conditions previously established. The solutions were filtered and then the concentration of heavy metals in the filtrates was determined using AAS. The concentration of the metal ions with the highest uptake was taken to be optimal which was 2 mg/L. for the three metal ions.

### 3.10.5 Determination of Optimum pH

The pH of synthetic pollutant solutions of Cu<sup>2+</sup>, Cd<sup>2+,</sup> and Pb<sup>2+</sup>were varied from 2, 5, 7, 9 to 12. The optimum Concentration of Synthetic Pollutant Solutions of each metal ions were adjusted using a small amount of dilute hydrochloric acid (0.1 M) in order to maintain pH 2 and 5 or sodium hydroxide solution (0.1 M) to obtained pH 9 and 12 at room temperature by use of pH-Meter. After attaining the pH that ranges from 2,5,7,9 to 12 in different flasks. The 20 mL of stock solutions of each metal ion and 0.250 g of rice husk biochar was added into each conical flask and were subjected to agitation at a contact speed of 200 rpm while maintaining optimal conditions previously established. The concentration of metal ions in the filtrates was determined using AAS. The pH where maximum uptake was obtained was considered optimal and was at pH 7 for the metal ions.

### **3.10.6 Determination of Optimum Temperature**

The purpose of this study was to evaluate the effect of temperature on the adsorption of the three metal ions solution of synthetic pollutants using RHBT500 the optimum biochar by varying temperatures from 25, 35 and 45°C. The 20 mL of stock solutions of each metal ion and 0.250 g of rice husk biochar was added into each conical flask and were subjected to agitation at a contact speed of 200 rpm in orbital shaker incubator at specified temperature while other optimal parameters previously established were used. The solutions were then filtered and the metal ion concentration was determined using AAS. The temperature with the highest efficiency removal of each metal ion was considered optimal and was 35°C for metals ions.

### 3.10.7 Comparative Test of Sorption Biomass

After attaining all the optimal conditions for adsorption, a comparative test was done for the three biomasses namely; the chemically activated biochar (RHBT500), untreated biochar (RHB500), and commercial activated carbon (AC). The purpose of this study was to evaluate the viability of the optimal biochar in the adsorption of heavy metal ions from aqueous solutions. All the optimum conditions previously established were used as the solutions were agitated. The solutions from each biomass were filtered and the concentration of metal ions in the filtrates was determined using AAS. The biomass where maximum uptake was obtained for each metal ion solution was considered optimum.

### 3.11 Determination of Adsorption Capacity

The experiment was carried out by varying the amount of adsorbent dosage from (0.125, 0.25, 0.5 and 1 g). The adsorption efficiency of Cd<sup>2+</sup>, Cu<sup>2+,</sup> and Pb<sup>2+</sup> was studied by keeping the pH constant and with some modification as per the procedure by Onyeji and Aboje (2011). 20 mL of 1 mg/L standard solutions of copper, lead, and cadmium were transferred to a 100 mL conical flask and 0.125 g of rice husk biochar was added to each conical flask.

The suspensions were stirred mechanically at 200 rpm at room temperature (298 K) in the optimal contact time of each metal ion in an incubator orbital shaker. The conical flasks were withdrawn from the incubator at some predetermined time. The solutions were filtered and the metal ion concentration was determined using AAS. The same procedure was repeated for 0.250, 0.50, and 1 g. The percent removal (%E) of metal ion and amount of metal ion adsorbed on rice husk biochar ( $Q_e$ )were calculated by using equations 3.3 and 3.4 respectively:

$$\%E = \frac{c_o - c_e}{c_o} x100.....3.3$$

Where  $C_o$  is the initial (equilibrium) concentrations of the metal ion in solution (mg/L),  $C_e$  is the final (equilibrium) concentrations of the metal ion in solution mg/L and %E is the removal efficiency in percentage.

Adsorption capacity  $(Q_e)$  after reaching equilibrium was calculated using equation (3.4)

$$Q_e = \frac{(C_o - C_e)V}{W}.....3.4$$

Where, *V* is the volume (mL) of solution and *W* is the mass (g) of RHB. All adsorption experiments were performed in triplicate and the mean values were used in data analysis.

# 3.11.1 Determination of Adsorption Kinetic

To evaluate the validity of the adsorption kinetic models, the method proposed by Adouby *et al.* (2007), was used. The adsorption capacity of the heavy metal ions by rice husk biochar was investigated using the established optimum conditions obtained. The experiments were carried out by shaking the optimal amount of rice husk biochar in 20 mL of the optimal metal ion concentration at room temperature. The suspension was agitated at 200 rpm by varying the time. At the end of each time, the mixture was filtered and the metal ion concentration in the filtrate was analyzed using AAS. The experimental data were fitted using the pseudo first order, pseudo second order, and Elovich diffusion models.

### 3.12 Determination of Adsorption Isotherm

In this study, the analysis of the adsorption isotherms of the three heavy metal ions was carried out by applying the Langmuir, Jovanovic, Freundlich, and Temkin equations. The experiment was carried out by varying the amount of adsorbent dose from 0.125, 0.250, 0.50 to 1 g. 20 mL of optimal concentrations of metal ion was transferred to 100 mL conical flask and 0.1250 g of rice husk biochar was added to each conical flask. The same procedures were repeated for 0.250, 0.50 and 1 g respectively. The suspensions were stirred mechanically at 200 rpm at room temperature (298 K) in the optimum contact time for each metal ion in an incubated orbital shaker. The conical flasks were

drawn at predetermined times. The solutions were filtered and the concentration of a metal ion in the filtrate was determined using AAS. Statistical analysis using ANOVA will be used to determine the significance of the data.

# **CHAPTER FOUR**

# **RESULTS AND DISCUSSION**

# 4.1 Determination of Physical Parameters

### 4.1.1 The pH of Unpyrolyzed Rice Husks and Pyrolyzed Biochar Samples

Figure 4.1 indicates the change in pH with increase of pyrolytic temperatures of the biochar.



# Figure 4.1: Plot of pH values of unpyrolyzed rice husk (RH0) and the biochar samples obtained at different pyrolytic temperatures

The results obtained of the pH of unpyrolyzed rice husk (RH0) was neutral this could be due to intact organic matrix while that of biochar samples produced at different temperatures increased from 5.6 to 9.4 as shown in Figure 4.1. The pH 5.6 of RHB300 was attributed to the formation of weak carbonic acid through the reaction of carbon dioxide in biochar and water. Inyang *et al.*, (2016) and Kimetu and Lehmann (2010), observed that the pH of biochar samples ranged from 7.1 to 10.5 and this was attributed to the formation. The increase of pH value from 5.6 to 9.4 could be attributed

to the progressive separation of alkali salts from organic materials, decomposition of the organic matrix and formation of carbonates and the results aligned to (García-Jaramillo *et al.*, 2015, Tomczyk *et al.*, 2020 andYuan *et al.*, 2011). At higher temperatures the pH of RHB600 and 700 becomes almost constant because there was no more formation of carbonates the results aligned to (Yuan *et al.*, 2011 and Zhao *et al.*, 2017).

# 4.1.2 Determination of Ash Content of Inactivated Unpyrolyzed Rice Husk and Activated Biochar Samples



Figure 4.2 represents the percentage ash content of the inactivated and activated biochar.

Figure 4.2 Percentage ash content of inactivated and activated biochar against different pyrolytic temperatures

The result obtained in figure 4.2 show a decrease in the PAC as the pyrolytic temperatures increases in both treated and untreated biochar samples. The PAC of untreated raw rice husk (RH) and rice husk biochar (RHB) produced at different temperatures ranging from 78 to 36%. The ash content was highest in unpyrolyzed rice biomass for activated and inactivated this could be attributed to the presence of silica. The PAC was lowest in the biochar pyrolyzed at 700 °C for both activated and

inactivated this could be due to the development of a well-defined structure within the biomass because the activating agents are capable of penetrating inside the biomass and breaking down the cross-linkage of cellulosic material and other minerals component the results aligned with Komnitsas and Zaharaki (2016) and Salleh *et al.*, (2014). The decrease of PAC as the pyrolysis temperature increases could be attributed to volatilization and decomposition of lignin, cellulose, hemicellulose, other organic matter with strong chemical bonds, and inorganic compounds into gas and liquid (Ding *et al.*, 2016 and Li *et al.*, 2013b).

According to Ahiduzzaman and Sadrul Islam (2016), rice husk biochar contains more than 50% ash, which causes problem in pore development in the biochar. As a result, the rice husk biochars were chemically activated with sodium hydroxide, which reacted with silica and this increased the porosity of the biochar significantly. The rice husk biochar samples were further activation with zinc chloride for surface modification and this lowed ash content, developed more pores, increase surface area, and more binding sites this corresponded to (Qu *et al.*, 2015) results . After chemical activation of the rice husk and biochar samples, the PAC ranged from 60 to 21%.

# 4.2 Characterization of the rice husk biochar

### 4.2.1 Fourier Transform Infra-Red Spectroscopy Characterization

The results obtained as in figure 4.3 shows the FT-IR spectra of unpyrolyzed rice husk (RH) and inactivated biochar produced at 300 and 700°C, they were denoted as RHB300 and RHB700 and adsorption with  $Cd^{2+}$ ,  $Cu^{2+}$  and  $Pb^{2+}$  metal ions had not taken place.



