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Application of rice and corn husk biochar for removal of heavy metal ions from industrial wastewater

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**APPLICATION OF RICE AND CORN HUSK BIOCHAR FOR REMOVAL
OF HEAVY METAL IONS FROM INDUSTRIAL WASTEWATER**

Paulo Martin Sanka

**Dissertation Submitted in Partial Fulfilment of the Requirements for the Degree of
Master's in Hydrology and Water Resources Engineering of the Nelson Mandela African
Institution of Science and Technology, Arusha, Tanzania.**

January, 2020

ABSTRACT

This study investigated the removal of heavy metal ions from industrial wastewater by using rice and corn husk biochar. The choice of the materials was influenced by their largest surface area, plentiful functional groups and their availability in the local environment. Rice and corn husks were pyrolysed at 500, 600, and 700 °C to make biochars that were used to treat low quality industrial wastewater. Carbonisation of rice husks at 600 °C produced the best removal efficiencies for Cr (65%), Fe (90%) and Pb (> 90%). The carbonisation of corn husks at 600 °C produced the worst removal efficiencies for Cr (only 20%) and Pb (slightly > 35%). Regardless of the carbonisation temperature, rice husk biochars performed better than corn husk biochars. All data fitted well in both the Langmuir and Freundlich isotherm models (R^2 values ranging between 0.82 and 0.99). The Langmuir separation factor R_L was had negative values; probably due to the low initial concentration of the adsorbates in the raw wastewater. All the biochars showed a relatively short contact time (20 to 30 min) to attain maximum adsorption efficiencies – a promising feature for future industrial applications. The studied biochar materials from rice and corn husk have the potential to remove heavy metal ions from industrial wastewater; rice husk biochar showed higher removal capacity than corn husk.

DECLARATION

I, Paulo Martin Sanka, do hereby declare to the Senate of Nelson Mandela African Institution of Science and Technology that this dissertation is my own original work and that it has neither been submitted nor being concurrently submitted for degree award in any other institution.

Paulo Martin Sanka _____

Name and signature of candidate

Date

The above declaration is confirmed

Dr. Mwemezi Johaiven. Rwiza _____

Name and signature of supervisor (1)

Date

Dr. Kelvin Mark Mtei _____

Name and signature of supervisor (2)

Date

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Dr. Mwemezi Johaiven Rwiza

Date

Dr. Kelvin Mark Mtei

Date

CERTIFICATION

The undersigned certifies that they have read and hereby recommend for acceptance by the Nelson Mandela Institution of Science and Technology a dissertation titled “**Removal of Heavy Metal Ions from Industrial Wastewater by using Rice and Corn Husk Biochar**” in fulfilment of the requirements for the Degree of Master’s of Hydrology and Water Resources Engineering (Water Supply and Sanitation) at the Nelson Mandela African Institution of Science and Technology Arusha, Tanzania.

Dr. Mwemezi Johaiven Rwiza

(Principal supervisor)

Date _____

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Finally, most sincere gratitude to my family, close friends, and relatives for all forms of support accorded during the entire study time.

DEDICATION

I dedicate this work to all my loved ones.

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LIST OF ABBREVIATIONS AND SYMBOLS

ACE	African Center of Excellence
ACS	American Chemical Society
BET	Brunauer, Emmet and Teller
CoCSE	Computational and Communication Sciences and Engineering
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
FTIR	Fourier Transforms Infrared Spectroscopy
ICP-MS	Inductively Coupled Mass Spectrometry
LiSBE	Life Sciences and Bio-Engineering
MEWES	Material, Energy, Water, and Environmental Science and Engineering
NM-AIST	The Nelson Mandela African Institution of Science and Technology
URT	United Republic of Tanzania
WHO	World Health Organization
WISE-Future	Water Infrastructure and Sustainable Energy Futures
WSPs	Waste Stabilization Ponds

CHAPTER ONE

INTRODUCTION

1.0 Overview

Wastewater management has become one of the significant social and environmental challenges in most developing countries. These challenges are due to urbanisation, rapid population growth, demand towards industrial development as well as inadequate resources to cater to the growing quantity and lessening the quality of wastewater generated in most of the developing countries (Connor *et al.*, 2017). Wastewater contains pollutants that are detrimental to human and environmental health. Pollutants of human and environmental concerns may include pathogenic microorganisms, nutrients such as organic matter, phosphorus and nitrogen, endocrine disruptors, hydrocarbons, and heavy metals (Akpor *et al.*, 2014). Wastewater containing such pollutants originates from different anthropogenic activities such as industry, agriculture, mining, domestic waste, urban run-off and effluents from improperly treated wastewater through the use of conventional treatment units (Jeff, 2008; Simon *et al.*, 2016).

Heavy metals are of significant concern as they are non-biodegradable and have a tendency to bioaccumulate in the living materials (Lakherwal, 2014). Physiological functioning of living organisms requires limited quantities of heavy metals such as iron, copper, cobalt, zinc, manganese, and iron but when these metals surpass maximum acceptable limits, they become toxic (Simon *et al.*, 2016). However, some heavy metals, like lead and mercury, are extraordinarily lethal to organisms. Even at small levels of exposure, these heavy metals can cause multiple organ damage and have no known beneficial function on organisms (Majid, 2010; Tchounwou *et al.*, 2012). Therefore, proper methods to reduce their concentration or limit their presence in wastewater released to the environment are highly needed.

Various methods, such as ion exchange, membrane techniques, adsorption into activated carbon, electrolytic techniques and lime precipitation, are used for the removal of heavy metals from industrial wastewater (Barakat, 2011). However, these approaches are limited since they often involve high investment and operational costs in terms of power consumption and working hour

requirements (Kapoor *et al.*, 1995). Also, conventional wastewater treatment systems require expert knowledge and produce high amounts of sludge (Rwiza *et al.*, 2018). Recently, there has more focus on safe and cost-effective alternative approaches for the elimination of heavy metals from wastewaters compared to other commercially available approaches.

Biological materials that are accessible in large amounts are potential low-cost adsorbents, as they signify unexploited resources that are environmentally friendly and with high removal efficiencies even at low pollutant concentrations (Rwiza *et al.*, 2018). These biological materials can be converted into biochar with increase surface area, plentiful functional groups, large pore volume, which are essential features for pollutant adsorption. Biochars, when used for pollutant adsorption, have shown good pollutant removal results with high efficiency, howbeit the treatment process being environmentally friendly and cost-effective. Other applications of biochar include soil conditioning, bio-fuel, i.e. heating and cooking, and carbon sequestration (Deng *et al.*, 2017). Therefore, corn and rice husk-based biochars were used in this stud to remove selected inorganic pollutants from industrial wastewater. Corn and rice husks were chosen as precursor materials because of their abundance in Tanzania, where the study was carried out.

1.1 Problem statement

In Tanzania, rice and corn husks are abundantly available in most parts of the country. They represent the unused resources, that can be quickly processed, applied and recovered without adverse impacts on the environment (Duku *et al.*, 2016; Nguyen *et al.*, 2013). Nevertheless, there is a lack of awareness and capacity to modify most of the corn and rice husks into the materials that can remove heavy metals. Many studies applied synthetic wastewater to remove heavy metals without testing real wastewater. Since wastewater contains not only heavy metals as synthetic solutions, the removal capacity of the adsorbents may be affected by the presence of added materials like petroleum products, and corrosive inorganic acid present in the wastewater. Therefore, this study will concentrate on assessing the capacity of corn and rice husks biochar for heavy metal removal from industrial wastewater effluent from Lemara waste stabilisation ponds (WSP). A recent study has shown the effluent from Lemara waste stabilisation ponds in Arusha is having the level of Cr above the acceptable level for irrigation as prescribed by FAO as well as above the recommended level of Pb and Fe as prescribed by WHO (Chuma, 2014).

1.2 Significance of the study

In developing countries, vast volumes of wastewater are usually pumped directly into receiving water bodies without proper pre-treatment. When released into the receiving water bodies, untreated wastewater may harm the ecosystem and may also result in the health and safety problems for the surrounding communities (Pillay, 2008). This, when coupled with the rapidly increasing population, water scarcity and the reuse potential of wastewater, the need to use wastewater to generate income, makes the problem even worse (URT, 2013). This study, therefore, assessed the applicability of agricultural wastes, i.e. rice and corn husk biochar, to scavenge Cr, Fe, and Pb from industrial wastewater to resolve an environmental problem.