Figure 4.3 FT-IR spectra for unpyrolyzed rice husk (RH) and biochar produced at 300 and 700°C

The results obtained in Figure 4.3 display the spectra for biochar samples labeled RH, RHB300, and RHB700, which are almost similar as most functional groups have shown same frequency like -OH stretch vibrations. The FTIR spectra displayed many peaks and even in finger print region which indicated the complex nature of adsorbents and their capabilities of adsorption of heavy metal ions (Khan *et al.*, 2017). The absorption bands were  $V_{max}$  3411 cm<sup>-1</sup> for RHB700 and 3418 cm<sup>-1</sup> for RH and RHB300 were assigned to - OH stretching vibration due to hydroxyl group in biochar like carboxylic acid in cellulose and lignin (Batagarawa and Ajibola, 2019 and Wang *et al.*, 2019). The bands  $V_{max}$  1636 cm<sup>-1</sup> for RHB700 and 1644 cm<sup>-1</sup> for RH indicated the presence of carbon C=C due to conjugated alkene and C=O stretch respectively due to conjugated ketone and quinones (Mahmoud *et al.*, 2018 and Zhao *et al.*, 2017). The band at  $V_{max}$  1549 cm<sup>-1</sup> indicated vibration of N-O due to the nitro group (Wang *et al.*, 2019). The peak at  $V_{max}$ 1403 cm<sup>-1</sup> was assigned to the aromatic vibration of C-C. The peak  $V_{max}$  1249 cm<sup>-1</sup> corresponds to C-O stretching in lignin and hemicellulose of adsorbent biochar (Shrestha

*et al.*, 2019 and Wang, Li, *et al.*, 2013b). The peaks in figure prints region around  $V_{max}$  731-738 cm<sup>-1</sup> indicated -CH bend vibration (Njoki *et al.*, 2016). The peak at  $V_{max}$  490 cm<sup>-1</sup> was due to Si-O vibration which is the major chemical compound in the rice material (Jindo *et al.*, 2014, Ligate and Mdoe, 2015 and Shrestha *et al.*, 2019).

Figure 4.4 to 4.6 shows FT-IR spectra for biochar produced at 400, 500 and 600°C where the unloaded is before and loaded is after adsorption of the selected metal ions.



Figure 4.4 FT-IR spectra for rice husk biochar produced at 400°C (RHBT400) before and after adsorption



Figure 4.5: FT- IR spectra for rice husk biochar produced at 500°C (RHBT500) before and after adsorption



Figure 4.6 FT- IR spectra for rice husk biochar produced at 600°C (RHBT600) before and after adsorption

FT-IR data obtained before and after adsorption of rice husk biochar with Cu<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> produced at three different pyrolytic temperatures 400, 500 and 600°C labeled as RHB400, RHB500 and RHB 600 respectively, showed that the principal functional groups present in rice husk biochar are -OH, C-H, C=C, N-O, C-C, C-O and Si-O. The -OH group was predominantly present in all rice husk biochar. Based on the results, the good adsorption properties of the adsorbent to metal ions are attributed to the presence of these functional groups in the rice biochar, which acted as the binding sites. It was evident that there was a shift of most spectra after adsorption of metal ions as indicated to Figure 4.4 by an increase of wavenumber for  $Cd^{2+}$  and  $Pb^{2+}$  from 3426 cm<sup>-1</sup> to 3432 cm<sup>-1</sup>, also overlapping of spectra at 3432 cm<sup>-1</sup> and a decrease of wavenumber from 3426  $cm^{-1}$  to 3218  $cm^{-1}$  for  $Cu^{2+}$  due to interaction of metal ions with the functional group. The Figure 4.5 for result of optimal biochar indicated there was an increase of wave number for Cu<sup>2+</sup> and Pb<sup>2+</sup> from 3404 cm<sup>-1</sup> to 3426 cm<sup>-1</sup> and 3411cm<sup>-1</sup> and decrease of wave number from 3404 cm<sup>-1</sup> to 3396 cm<sup>-1</sup> for Cd<sup>2+</sup> after adsorption. The results obtained in Figure 4.6 show increase of wave number after adsorption of  $Cu^{2+}$  and  $Pb^{2+}$ ions from 3426 cm<sup>-1</sup> to 3440 cm<sup>-1</sup> and 3432 cm<sup>-1</sup> respectively. There was also overlapping of spectra for unloaded biochar and Cd<sup>2+</sup> metal ion at 3426 cm<sup>-1</sup>. The possible mechanisms for sorption of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Pb^{2+}$  on the adsorbent surface were due to the complexation between the metal ions onto negatively charged hydroxylating and carboxylate anions and results aligned to results obtained by Prapagdee et al., (2016) and Wang et al., (2019).

Copper, lead, and cadmium are transitional elements and have a greater tendency of binding via dative bonding. This is because of the presence of vacant d-orbital and hence they bind through dative bonding with lone pairs of the functional groups containing oxygen and nitrogen groups (Albadarin *et al.*, 2011 and Prapagdee *et al.*, 2016). The results correspond to results obtained by Shrestha *et al.*, (2019), which indicated the presence of oxygen and nitrogen functional groups such as carboxylic, hydroxyl, phenolic, and carboxyl groups on the surface of the biochar. The findings also suggested

that both the chemically activated and the non-activated biochar have similar functional groups, which for the most part remained intact during activation with sodium hydroxide and dilute zinc chloride (Figures 4.4 to 4.6). The chemically activated biochar are the ones that were loaded with metal ions. Prapagdee *et al.* (2016), in his study of physico-chemical activation on rice husk biochar for enhancing cadmium removal from aqueous solution observed similar trends.

### 4.2.2 Scanning Electron Microscopy Analysis

The shape and morphology of unpyrolyzed rice husk inactivated rice husk biochar produced at 500°C and chemically activated rice husk biochars (RHBT 400, RHBT 500, and RHBT 600) with sodium hydroxide and further activation with zinc chloride solutions were analyzed in this research work.



Plate 4.1: SEM micrograph of the unpyrolyzed RH

and inactivated biochar RHB500 and plate 4.2 display the micrographs for activated rice husk biochar RHBT400, RHBT500, and RHBT600.



Plate 4.2: SEM image of chemically inactivated (RHB500 a) and activated (RHBT500b) optimum rice husk biochar



Plate 4.3: SEM image of chemically activated RHBT400 (a) and RHBT600(b)

The SEM image reveals that the shape and morphology of unpyrolyzed rice husk adsorbent contained few pores on the surface of biochar material and the active sites were not well defined (Plate 4.1). The optimal inactivated biochar (RHB500) and activated (RHBT500) pyrolyzed at 500°C (Plate 4.2a and b) showed that the surface topography did not have well-defined pores for inactivated biochar. Through the chemical activation with sodium hydroxide and further, with zinc chloride solutions, the biochar that gave optimal adsorption properties RHBT500 as shown in (Plate 4.2b) had a

variety of regularly shaped pores that acted as active sites for adsorption. It had welldeveloped uniform fine pores structures, which were homogenously distributed on the surface of rice husk biochar making it to the best adsorbent material and the results corresponded to results obtained by (Ahiduzzaman and Sadrul, 2016, Bernard *et al.*, 2013, Salleh *et al.*, 2014 and Taha *et al.*, 2011).

The results obtained in the (Plate 4.3a), indicated that the RHBT400 had well-defined pores, a consistent interconnection of the network of the pores but they were gaps on surface of biochar. The activated biochar produced at 600°C shows regular shaped, well-developed pores which were uniformly distributed and there was the formation of a hollow tunnel at the surface of biochar (Plate 4.3b). The two biochars of lower (RHBT400) and upper (RHBT600) limit of the optimum biochar were not good adsorbent material for adsorption because of the gaps and hollow tunnel and this limit the active adsorption sites. According to Mopoung *et al.* (2020), the temperatures above 500°C, causes complete degradation of volatile matter and hence the destruction of adjacent walls and subsequent reduction in the number of binding sites on the sample surface. Also, there was the observation of many cracks on the surface of RHBT600. Jia *et al.*, (2018) and Mopoung *et al.* (2020), indicated these were attributed to higher temperatures.

The SEM analysis verifies the effect of chemical activation on the rice husk biochar surface. The results showed that the surface and pore structure were significantly affected when compared to the SEM images of unpyrolyzed rice husk and inactivated rice husk carbonized at 500°C (Plate 4.1, 4.2a and 4.2b). There was the creation of fine and more uniform pores in chemically activated biochar as compared to the inactivated biochar. According to Salleh *et al.* (2014), the development of small fine pores when pyrolysis temperatures were increased was due to the extraction of volatile materials and breakup of lignin and other mineral components. The rice husk biochar pore diameter was 100 nm indicating it is a porous material (Shrestha *et al.*, 2019).
### 4.2.3 Brunauer Emmert Teller Analysis

Figure 4.7 and 4.8 shows the adsorption and desorption isotherms of the RH and chemically activated rice biochar pyrolyzed at different temperatures (400, 500, and 600°C) and a comparison curve at 500°C between the inactivated and the chemically activated optimal biochar.



Figure 4.7 Adsorption and desorption isotherms of RH, RHBT400, RHBT500, and RHBT600



Figure 4.8 Adsorption and desorption isotherms of RHB500 and RHBT500

The results obtained in Figure 4.7 shows the rate of adsorption and desorption for the unpyrolyzed rice husk (RH) and rice husk biochar samples RHBT400, RHBT600 RHBT500. The lower portion of the loop indicated the adsorption loop and the uppermost portion is desorption. The adsorption process of unpyrolyzed rice husk (RH) showed that the adsorption and desorption forces were relatively weak as compared to RHBT400, RHBT500 and RHBT600 (Figure 4.7). The adsorption for the RHBT600 was higher and faster compared to RH, RHBT400 and RHBT500 indicating that pyrolysis temperature affects adsorption-desorption and chemical activation. The results corresponded to those of Sakr (2014), while investigating the effect of burning temperature and soaking time and indicated that as temperature increased adsorption and desorption increased. The BET analysis for rice husk biochar showed the particle size and pore structure. The lower the size of particles the higher the surface area and the more porous the particles. The results indicated that chemical activation greatly

contributed to the increase of adsorption and desorption processes since RHBT500 had the highest adsorption of two matrices Figure 4.8.