1.3 General objective

To investigate the application of rice and corn husk biochar for heavy metal ions removal from industrial wastewater effluents.

1.4 Specific objectives

- (1) To synthesize and characterize biochar from corn and rice husks.
- (2) To assess the efficiency of rice and corn husk biochar for heavy metal removal in the industrial wastewater effluents.

1.5 Research questions

- (1) What are the characteristics of biochar derived from rice and corn husks?
- (2) What is the efficiency of corn and rice husks biochar for heavy metals removal of Cr, Fe, and Pb in the industrial wastewater?

CHAPTER TWO

LITERATURE REVIEW

2.0 Heavy metals in the environment

Heavy metals toxicity is a major risk to the environments and humans all over the world. They mainly act as environmental pollutants, and they can be of severe threat to human and animal health through their lasting persistence in the environment (Tchounwou *et al.*, 2012). Usually, most of the study on the heavy metal pollutants is focused on non-vital heavy metals like Cr and Pb and vital heavy metals such as Co, Ni and Se which are toxic could cause health problems (Patra *et al.*, 2017).

Chromium occurs in the environment, mostly in two forms, Cr (III), which is less toxic and Cr (VI), which is highly toxic (Oliveira, 2012). The main contribution to Cr release includes stainless steel welding, metal processing, ferrochrome, chromate production, chrome pigment production and tannery facilities (Jacobs *et al.*, 2005). Cr (VI) at high levels causes sneezing, irritate the nose and itching, nosebleeds, holes in the nasal septum, ulcers, and the long-term exposure can result into a lung cancer (Teklay, 2016). Cr (VI) is absorbed into the human body than Cr (III) as the structure of the active form of Cr (VI) as chromate resembles sulfate and therefore quickly enters cell membranes through the sulfate transporters (Achmad, 2017).

Iron is among the most abundant and vital elements in nature, and it is used widely in both water and wastewater treatment and may exist in both ferrous (Fe (II)) and ferric (Fe (III)) states (Waite, 2002). Under the occurrence of oxygen, ferrous iron (Fe^{2+} and FeOH^+) is oxidised to ferric species (Fe^{3+} , FeOH^{2+} , Fe(OH)^{+2}) (Gurzau *et al.*, 2003; Waite, 2002). Iron can accept and give electrons readily which make makes it physiologically vital, as a useful element of cytochromes and oxygen-binding molecules (Emerit *et al.*, 2001). However, Fe is also biochemically dangerous since it can harm the tissues through catalysing the conversion of hydrogen peroxide to free-radical ions that attack protein, DNA, and cellular membranes (Gurzau *et al.*, 2003).

Lead is an essential toxic element in the environment as it is non-biodegradable. Its essential properties like ductility, softness, malleability, poor conductivity and resistance to corrosion

appear to make it challenging to give up its use (Wani *et al.*, 2015). Pb is a highly poisonous metal affecting almost every organ in the body, and it damages the peripheral and central nervous system; the body's ability to regulate vitamin D and the kidneys. Pb disturbs the development of red blood cells and can cause coma at a high level, seizures, and death. A child can suffer from the developmental delay at lower levels of exposure, hyperactivity, learning disabilities, lower IQ, impaired hearing, behavioural problems, and stunted growth (Flora *et al.*, 2006; Harper *et al.*, 2003). Pb is introduced into the environment through paints, leaded petrol, food cans, traditional remedies, ceramics, batteries and make-up. A human can be exposed to Pb through ingestion or inhalation and, to a small degree for organic lead compounds and dermal absorption (Asante-Duah, 2002; Carolyn, 2005).