Table 4.1 shows the specific surface area, pore size, total pore volume, micro pore, and external surface.

Samples	Specific surface area (M <sup>2</sup> /g <sup>-1</sup> )	Pore size/width (Å)	Total pore volume (Cm <sup>3</sup> /g <sup>-1</sup> )	Micro pores (M <sup>2</sup> /g)	External surface area (M <sup>2</sup> /g)
RH	0.1927	77.662	30.0037	0.0008	0.5048
RHBT400	81.6524	30.578	30.0581	38.7402	42.9122
RHB500	54.0172	33.642	30.044	30.8158	30.5804
RHBT500	124.3960	28.471	30.095094	61.8157	62.5804
RHBT600	296.0646	25.553	30.189136	154.8370	141.2276

Table 4.1: The specific surface area, pore size, total pore volume, micro pores, and external surface area

The specific surface area was observed to increase as pyrolysis temperature increased and the highest was in RHBT600 while unpyrolyzed rice husk had the lowest (Table 4.1). This could be due to the release of certain volatile components from the biochar and the degradation of organic matter like cellulose and lignin (Tomczyk *et al.*, 2020). The same trend was observed by Angin and Şensöz (2014), in the effect of pyrolysis temperature on chemical and surface properties of biochar of rapeseed (*Brassica napus*) where the surface area increased as pyrolysis temperature increased. Chemical activation was also observed to affect the surface area of biochar since the activated optimum biochar (RHBT500) displayed a double increase in the surface area as compared to the inactivated one (Table 4.1). Similarly, the surface area of RHBT400 was higher than that of inactivated biochar pyrolyzed at RHB500. Similar results were reported by Angin and Şensöz (2014) and Prapagdee *et al.* (2016), who also observed that the larger the surface

area, the faster the reaction rate. The average adsorption pore width was observed to decrease as surface area per unit mass increased. It was lowest in RHBT600 (25.553 Å) and highest in raw rice husk (77.662 Å). The activated RHBT500 had a lower pore size (30.578 Å) compared to inactivated RHB500 (33.642 Å). The higher surface areas and smaller pore diameters indicated that the rice husk biochar is highly porous. The total pore volume for RHBT600 was 30.189136 cm<sup>3</sup>/g which was slightly bigger than that for untreated rice husk (RH 30.003746 cm<sup>3</sup>/g). The pores volume for chemically treated RHBT500 was higher (30.095094 cm<sup>3</sup>/g) than that for untreated RHB500 which had a valve of (30.058119 cm<sup>3</sup>/g).

According to Srivastava *et al.* (2017), BET analysis is based on the principle, that the rate of adsorption is equal to the rate of desorption on a homogeneous surface. The results obtained in this study showed that there was a relatively equal adsorption-desorption efficiency. This indicated that the adsorbent is highly reusable and that it has good stability. This could be attributed to the porous structure of rice husk particles which enhanced adsorbent stability towards the removal of metal ions from aqueous solution (Srivastava *et al.*, 2017). This attribute makes rice husk biochar to be economically viable and proves its suitability as an adsorbent for the treatment of wastewater.

# 4.3 Optimization of the Adsorption Parameters

# 4.3.1 Optimization of the Pyrolytic Temperature for Synthesizing Biochar Samples

Lead, copper, and cadmium solutions with different concentrations of 1, 2 and 4 mg/L were used as synthetic metal ion pollutants to enable the identification of the optimum temperature for the production of the most efficient and effective biochar for adsorption. The adsorption of all the three metals ions was done using 0.125g of adsorbent, room temperature, pH7 for synthetic pollutants solutions while varying the temperature from 300 to 700°C.

# 4.3.1.1 Determination of the Optimum Pyrolytic Temperature of Lead Ion

Figure 4.9 represents the graph for optimization of pyrolysis temperatures using the three concentrations of lead metal ions.



Figure 4.9 Plot of percent removal of Pb<sup>2+</sup> against biochar pyrolyzed at different temperatures

The percentage efficiency removal of metal ions in the adsorbent samples synthesized at different temperatures in all three concentrations had a common trend of increasing with pyrolytic temperatures as in Figure 4.9. According to Baccar *et al.*, (2009) and Jia *et al.* (2018), this was attributed to the decomposition of organic matter, which subsequently leads to the increase in the surface area and the size of the diameter of the pores. After attaining maximum adsorption at 500 and 600°C, in the 1 mg/L solution decreased slightly (Figure 4.9). The decrease in adsorption of the metal ions at higher temperatures was attributed to complete degradation of volatile matter at temperatures greater than 500°C and destruction of adjacent walls and hence reducing the number of the binding

sites on the surface (Jia *et al.*, 2018). In 1 mg/L efficiency removal of metal ions by chars from 300 to 500°C ranged from 22 to 80% and from 600 to 700°C it decreased from 78 to 64%. For 2 and 4 mg/L, the maximum efficiency removal of lead ions was achieved in the char produced at 500°C and was 100% (Figure 4.11). For 1 mg/L and 2 mg/L, the decrease remained constant at 88% for chars at 600 and 700°C. The optimum char was identified as the one synthesized at 500°C (RHBT500). The rapid uptake of lead metal ions by the char was due to competition of available binding sites on adsorbents by metal ions (Aderonke *et al.*, 2014 and Pakade *et al.*, 2017). According to Wang *et al.* (2010), the total availability of binding sites is limited, therefore, the decrease of adsorption was due to exhaustion of the number of the binding sites. Statistical analysis using ANOVA reveal that there was a significant difference ( $p \le 0.05$ ) for the three concentrations of Pb<sup>2+</sup> adsorption at different temperatures (Appendix I).

# 4.3.1.2 Optimization of Pyrolysis Temperature using Copper

Figure 4.10 indicates optimization of pyrolysis temperature using 1, 2 and 4 mg/L as the initial concentrations of  $Cu^{2+}$ .



# Figure 4.10 Plot of percent removal of copper ions against the biochar pyrolyzed at different temperatures

The efficiency removal was highest at 1 mg/L ranging from 98 to 100%, followed by 2 mg/L with a range of 75% to 100% and the lowest was 4 mg/L ranging from 35% to 70%. The adsorbents had a common trend of the rapid uptake of metal ions and after attaining the optimum adsorption the removal of copper either remained constant or decreased (Figure 4.10). Initially, a large percentage of copper ions was adsorbed most probably due to the availability of binding sites. Adsorption at 4 mg/L was the lowest of the three copper ion concentrations and it was, therefore noted that adsorption decreased with increasing concentration. This trend was most probably because the exchange sites on rice husk biochar were saturated with copper ions therefore, due to the common ion effect there was repulsion between the adsorbed and free copper ions (Hossain *et al.*, 2012b). The optimum char was identified as the one synthesized at 500°C (RHBT500). Statistical analysis using ANOVA show that there was a significant difference ( $p \le 0.05$ ) for the three concentrations of Cu<sup>2+</sup> adsorption at different temperatures (Appendix II).

## 4.3.1.3 Optimization of Pyrolysis Temperature using Cadmium

Figure 4.11 displays the adsorption curve for  $Cd^{2+}$  adsorbed by the various biochar samples from initial concentration of 1, 2, and 4 mg/L.



Figure 4.11 Plot of percent removal of cadmium ions against the biochar pyrolyzed at different temperatures

The adsorption trend observed was similar to the one for lead and copper that is, adsorption increased with pyrolytic temperature up till the biochar produced at 500°C and then decreased. However, unlike lead and copper, the initial cadmium concentration did not significantly affect the amount of cadmium adsorbed. Maximum ion adsorption of 98, 99 and 100% was attained for 1, 2, and 4 mg/L respectively at 500°C. At the higher temperatures of 600 and 700°C percentage adsorption decreased from 94 to 85% for 1 mg/L, 2 mg/L from 99 to 73% and 4 mg/L 97 to71% (Figure 4.11). The biochar produced at 500°C was considered to be the optimum biochar (RHBT500). This biochar (RHBT500) was used in subsequent adsorption experiments. Statistical analysis

Appendix (III) using ANOVA reveal that there was a significant difference ( $p \le 0.05$ ) for the three concentrations of Cd<sup>2+</sup> adsorption at different temperature.

# 4.3.2 Optimization of Contact Time

The contact time plays a major role in the adsorption process as it helps to determine the point at which the process achieves equilibrium between the adsorbate and adsorbent (Ocreto *et al.*, 2019). The adsorption of all the three metals ions was done using 0.125g of optimum biochar (RHBT500), room temperature and synthetic pollutants solutions were maintained at pH7. The time contact was varied from 3.75 to 120 minutes and adsorption was done using 1, 2, and 4 mg/L of lead, copper, and cadmium metal ions.

# 4.3.2.1 Optimization of Contact Time using Lead

Figure 4.12 shows the plot of percentage adsorption at various contact times using 1, 2, and 4 mg/L Pb<sup>2+</sup> concentrations.