2.1 Methods for heavy metals removal

Several methods are available for the removal of heavy metal ions in aqueous solution and the most commonly used are solvent extraction, membrane filtration, lime coagulation, chemical precipitation, reverse osmosis, electrodeposition, ion exchange and adsorption (Halnor, 2015). However, these methods are linked with various shortcomings like the generation of sludge, high reagent requirements, incomplete metal removal, energy requirements, fouling of the membranes and aggregation of metal precipitates (Kanamarlapudi *et al.*, 2018).

2.2 Adsorption

Adsorption is among the utmost effective methods for removing harmful heavy metals from the solvent phase because of its availability, environmental friendly in nature and low cost (Agarwal *et al.*, 2016; Burakov *et al.*, 2018). The deposition of chemical elements onto the surface of a solid is called adsorption as seen in Figure 1, and the adsorbed substance onto the surface of another is called an adsorbate whereas a substance that adsorbs another on its surface is called an adsorbent (Halnor, 2015). The attachment of adsorbate on the surface of solids and liquids may be divided into physisorption (physical adsorption) and chemisorption (chemical adsorption).

Physisorption involves a weak bonding force called van der Waals in which gas molecules get adsorbed on a solid surface. As the adsorption process releases energy (exothermic), the physical

adsorption happens readily at low temperatures and decreases with the rising temperature (Dash, 2012; Yang, 2013). Porous substances are suitable adsorbents as an increased surface area promotes adsorption (Summers *et al.*, 1988). The gas is more absorbent as it is easy to dissolve while depending on the case, the gas can have a single layer or multi-particle layer on the surface as seen in Figure 2 (Bartelt *et al.*, 1991).

Chemical adsorption can be characterised through the immersion of chemical bonds between the adsorbent surface and the gas molecules. Moreover; it results in a single layer (Bansal *et al.*, 2005). The bond between the surface particles of a metal and another substance in contact with are almost as strong as conventional chemical bonds, much stronger than the van der Waals forces characteristic of physical adsorption (Dash, 2012).

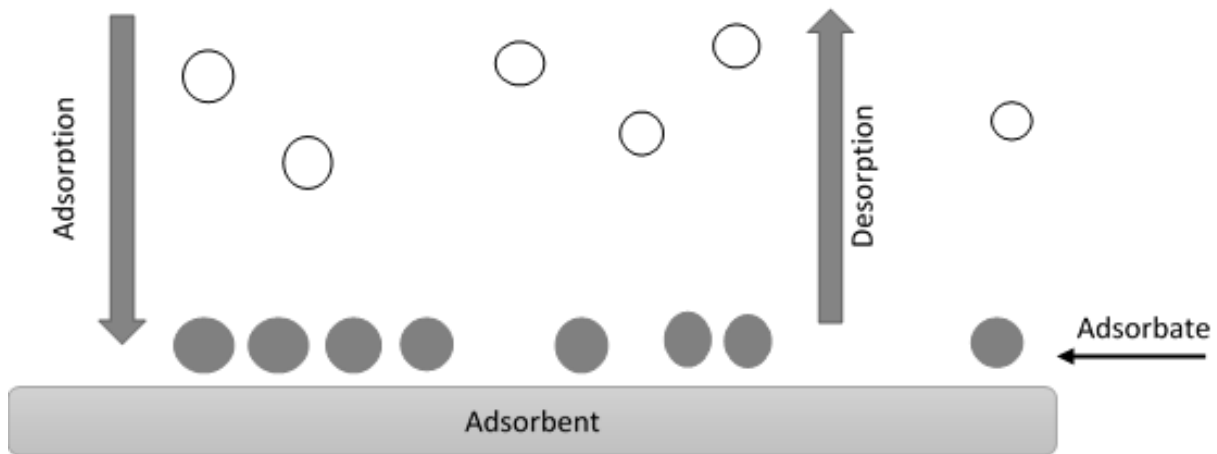


Figure 1. Illustration of adsorption and desorption processes (Kecili *et al.*, 2018; Premkumar *et al.*, 2018).