Figure 4.12: Percentage removal of lead ion concentration versus contact time

The removal efficiency at 3.75 minutes was almost the same for the three concentrations (Figure 4.12). The sorption of lead ions increased with contact time and then became constant after attaining equilibrium. This could be due to the saturation of the binding sites by the metal ions. The maximum adsorption values of 80, 100, and 98% for 1, 2, and 4 mg/L respectively were achieved at 60 minutes (Figure 4.12). The equilibrium time was therefore identified as 60 minutes for all three concentrations. The same trend corresponded by results obtained by Olu-owolabi *et al.*, (2012) and in their experiments after attaining the optimal contact time percentage adsorption gradually reduced. Statistical analysis using ANOVA reveal that there was a significant difference ( $p \le 0.05$ ) for the three concentrations of Pb<sup>2+</sup> adsorption at varied contact time (Appendix IV).

# 4.3.2.2 Optimization of Contact Time using Copper

Figure 4.13 shows the percentage removal of  $Cu^{2+}$  at different contact times.



Figure 4.13: Plot of percentage removal of copper versus contact time

The sorption of the copper ion decreased with copper concentration used, this showed the trend from highest to lowest as 1, 2, and 4 mg/L (Figure 4.13). This could be as a result of repulsion forces between the adsorbed copper ions and free copper ions (Ngugi, 2015). The adsorption efficiency for the three initial concentrations increased with an increase in the residence time and after attaining the equilibrium point there was no further increment in heavy metal ions adsorption. This was indicated that adsorption sites available on the char were exhausted after attaining the equilibrium (Renu *et al.*, 2017b). The maximum sorption for the three concentrations was achieved at 60 minutes for 1 and 2 mg/L was 100%, and 4 mg/L was 90% (Figure 4.13). The optimum contact time in all the concentrations in copper was, therefore identified as 60 minutes. Similar trends were obtained by Chen *et al.*, (2008) and Hossain *et al.* (2012a), where there were no significant increases after 60 minutes of adsorption. Statistical analysis using ANOVA reveal that there was a significant difference ( $p \le 0.05$ ) for the three concentrations of Cu<sup>2+</sup> adsorption at varied contact time (Appendix V).

### 4.3.2.3 Optimization of Contact Time using Cadmium

Figure 4.14 shows the percentage removal of Cd<sup>2+</sup> against contact time



Figure 4.14: Percentage removal of cadmium in RHBT500 versus contact time

The relationship between the contact time and percentage removal efficiency of cadmium ions is illustrated in Figure 4.14 where contact time was varied from 3.75 to 120 minutes. The efficiency removal increased with an increase in contact time until a maximum of 30 minutes in all three concentrations. The adsorption for 3.75 minutes was the highest in the concentration 2 mg/L 96% and lowest in the initial concentration of 4 mg/L 80%. The maximum cadmium adsorbed at 30 minutes for different concentrations was observed to be 1 mg/L (94%), 2 mg/L (99%) and 4 mg/L (99%). It was observed that the sorption of cadmium ions on the biochar decreased after equilibrium was attained. The same trend of reduction of adsorption after reaching equilibrium was found by Wang *et al.* (2010), who realized that the adsorption capacity of cadmium on bamboo charcoal increased slowly with contact time before reaching a plateau value after the contact time of 30 minutes for all cadmium concentrations, which was considered sufficient for the removal of Cd<sup>2+</sup> by this adsorbent. Statistical analysis using ANOVA revealed

that there was a significant difference ( $p \le 0.05$ ) for the three concentrations of Cd<sup>2+</sup> adsorption at varied contact time (Appendix VI).

#### 4.3.3 Optimization of Biochar Dosage

The adsorption of all the three metals ions was done using optimum biochar (RHBT500) which was varied from 0.1250 to 1.0g, optimum contact time. Obtained for each metal ion, room temperature, synthetic pollutants solutions at pH7 and initial concentration of 1 mg/L of all the metal this was because, the initial concentration from previous experimental data obtained didn't predict the optimum conditions.

## 4.3.4 Optimization of Concentration of Synthetic Pollutants

The adsorption of all the three metals ions was done using 0.250 g of optimum biochar (RHBT500), optimum contact time ( $Cu^{2+}$  and  $Pb^{2+}$  60 mins and  $Cd^{2+}$  30 mins) room temperature, synthetic pollutants solutions at pH7. The initial concentration of metal ions was varied from 1 to 8 mg/L.

Figure 4.15 shows adsorption trends observed when the initial concentration of the metal ions was 1, 2, 4, and 8 mg/L.



Figure 4.15: Percentage removal of  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  versus concentration of metal ion

The results obtained in Figure 4.15 indicate that the adsorption capacity of the RHBT500 increased as the concentration increased for all the metal ions. The highest efficiency removal of the three metal ions for cadmium 95%, copper was 94%, and lead (88%) was observed with 2 mg/L (Figure 4.15). In addition, the sorption for cadmium, copper and lead was observed to decrease as the concentration levels increased. This could be due to the limited number of active sites after the adsorbent attained saturation over a certain concentration and therefore in a solution with higher concentrations, more metal ions were left un-adsorbed (Lee et al., 2017a and Ocreto et al., 2019). The optimum concentration for cadmium, copper and lead was 2 mg/L. It can be concluded that the number of metal ions adsorbed into the unit mass of the rice husk biochar at equilibrium (the adsorption capacity) rapidly increased at the low initial metal ions concentration and then it began to decrease as the metal ion concentration increased. Similar results were obtained by Abdus et al., (2016) and Giwa et al. (2013), indicating that the favorable sites become less energetic as concentrations of metal ions increased and the binding sites become almost completely covered. Statistical analysis using ANOVA reveal that there was a significant difference ( $p \le 0.05$ ) in the synthetic pollutant removal of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  for the three concentrations (Appendix X to XII).

#### **4.3.5** Optimization of pH of Synthetic Pollutants

Figure 4.16 shows the trend of change of pH with adsorption.



Figure 4.16: Plot of percentage removal of metal ions concentration versus pH

pH is a very crucial factor as it affects the biosorption of the metal ions, their chemistry in solution, and the surface chemistry of adsorbents (Priyantha *et al.*, 2018 and Saeed *et al.*, 2021). Figure 4.16 shows the effect of pH on removal efficiency of  $Cu^{2+}$ , Pb<sup>2+</sup> and Cd<sup>2+</sup>. The experiments were performed under optimal conditions acquired previously. The results showed that an increase in the solution pH from 2 to 12 had a significant effect on the adsorption of the three metal ions. At lower pH values (pH 2), the percentage removal of the three metal ions was lowest for cadmium (19%). According to Priyantha *et al.* (2018), this could be due to the competition of metal ions with H<sub>3</sub>O<sup>+</sup> and H<sup>+</sup> limiting the number of active sites in the adsorbent and preventing the  $Cu^{2+}$ , Pb<sup>2+</sup> and Cd<sup>2+</sup> ions from approaching the adsorption sites. According to Overah *et al.*, (2011) and Wang *et al.* (2019), the lower percentage removal of the three metal ions was due to the protonation of functional groups in the adsorbents, hence reducing binding sites available for adsorption of metals ions and also due to the existence of repulsion forces between the protonated functional groups and positively charged  $Cu^{2+}$ , Pb<sup>2+</sup> and Cd<sup>2+</sup> ions, thereby impeding the reaction of the adsorbent with metal ions.

The pH 7 was established to be the optimal pH for adsorption of  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  (Figure 4.16). According to Musumba *et al.* (2020), Nworie *et al.* (2019) and Wang *et al.* (2019), the adsorption of metal ions increased with an increase in pH due to the increase in the negative charge density on the biochar surface, enhancing the electrostatic attraction with the positively charged metal ions, therefore, resulting in higher percentage removal. At pH values beyond the optimum there was a decrease in adsorption for  $Cu^{2+}$  and  $Pb^{2+}$  while that for  $Cd^{2+}$  remained constant (Figure 4.16). This could be due to the precipitation of low soluble metal hydroxides which interfered with the biosorption process by immobilizing the metal ions making them unavailable for adsorption (Jellali *et al.*, 2021 and Musumba *et al.*, 2020). This leads to low removal of metal ions by the biochar as described by chemical equation 4.1

$$M^{2+} + 20H^- \longrightarrow M(OH)_2$$
.....4.1

These results agree with other adsorption studies (Kariuki *et al.*, 2017 and Ouyang *et al.*, 2019) who observed that percentage removal increased as pH increased and that after attaining the optimal pH, adsorption started to decline. Statistical analysis using ANOVA reveal that there was a significant difference ( $p \le 0.05$ ) in the change of pH for removal of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> (Appendix XIII to XV).

# 4.3.6 Optimization of Adsorption Temperature

Figure 4.17 shows the effect of temperature changes on the removal of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  using an aqueous solution of RHBT500 activated biochar.



# Figure 4.17: Plot of percentage removal of lead, copper, and cadmium metal ion versus temperature

Temperature is a crucial parameter in the adsorption of metal ions because temperature greatly affects the intermolecular forces between the adsorbate and adsorbent. On investigating the effect of temperature on metal ion adsorption, the adsorption capacity was observed to increase with increased temperature (Figure 4.17). This trend could be attributed to an increase in the rate of reaction as the average velocity and diffusion of metal ions increased and adhered to the surface of the adsorbent (Manyangadze *et al.*, 2020). The maximum adsorption for the three metal ions was found to be at 35°C (Figure

4.17). The magnitude of adsorption efficiency declined after attaining the optimal temperature when the temperature was increased from 35 to 45°C. This could be due to weak adsorption interaction between rice husk biochar and metal ions because of weakened physical and chemical attractive forces, hence reduced adsorption ability results corresponded to results obtained by (Ariffin *et al.*, 2017, Ugwu *et al.*, 2020 and Ullah *et al.*, 2020). The adsorption process for the three metal ions was observed to increase from 25 to 35°C this is because the increase in temperature favored the adsorption equilibrium. The adsorption process of the three metal ions indicated to be exothermic in nature this is because, the surface particles on biochar surface were unstable and when the metal ions were adsorbed the energy of the adsorbent decrease and this results in the evolution of heat. Similar results were observed by Flores-Cano *et al.*, (2013), Manyangadze *et al.*, (2020), Ngugi (2015) and Ugwu *et al.*, (2020). Statistical analysis using ANOVA revealed that there was a significant difference ( $p \le 0.05$ ) in the adsorption temperature removal of Cu<sup>2+</sup> (Appendix XVII) while the was a significant difference for Pb<sup>2+</sup> and Cd<sup>2+</sup> as in Appendix XVI and XVII respectively.

## 4.4 Comparative Test of Biomass Sorption

The sorption comparative tests of all the three sorption biomasses used 0,250g of optimum biochar (RHB500 and RHBT500) and activated charcoal, optimum contact time ( $Cu^{2+}$  and  $Pb^{2+}60$  mins and  $Cd^{2+}$  30mins), synthetic pollutants solutions at pH7, adsorption temperature 35°C and initial concentration of metal ions 2 mg/L.

Figure 4.18 shows sorption comparative tests for the treated, untreated, and activated biochar.



Figure 4.18: Plot of percentage removal of metal ion concentration versus biomass

Comparative tests for three biomasses that is: untreated rice husk biochar, chemically treated rice husk biochar, and commercial activated carbon were done using the obtained optimal conditions. The results obtained (Figure 4.18) indicated that the chemically activated biochar was the most effective adsorbent for efficient removal of lead (91%), copper (97%) and cadmium (95%) was observed. It was followed by commercially activated carbon with efficient removal of Pb<sup>2+</sup> 90%, Cu<sup>2+</sup> 96% and Cd<sup>2+</sup> 92% and finally the untreated biochar was having efficiency removal of Pb<sup>2+</sup> 85%, Cu<sup>2+</sup> 92% and Cd<sup>2+</sup> 90%. Similar results were obtained by Taha *et al.* (2014), when they investigated the adsorption of 15 different pesticides on untreated biochar, phosphoric acid-treated biochar, and charcoal. Generally, chemically modified biochar has greater potential in the adsorption of metal ions from aqueous solutions (Kareema *et al.*, 2021, Mao *et al.*, 2015, Sikdar *et al.*, 2020 and Ullah *et al.*, 2020). The treated rice husk biochar has proven to be viable adsorbents for the purification of contaminated water because it is more efficient and effective in the removal of metal ions.

#### 4.5 Biosorption Equilibrium

## 4.5.1 Adsorption Kinetics models

The experimental data of time-dependence biosorption of lead, copper, and cadmium on the biochar was determined using three kinetic models; namely the pseudo first order, pseudo second order and Elovich diffusion. The corresponding constant K, correlation coefficient ( $R^2$ ) and  $q_e$  were used to reveal the most suitable kinetic equation, which could predict the biosorption mechanism of the metal ions. The equations applied to kinetic study are shown in equations 2.1, 2.2, and 2.3 and the data used to plot the graphs are shown in Appendix XXVIII, XXIX and XXX respectively.

# **4.5.1.1 Pseudo First Order Adsorption Kinetics for Lead, Copper, and Cadmium** Figure 4.19 shows the Pseudo first order plot for adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> for

the optimum activated biochar against time (t).



Figure 4.19: Pseudo first order plot for the biosorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> onto activated rice husk biochar against time

The summary of regression coefficient ( $R^2$ ) deduced from the graph (Figure 4.19) and Table 4.2 show quite low correlation coefficient values ( $R^2$ ) for pseudo first order equation, lead 0.356, copper 0.349 and cadmium 0.231 indicating that the model did not satisfactorily fit adsorption of metal ions. The adsorption capacity at equilibrium ( $q_e$ mg/g) followed the trend copper (16.128), lead (1.198) and cadmium (0.998), this is because copper has a large ionic radius thus less nuclear charge lending to higher attraction of the biochar. Similar results were obtained by Din *et al.*, 2013 and Zhang *et al.* 2020), in the removal of heavy metal ions by the use of treated human hair.

Table 4.2: Pseudo first order kinetic parameters for adsorption of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$ 

Metal	<i>q</i> <sub>e</sub> (mg/g)	$q_t (\min^{-1})$	R <sup>2</sup>
Pb <sup>2+</sup>	1.198	0.714	0.356
$Cu^{2+}$ $Cd^{2+}$	16.128 0.998	0.032 2.299	0.349 0.231

# 4.5.1.2 Pseudo Second Order Adsorption Kinetics for Lead, Copper, and Cadmium

Figure 4.20 indicates the Pseudo second order plot for adsorption of  $Pb^{2+}$ ,  $Cu^{2+}$  and  $Cd^{2+}$  onto optimum activated biochar against time.



Figure 4.20: Pseudo second order plot for the biosorption of Pb<sup>2+</sup>, Cu<sup>2+</sup>and Cd<sup>2+</sup> onto activated rice husk biochar against time

The summary of regression coefficient ( $\mathbb{R}^2$ ) indicated pseudo second order kinetic model fitted the adsorption process quite well, with higher  $\mathbb{R}^2$  values as follows  $\mathbb{Cd}^{2+}$ ,  $\mathbb{Pb}^{2+}$  and  $\mathbb{Cu}^{2+}$  (Figure 4.20). The adsorption capacities of adsorbate at equilibrium (mg/g) as shown in Table 4.3 were: for lead 0.099, for copper 0.444 and for cadmium 0.059. The results indicated adsorption process was chemisorption since there was a formation of chemical bond between the metal ions and adsorbent. Similar results were obtained by Zhang *et al.* (2020), in the removal of heavy metals in chemically treated hair waste and also by Alamin and Kaewsichan, (2015) in the removal of  $\mathbb{Cd}^{2+}$  ions by using bamboo biochar.

Table 4.3: Pseudo second order kinetic parameters for adsorption of  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$ 

	Pseudo Second Order		
Metal	$q_e^2$ (mg/g)	$q_t (\min^{-1})$	$\mathbf{R}^2$

Pb <sup>2+</sup>	0.099	0.654	0.995
$Cu^{2+}$	0.444	0.012	0.791
$Cd^{2+}$	0.059	6.177	0.999

# 4.5.1.3 Elovich Model Adsorption Kinetics for Lead, Copper, and Cadmium

Figure 4.21 shows Elovich diffusion for the biosorption of  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$  onto activated rice husk biochar.



Figure 4.21: Elovich diffusion plot for the biosorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> onto activated rice husk biochar

The subjection of the kinetic data to the Elovich model revealed very low correlation coefficient values ( $\mathbb{R}^2$ ) values as shown in Figure 4.21 for  $\mathbb{Cu}^{2+}$ ,  $\mathbb{Pb}^{2+}$  and  $\mathbb{Cd}^{2+}$ . This indicated that this model was not applicable for the adsorption of  $\mathbb{Cu}^{2+}$ ,  $\mathbb{Pb}^{2+}$  and  $\mathbb{Cd}^{2+}$  metal ions. Table 4.4 indicate low level of initial rate of adsorption (*A*) and coefficient of desorption (*B*) for all the selected metal ions. Studies by Hossain *et al.* (2012b), in the biosorption of  $\mathbb{Cu}^{2+}$  from water by banana peels.

Metal	Elovich diffusion A (g/mg/min)	B (mg/g/mol)	R <sup>2</sup>
$Pb^{2+}$	0.0379	0.0719	0.4527
Cu <sup>2+</sup>	0.0198	0.1068	0.4737
$\mathrm{Cd}^{2+}$	0.0062	0.2351	0.3948

Table 4.4: Parameters for adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup>

Table 4.5: Comparison of kinetics parameters for Pseudo first, Pseudo second order kinetics and Elovich for biosorption of Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> onto activated rice husk biochar