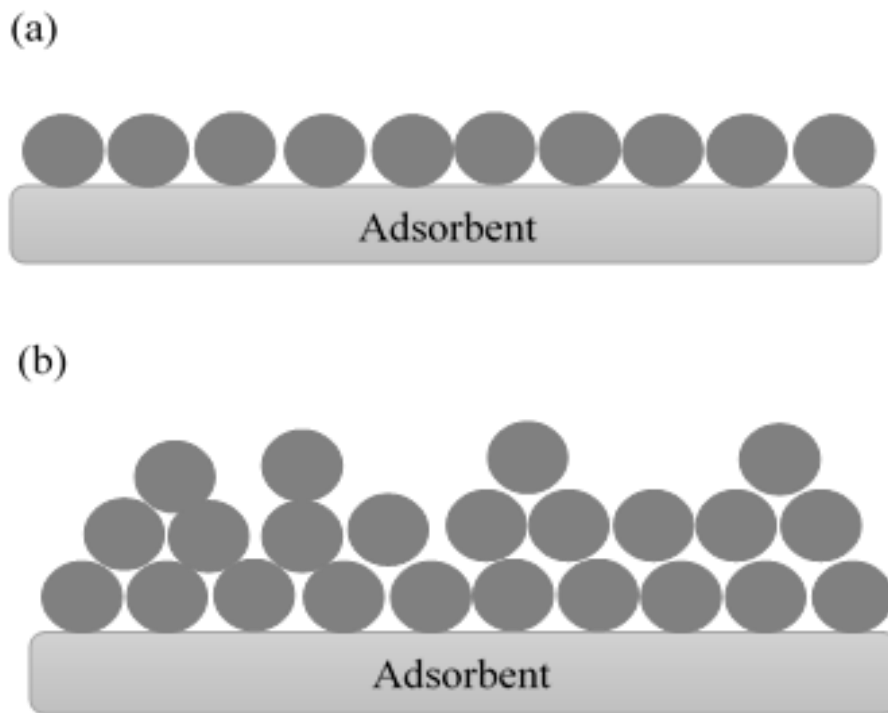


Figure 2. (a) Monolayer and (b) multilayer adsorption (Kecili *et al.*, 2018; Premkumar *et al.*, 2018).

Table 1. Physical adsorption and chemical adsorption comparison (Kecili *et al.*, 2018).

Physical adsorption	Chemical adsorption
It involves electrostatic interactions and Van der Waals forces	The formation of covalent bonds between the adsorbed molecules and the surface
It is reversible	It is irreversible
It is fast	It is slow
Multilayer is formed	Monolayer is formed
Not very specific	It is very specific
It does require the activation energy	It requires the activation energy
Occurs at low-temperature	Occurs at high temperature

2.3 Biochar and heavy metals removal

Biochar is the product rich in carbon obtained when biomass (wood, agricultural waste and solid waste) is heated under a limited supply of oxygen and at a relatively low temperature ($<700\text{ }^{\circ}\text{C}$) (Nartey *et al.*, 2014). The pyrolysis of organic materials increases the surface area and effective cation exchange capacity as compared to the un-charred organic materials, but the decomposition rate is lower compared to un-charred materials (Beesley *et al.*, 2015).

Biochar having a high surface area and pore volumes have a superior affinity for metals as metallic ions are sorbed physically onto the char surface and kept inside the pores (Inyang *et al.*, 2016). Figure 3 shows various mechanisms in heavy metals removal from the solutions by using biochar, including ion exchange, precipitation, chemisorption, complexation, and physical sorption (Beesley *et al.* (2015); Patra *et al.*, 2017). Mechanisms of heavy metal adsorption by biochars can be thoroughly studied by using different methods, including adsorption isotherms and technical analysis including BET and FTIR (Nartey *et al.*, 2014).