seudo first order Pseudo second order			Elovich diffusion					
$q_e$	$q_t$	$\mathbf{R}^2$	$q_e^2$	$q_t$	$\mathbf{R}^2$	Α	В	$\mathbf{R}^2$
(mg/g)	( <b>min</b> <sup>-1</sup> )		(mg/g)	( <b>min</b> <sup>-1</sup> )				
1.198	0.714	0.356	0.099	0.654	0.994	0.037	0.071	0.452
16.128	0.032	0.349	0.444	0.012	0.791	0.019	0.106	0.473
0.998	2.299	0.231	0.059	6.177	0.999	0.006	0.235	0.394
1	first orde <i>q<sub>e</sub></i> (mg/g) 1.198 16.128 0.998	first order         q_e       q_t         (mg/g)       (min <sup>-1</sup> )         1.198       0.714         16.128       0.032         0.998       2.299	first order $q_e$ $q_t$ $\mathbb{R}^2$ (mg/g)(min <sup>-1</sup> ) $\cdot$ 1.1980.7140.35616.1280.0320.3490.9982.2990.231	first order       Pseudo set $q_e$ $q_t$ $\mathbb{R}^2$ $q_e^2$ (mg/g)       (min <sup>-1</sup> )       (mg/g)         1.198       0.714       0.356       0.099         16.128       0.032       0.349       0.444         0.998       2.299       0.231       0.059	first order       Pseudo second ord $q_e$ $q_t$ $\mathbb{R}^2$ $q_e^2$ $q_t$ (mg/g)       (min <sup>-1</sup> )       (mg/g)       (min <sup>-1</sup> )         1.198       0.714       0.356       0.099       0.654         16.128       0.032       0.349       0.444       0.012         0.998       2.299       0.231       0.059       6.177	First order       Pseudo second order $q_e$ $q_t$ $\mathbb{R}^2$ $q_e^2$ $q_t$ $\mathbb{R}^2$ (mg/g)       (min <sup>-1</sup> )       (mg/g)       (min <sup>-1</sup> ) $\mathbb{R}^2$ 1.198       0.714       0.356       0.099       0.654       0.994         16.128       0.032       0.349       0.444       0.012       0.791         0.998       2.299       0.231       0.059       6.177       0.999	first order       Pseudo second order       Elovic $q_e$ $q_t$ $\mathbb{R}^2$ $q_e^2$ $q_t$ $\mathbb{R}^2$ $\mathbb{A}$ (mg/g)       (min <sup>-1</sup> )       (mg/g)       (min <sup>-1</sup> ) $\mathbb{C}^2$ </td <td>First order       Pseudo second order       Elovich diffus         <math>q_e</math> <math>q_t</math> <math>\mathbb{R}^2</math> <math>q_e^2</math> <math>q_t</math> <math>\mathbb{R}^2</math> <math>\mathbb{A}</math> <math>\mathbb{B}</math>         (mg/g)       (min<sup>-1</sup>)       (mg/g)       (min<sup>-1</sup>)       (mg/g)       (min<sup>-1</sup>)       <math>\mathbb{C}</math> <math>\mathbb{C}</math>         1.198       0.714       0.356       0.099       0.654       0.994       0.037       0.071         16.128       0.032       0.349       0.444       0.012       0.791       0.019       0.106         0.998       2.299       0.231       0.059       6.177       0.999       0.006       0.235</td>	First order       Pseudo second order       Elovich diffus $q_e$ $q_t$ $\mathbb{R}^2$ $q_e^2$ $q_t$ $\mathbb{R}^2$ $\mathbb{A}$ $\mathbb{B}$ (mg/g)       (min <sup>-1</sup> )       (mg/g)       (min <sup>-1</sup> )       (mg/g)       (min <sup>-1</sup> ) $\mathbb{C}$ $\mathbb{C}$ 1.198       0.714       0.356       0.099       0.654       0.994       0.037       0.071         16.128       0.032       0.349       0.444       0.012       0.791       0.019       0.106         0.998       2.299       0.231       0.059       6.177       0.999       0.006       0.235

The biosorption process of the three heavy metal ions was observed to follow Pseudo second order kinetics, which involved the formation of chemical bonds due to sharing or exchange of electrons between the adsorbate and adsorbent. Therefore, experimental data shows that the rate-limiting step of the sorption process was chemical sorption. Similar results were obtained by Kołodyńska *et al.* (2012), in kinetic studies and adsorptive characterization of biochar in the removal Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> ions by Overah *et al.*, (2011) and Priyantha *et al.* (2018), when studying the removal of trace elements and their derivatives from the environment. Also in the removal of various trace metals Cd, Cr, Cu, and Pb by Khare (2013), from acidic solutions using plant waste-derived biochar, it was observed that adsorption favored Pseudo second order kinetics. These findings were in line with sorption studies reviewed by Bakyayita

(2014), Batagarawa and Ajibola (2019) and Wan Ngah and Hanafiah (2008), who opined that the biosorption processes followed Pseudo second order kinetics.

In conclusion, the results from this study revealed that the adsorption of  $Pb^{2+}$ ,  $Cu^{2+}$ , and  $Cd^{2+}$  follows pseudo second order kinetics but not by the pseudo first order or Elovich diffusion. From the principle on which pseudo second order is established, the adsorption involves chemisorption as the operative reaction mechanism. The same conclusion was made in this study, that the mode of adsorption was chemisorption.

#### 4.5.2 Adsorption Isotherms Models

In this study, the equilibrium data for  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  was determined using initial concentrations between 1 to 8 mg/L and using four adsorption isotherms namely; Langmuir, Jovanovich, Freundlich, and Tempkin. The equations applied to the adsorption isotherm models study are shown in equations 2.4, 2.5, 2.6, 2.8 and 2.9 and the data used for plotting the graphs are given in Appendix XXXI, XXXII and XXXIII respectively.

**4.5.2.1** The Langmuir Isotherms for adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup>, and Cd<sup>2+</sup> Figure 4.22 indicates the Langmuir isotherms of Pb<sup>2+</sup>, Cu<sup>2+,</sup> and Cd<sup>2+</sup>.



Figure 4.22: Langmuir isotherms for Cu<sup>2+</sup>, Pb<sup>2+,</sup> and Cd<sup>2+</sup> adsorption onto rice husk

The results obtained in Figure 4.22 shows that the equilibrium fitted well for the three metals ions to the Langmuir equation with a higher correlation coefficient ( $\mathbb{R}^2$ ). From Table 4.6, the values for maximum adsorption quantity ( $q_{max}$ ) followed the pattern Pb<sup>2+</sup>, Cd<sup>2+</sup> and Cu<sup>2+</sup>. The Langmuir constant values ( $K_L$ ) indicated Cu<sup>2+</sup> was more superior than for Cd<sup>2+</sup> and Pb<sup>2+</sup> this signifies that bio sorbent has a higher binding affinity for Cu<sup>2+</sup> than the other metal ions. This could be attributed to the fact that Pb<sup>2+</sup> ions are bigger than copper ions and therefore the repulsion may be greater and also the ions may not fit as snugly as the copper ions in the binding sites.

The equilibrium parameter ( $R_L$ ) which usually indicates adsorption system is either; unfavorable ( $R_L$ >1) linear ( $R_L$ =1), favorable (0< $R_L$ >1),  $K_L$  and irreversible  $R_L$ =0. The  $R_L$ were found to be,  $Cu^{2+}$  0.03678,  $Pb^{2+}$  0.06398 and  $Cd^{2+}$  0.06080. The adsorption was favorable for the three metal ions. Similar results were obtained by (Kamau *et al.* (2020), Olu-owolabi *et al.*, (2012) and Overah *et al.*, (2011).

Table 4.6: Langmuir isotherm model parameters for adsorption of  $Cu^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$ 

Langmuir Isotherm	Metal		
	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Cd <sup>2+</sup>
$q_{max} (mg^{-1})$ $K_L (Lmg^{-1})$	0.4170	1.0486	0.9471
R.	2.3981	0.9537	1.0558
$\mathbf{n}_L^2$	0.03678	0.06398	0.06080
ĸ	0.9894	0.9863	0.9537

# 4.5.2.2 The Jovanovich Isotherms for Adsorption of Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup>

Figure 4.26 shows the adsorption of  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  onto the biochar by use of the Jovanovich model.



Figure 4.23: Jovanovich isotherm for Pb<sup>2+</sup>, Cu<sup>2+</sup> and Cd<sup>2+</sup> adsorption onto rice husk biochar

The Jovanovich isotherm model was used to fit experimental data (Figure 4.23). Cadmium fitted well to the Jovanovich isotherm model as it displayed a higher correlation coefficient ( $\mathbb{R}^2$ ) as in Table 4.7. The maximum amount of adsorbate adsorbed per unit mass of adsorbent followed the trend  $Cd^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ . According to Quiñones and Guiochon (1998), Jovanovich favored metal ions with low detection limits like cadmium hence the adsorption system was a monolayer isotherm.

Table 4.7: Jovanovich isotherm model parameters for adsorption of  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ 

Jovanovich Isotherm	Metal		
	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Cd <sup>2+</sup>
$K_J (Lg^{-1})$	-2.0739	-2.3933	-3.3647
$q_{max} (mgg^{-1})$	0.4715	1.1151	10.5173
$R^2$	0.4270	0.7135	0.9994

### 4.5.2.3 Freundlich Isotherm for Cu2+, Pb2+ and Cd2+

Figure 4.24 Indicates the adsorption of  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  onto the char by use of Freundlich isotherm.



Figure 4.24: Freundlich isotherm for Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> adsorption onto rice husk biochar

Freundlich model was also used to fit adsorption data using equation 2.6 to find the Kf (mg/L) and n which are the constants for incorporating all factors affecting the adsorption process (that is indicator of adsorption capacity and intensity). The results

obtained in Table 4.8 Kf (mg/L) were: Pb<sup>2+</sup> 6.0653, Cu<sup>2+</sup> 4.2474 and Cd<sup>2+</sup> 0.5234, the high values for sorption of Cu<sup>2+</sup> and Pb<sup>2+</sup> ions onto rice husk biochar biosorbents indicated that these sorbents have heterogeneous site binding affinities. The *n* values followed this trend from the highest binding intensity Pb<sup>2+</sup>, Cu<sup>2+</sup>and Cd<sup>2+</sup>. The adsorption process was favorable for Cu<sup>2+</sup> and Pb<sup>2+</sup> because *n* values were greater than one (Lee *et al.*, 2017b and Priyantha *et al.*, 2018) and also indicated a strong bond between rice husk biochar and the two metal ions but, for Cd<sup>2+</sup> was normal adsorption since *n* value was less than one. The correlation coefficient (R<sup>2</sup>) Figure 4.24 for Cu<sup>2+</sup> and Pb<sup>2+</sup> was higher indicating they undergo multilayer (physisorption) adsorption. The R<sup>2</sup> value for cadmium was very low meaning that it does not follow the Freundlich isotherm model.

Table 4.8: Freundlich isotherm model parameters for adsorption of  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ 

Freundlich Isotherm	Metals		
	Cu <sup>2+</sup>	$Pb^{2+}$	$Cd^{2+}$
n	1.8261	2.3229	0.2349
$Kf_{(mg/L)}$	4.2474	6.0653	0.5234
$\mathbf{R}^2$	0.85181	0.9675	0.3989

<sup>4.5.3</sup> 4.5.3 Temkin isotherm for Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup>

Figure 4.25 shows Tempkin isotherm for  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  adsorption onto rice husk biochar.



Figure 4.25: Temkin isotherm for Cu<sup>2+</sup>, Pb<sup>2+</sup> and Cd<sup>2+</sup> adsorption onto rice husk biochar

Temkin model was used to fit experimental data for the biochar (Figure 4.25). The correlation coefficient ( $\mathbb{R}^2$ ) values observed in Table 4.9 were high for the three metal ions, indicating the suitability of the model in the adsorption. The T values of the heat of adsorption were less than unit for Cu<sup>2+</sup> 0.088, Pb<sup>2+</sup> 0.17487 and Cd<sup>2+</sup> 0.26282 and Temkin isotherm constant b<sub>T</sub> was Cu<sup>2+</sup> 0.33133, Pb<sup>2+</sup> 0.39537 and Cd<sup>2+</sup> 0.73526 (Table 4.9). Similar results were obtained by Kamau *et al.* (2020), in the removal of lead and cadmium from wastewater using Macadamia Nutshell biochar.

Table 4.9: Temkin isotherm model parameters for adsorption of  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ 

Temkin Isotherm	Metal		
	Cu <sup>2+</sup>	$Pb^{2+}$	$\mathrm{Cd}^{2+}$
T (Lmg-1)	0.0888	0.1748	0.2628
b <sub>T (KJmol-1)</sub>	0.3313	0.3953	0.7354

0.9780 0.9729 0.9	115
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Table 4.10: Comparison of various sorption isotherm parameters for  $Cu^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$  adsorption

 $\mathbf{R}^2$ 

Isotherms Models Parameters	Metals		
Langmuir Isotherm	Cu <sup>2+</sup>	Pb <sup>2+</sup>	Cd <sup>2+</sup>
<i>q<sub>max</sub></i> (mg <sup>-1</sup> ) <i>K<sub>L</sub></i> (Lmg <sup>-1</sup> ) <i>R<sub>L</sub></i> R <sup>2</sup> Jovanovich Isotherm	0.4170 2.3981 0.03678 0.9894	1.0486 0.9537 0.06398 0.9863	0.9471 1.0558 0.06080 0.9537
$K_J$ (Lg <sup>-1</sup> )	-2.0739	-2.3932	-3.3647
$q_{max} (\mathrm{mg/g})$	0.4715	1.1151	10.517
$\mathbf{R}^2$	0.42706	0.71355	0.9994
Freundlich Isotherm n $Kf_{(mg/L)}$ $R^2$	1.82615 4.2474 0.8518	2.3229 6.0653 0.9675	0.2349 0.5234 0.3989
<b>Temkin Isotherm</b> T (Lmg-1) b <sub>T (KJmol-1)</sub>	0.0888 0.3313	0.1748 0.3953	0.2628 0.7354
$R^2$	0.9780	0.9729	0.9115

The evaluated constants of stimulated data of  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$  are reported in Table 4.10 which shows the comparison of adsorption isotherms of the optimum biochar. The linear regression tool was used to determine the best fitting adsorption model because, it

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helped to identify the distribution of adsorbate, the adsorption system and verified the consistency of the theoretical assumption of the adsorption isotherm model.

In general, for the monolayer adsorption model, Langmuir fitted well in the metal ions and Jovanovich was more suitable for  $Cd^{2+}$ . In multilayer models, Freundlich isotherms fitted well in  $Cu^{2+}$  and  $Pb^{2+}$ , but not for  $Cd^{2+}$  ion. The Temkin model was suitable for three metal ions. This indicated that  $Cu^{2+}$ ,  $Pb^{2+}$ , and  $Cd^{2+}$  underwent both monolayer (chemisorption) and multilayer (physisorption) as also observed by Srivastava *et al.*, (2017). Similar results are found by Yahaya *et al*,. (2011), in adsorptive removal of  $Cu^{2+}$ by use of activated rice husk by using of ZnCl<sub>2</sub> solution.

#### **CHAPTER FIVE**

### CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Conclusions

In the current research on the removal of cadmium, lead and copper using rice husk biochar as potential adsorbent, the following findings were revealed;

i. The optimum biochar rice husk was produced at 500°C.

ii. The characterization of biochar revealed the presence of OH, CH- and C=O as the major functional groups which acted as binding sites during adsorption. SEM analysis displayed regular shaped pores. The BET analysis showed that specific surface area increased with increase in temperature.

iii. The optimized conditions for contact time, pH and optimal dosage for the metal ions varied with the metal ion.  $Cu^{2+}$  and  $Pb^{2+}$  displayed an optimal contact time of 60 minutes, whereas for  $Cd^{2+}$  it was 30 minutes. The optimum pH was 7 for  $Cd^{2+}$ ,  $Cu2^+$  and  $Pb^{2+}$ . The optimal dosage was 0.250 g, while the initial concentrations were 2 mg/L for  $Cd^{2+}$ ,  $Cu^{2+}$  and  $Pb^{2+}$ . The optimum temperature was found to be 35°C for all the selected metal ions.

iv. The experiment data was fitted into three kinetic models, the Pseudo first order, Pseudo second order, and Elovich diffusion. The Pseudo second order fitted the adsorption mechanism indicating chemisorption for the three metal ions which involved the formation of a chemical bond between the metal ions and the adsorbent.

v. The equilibrium data was subjected to four isotherm models; Langmuir, Jovanovich, Freundlich, and Temkin. The Langmuir adsorption system was found to be favorable for the three metal ions. The  $Cd^{2+}$  removal was observed to follow the Jovanovich model because of its low detection limit. The Freundlich adsorption process was favorable for

 $Cu^{2+}$  and  $Pb^{2+}$  because *n* value was greater than one, which indicated a strong bond between rice husk biochar and the metal ions.

vi. The comparative test for the three biomasses, namely; untreated rice husk biochar, chemically treated rice husk biochar, and commercial activated carbon revealed that the chemically activated biochar was the best adsorbent with efficiency removal for  $Cu^{2+}$ ,  $Pb^{2+}$  and  $Cd^{2+}$ . Generally, the chemically activated rice husk biochar proved to be a viable low-cost adsorbent, which was also eco-friendly and with excellent adsorption ability in the removal of the heavy metal ions.

# 5.2 Recommendations

From the above findings and conclusions, the following are recommended for further research;

i. The efficiency of the rice husk biochar in the removal of other types of contaminants like organic, other inorganic pollutants, pesticides, and pharmaceutical waste effluents should be investigated.

ii. The rice husk biochar should be tested for removal of heavy metal ions in real water samples.

iii. The recyclability analysis of the rice husk biochar and the cycles needed for complete desorption of metal ions from the biochar could be investigated

iv. The continuous adsorption model could be used as an adsorption process instead of the batch adsorption process, which was used in the current research project.

v. A comparative test on effectiveness and efficiency between rice husk, rice straw, and other biomass should be undertaken using different ratios.

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## APPENDICES

Appendix I:Variation (ANOVA) for optimization of pyrolytic temperature on lead ions removal

Source	of	SS	Df	MS	F	P-value	F crit
Variation							
Between Groups		0.556631	5	0.111326	10.61748	0.000445	3.105875
Within Groups		0.125822	12	0.010485			
Total		0.682454	17				

Appendix II: Variation (ANOVA) for optimization of pyrolytic temperature on copper ions removal

Source of Variation	SS	Df	MS	F	P-value	F crit
Between Groups	0.704492	5	0.140898	4.680584	0.013306	3.105875
Within Groups	0.361233	12	0.030103			
Total	1.065725	17				

Appendix III: Variation (ANOVA) for optimization of pyrolytic temperature on cadmium ions removal

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups Within Groups	0.4297 0.0005	5 12	0.0859 4.28E-05	2008.959	4.23E-17	3.105
Total	0.4303	17				

Appendix IV: Variation (ANOVA) for optimization of contact time for removal of lead ions

Source of						
Variation	SS	df	MS	F	<b>P-value</b>	F crit
Between Groups	2.0248	6	0.3374	346.8558	2.69E-08	3.865969
Within Groups	0.0068	7	0.0009			
Total	2.0316	13				

Appendix V: Variation (ANOVA) for optimization of contact time for removal of copper ion

Source of						
Variation	SS	df	MS	$\mathbf{F}$	<b>P-value</b>	F crit
Between Groups Within Groups	0.0350 0.0007	6 7	0.0058 0.0001	55.641	1.49E-05	3.865
Total	0.03577	13				

## Appendix VI: Variation (ANOVA) for optimization of contact time for removal of cadmium ions

Source of					P-	
Variation	SS	Df	MS	F	value	F crit
Between Groups Within Groups	1.29535796 0.00193509	6 7	0.21589 0.000276	780.971	1.58E1	3.86597
Total	1.297293054	13				

## Appendix VII: Variation (ANOVA) for optimization of dosage for removal of lead ion

Source of						
Variation	SS	df	MS	F	<b>P-value</b>	F crit
					7.54E-	
Between Groups	0.4553	3	0.151769	66492.42	10	6.591382
Within Groups	9.13E-06	4	2.28E-06			
Total	0.4553	7				

Appendix VIII: Variation (ANOVA) for optimization of dosage for removal of copper ions

Source of						
Variation	SS	df	MS	F	<b>P-value</b>	F crit
Between Groups	0.009874	3	0.003291	1.065775	0.457077	6.591382
Within Groups	0.012353	4	0.003088			
Total	0.022227	7				

Appendix IX: Variation (ANOVA) for optimization of dosage for removal of cadmium ions

Source of						
Variation	SS	Df	MS	F	<b>P-value</b>	F crit
Between Groups	0.0006304	3	0.0002	28.6523	0.003652	6.591382
			7.34E-			
Within Groups	0.00002934	4	06			
Total	0.000659835	7				

Appendix X: Variation (ANOVA) for optimization of synthetic pollutant concentration for removal of lead ions

Source of						
Variation	SS	Df	MS	F	<b>P-value</b>	F crit
Between Groups	2.988334	3	0.996111	81.7125	0.000481	6.591382
Within Groups	0.048762	4	0.01219			
Total	3.037096	7				

Appendix XI: Variation (ANOVA) for optimization of synthetic pollutant concentration for removal of copper ions

Source of						
Variation	SS	Df	MS	F	<b>P-value</b>	F crit
Between Groups Within Groups	9.08013 0.076149	3 4	3.02671 0.019037	158.988	0.00011	6.59138
Total	9.156283	7				

Appendix XII: Variation (ANOVA) for optimization of synthetic pollutant concentration for removal of cadmium ions

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00155	3	0.0005	9.12202	0.02916	6.59138
			5.7E-			
Within Groups	0.000228	4	05			
Total	0.001787	7				

Appendix XIII: Variation (ANOVA) for optimization of adsorption pH for removal of lead ions

Source of Variation	SS	df	MS	F	<b>P-value</b>	F crit
Between Groups	0.862927	4	0.215732	192.4271	1.17E-05	5.192168
Within Groups	0.005606	5	0.001121			
Total	0.868533	9				

Appendix XIV: Variation (ANOVA) for optimization of adsorption pH for removal of copper ions

Source of						
Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.876892	4	0.2192	287.067	4.32E-06	5.192168
Within Groups	0.003818	5	0.0007			
Total	0.88071	9				

Appendix XV: Variation (ANOVA) for optimization of adsorption pH for removal of cadmium ions

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	61.2909	4	15.3227	9141.90	7.65E-10	5.192168
Within Groups	0.00838	5	0.001676			
Total	61.29931	9				

Appendix XVI: Variation (ANOVA) for optimization of adsorption temperature for removal of lead ions

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0295780	2	0.01478	7.40351	0.0691	9.55209
	0.0059927		0.00199			
Within Groups	1	3	8			
Total	0.0355707	5				

Appendix XVII: Variation (ANOVA) for optimization of adsorption temperature for removal of copper ions

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.00415	2	0.00207	10.6411	0.04342	9.55209
Within Groups	0.000585	3	0.000195			
Total	0.00473	5				

Appendix XVIII: Variation (ANOVA) for optimization of adsorption temperature for removal of cadmium ions

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	0.0001	2	5.37E-05	6.255294	0.085063	9.552094
Within Groups	2.57E-05	3	8.58E-06			
Total	0.000133	5				

Appendix XIX : Calibration curve for the optimization of pyrolytic temperature for removal of lead ions



Appendix XX: Calibration curve for the optimization of pyrolytic temperature for removal of copper ions



Appendix XXI: Calibration curve for optimization of pyrolytic temperature for removal of cadmium ions



Appendix XXII: Calibration curve for the optimization of contact time, adsorbent dosage, pH, temperature and comparative test for biomasses for removal of lead ions



Appendix XXIII: Calibration curve for optimization of contact time, adsorbent dosage, pH, temperature and comparative test of biomasses in removal of copper ions



Appendix XXIV: Calibration curve for the optimization of contact time, adsorbent dosage, pH, temperature and comparative test of biomasses for removal cadmium ions





Appendix XXV: Calibration curve for the optimization of concentration for removal of lead ions









Appendix XXVIII: Data for the kinetic studies on lead metal ions using 2 mg/L

Time	Co	C <sub>f</sub>	qt	<b>q</b> e	<b>q</b> e- <b>q</b> t	In(q <sub>e</sub> -	t/q <sub>t</sub>	Int
(mins)						q <sub>t</sub> )		
3.75	1.7228	0.7189	0.1206	0.160	0.06	-1.8336	37.5	1.3218
7.5	1.7228	0.7189	0.1606	0.160	0.0394	-1.8336	62.1890	2.0149
15	1.7228	0.2233	0.2399	0.239	0.0293	-1.4323	71.5308	2.7081
30	1.7228	0.1372	0.2397	0.254	0.030	-1.3714	118.2499	3.4012
60	1.7228	0.1211	0.2537	0.294	0.0377	-1.2250	234.1001	4.0943
120	1.7228	0.1211	0.2563	0.294	0.0377	-1.2250	468.2013	4.7849

Time	Co	C <sub>f</sub>	qt	q <sub>e</sub>	<b>q</b> e- <b>q</b> t	In(q <sub>e</sub> -	t/q <sub>t</sub>	Int
(mins)						q <sub>t</sub> )		
3.75	1.9711	1.6471	0.0578	0.2116	0.21160	-	72.3938	1.3218
						1.5533		
7.5	1.9711	1.7434	0.0364	0.273	0.27296	-	206.0439	2.0149
						1.2984		
15	1.9711	1.7439	0.0364	0.278	0.27796	-	412.0879	2.7081
						1.2803		
30	1.9711	1.7443	0.0363	0.278	0.27796	-	826.4462	3.4012
						1.3803		
60	1.9711	1.7451	0.0362	0.312	0.3112	-	1657.4586	4.09443
						1.1649		
120	1.9711	1.7461	0.0360	0.322	0.32196	-	1666.6667	4.7849
						1.1333		

Appendix XXIX: Data for the kinetic studies on copper metal ions using 2 mg/L

Time	Co	C <sub>f</sub>	qt	<b>q</b> e	<b>q</b> e- <b>q</b> t	In(q <sub>e</sub> -	t/q <sub>t</sub>	Int
(mins)						q <sub>t</sub> )		
3.75	1.6472	0.0651	0.000250	0.252	0.2517	-	15	1.3218
						1.3793		
7.5	1.6472	0.0156	0.000261	0.260	0.2597	-	28.7356	2.0149
						1.3481		
15	1.6472	0.0267	0.000259	0.259	0.2587	-	57.8445	2.7081
						1.3519		
30	1.6472	0.0288	0.000258	0.258	0.2577	-	115.8449	3.4012
						1.3558		
60	1.6472	0.7814	0.000250	0.125	0.1248	-	239.0438	4.0943
						2.0810		
120	1.6472	1.2003	0.000244	0.190	0.1897	-	491.1993	4.7849
						1.6623		
120	1.6472	1.2003	0.000244	0.190	0.1897	2.0810 - 1.6623	491.1993	4.7849

Appendix XXX: Data for the kinetic studies on cadmium metal ions using 2 mg/L

Appendix XXXI: Data for the adsorption isotherms studies on copper metal ions

Co	C <sub>e</sub>	1/C <sub>e</sub>	<b>q</b> e	$C_e/q_e$	logC <sub>e</sub>	$\log q_{e}$	Inq <sub>e</sub>	InC <sub>e</sub>
0.9780	0.06933	14.4238	0.0725	0.9589	-	-	-	-2.6689
					1.1591	1.4096	2.6269	
2.0000	0.1025	9.7561	0.151	1.4804	-	-	-	-2.2779
					0.8210	0.9893	1.8903	
4.000	0.5229	1.91224	0.2773	1.8859	-	-	-	-0.6484
					0.4380	0.5571	1.2827	
7.9881	2.7416	0.3648	0.4167	7.5154	-	-	-	1.0085
					0.2816	0.3802	0.8754	

Appendix XXXII: Data for the adsorption isotherms studies on lead metal ions

Co	C <sub>e</sub>	1/C <sub>e</sub>	<b>q</b> e	$C_e/q_e$	logC <sub>e</sub>	logq <sub>e</sub>	Inq <sub>e</sub>	InC <sub>e</sub>
1.000	0.1360	7.3529	0.0684	1.9883	-0.8665	-1.1649	-2.6824	-1.9951
2.0117	0.2473	4.0437	0.1390	1.7791	-0.6068	-0.8570	-1.9733	-1.3972
4.000	0.5845	1.7109	0.2709	2.1576	-0.2332	-0.5672	-1.3060	-0.5370
7.9853	1.6571	0.6035	0.5044	3.2857	0.2193	-0.2972	-0.6844	-0.5051

Appendix XXXIII: Data for the adsorption isotherms studies on lead metal ions

Co	C <sub>e</sub>	1/C <sub>e</sub>	<b>q</b> e	$C_e/q_e$	logC <sub>e</sub>	logq <sub>e</sub>	lnq <sub>e</sub>	InC <sub>e</sub>
0.9597	0.0823	12.1507	0.07	0.1756	-	-1.1549	-2.4974	-2.6593
					1.0846			
2.0548	0.1180	12.6582	0.1523	0.1761	-	-0.8173	-2.5380	-1.8819
					1.1024			
3.9355	0.2108	12.0627	0.3076	0.2695	-	-0.5120	-2.4901	-1.7788
					1.0814			
8.0222	0.4188	9.0252	0.6291	0.5187	-	-0.2013	-2.200	-0.4635
					0.9555			