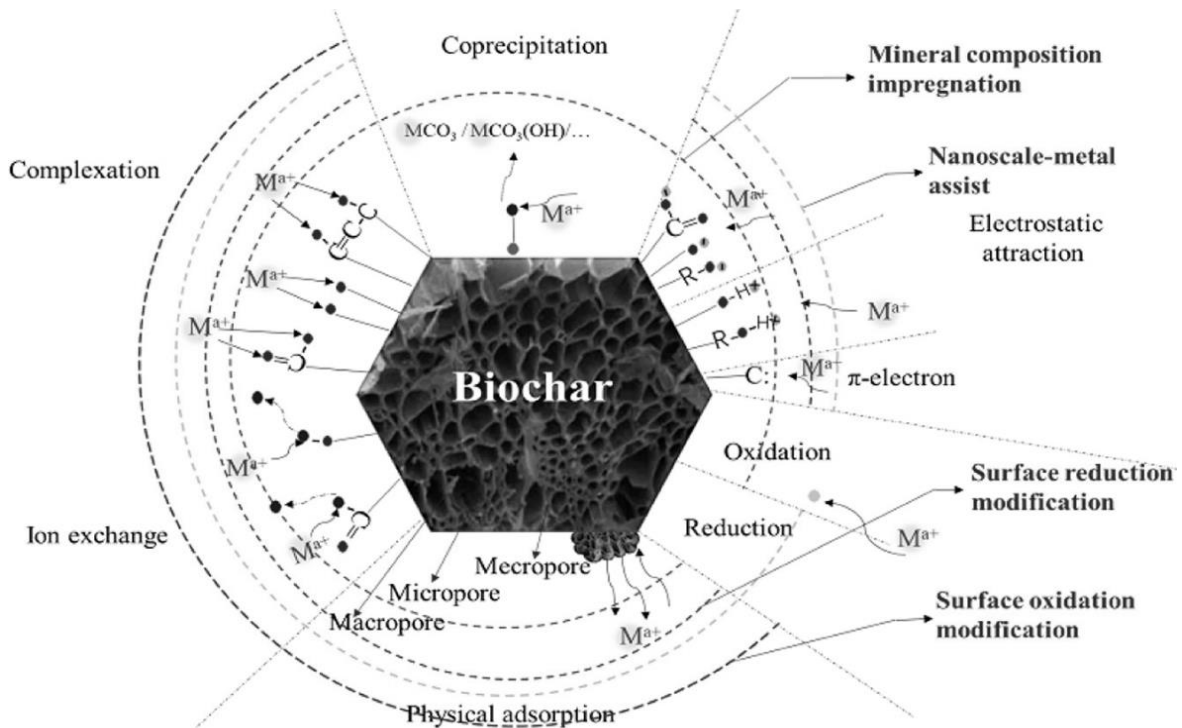


Figure 3. Mechanisms of metal sorption onto biochar (Wang *et al.*, 2019).

The usage of biochar made from biomass for the heavy metals removal of industrial effluents proposes a potential substitute to existing treatment technologies and has added outstanding reliability in recent years because of the excellent performance and low cost of this complexing material (Patra *et al.*, 2017; Sekhar *et al.*, 2003). Biochar has a well-structured carbon matrix similar to that of activated carbons which can play a vital part in controlling environmental contaminants (Rwiza *et al.*, 2018).

Numerous studies have discovered the production of biochar from cheap and locally available unused materials such as industrial wastes, sewage sludge, animal manures and plant residues which have proven to be effective in the heavy metals removal in the aqueous solutions (Li *et al.*, 2016). Sekhar *et al.* (2003) conducted a study on the Pb, Cr and Zn removal on the wastewater with the removal efficiency of 90% by using the root bark of *Indian Sarsaparilla*. Rwiza *et al.* (2018) also conducted a study on the Pb removal with corn and rice husks on synthetic wastewater, and the removal efficiency was 90%. Hegazi (2013) uses only rice husks for Fe and Pb removal on synthetic wastewater with the removal efficiency of 99.25% and 87.17%. Desta (2013) uses Teff Straw for Cr removal in the wastewater with the removal efficiency of 74.5%.

CHAPTER THREE

MATERIALS AND METHODS

3.0 Materials

Rice and corn husk were collected from Arusha and Manyara regions of northern Tanzania, and all the chemicals, including potassium hydroxide (KOH), nitric acid (HNO₃) and hydrochloric acid (HCl) used were of analytical grade. Wastewater samples were collected from a municipal waste stabilisation pond (WSP) in Arusha; at a point where industrial effluents enter the WSP. The pH of the sampled wastewater was recorded on-site by using the portable pH meter (GMH 3500 Series). The collected samples were stored in pre-cleansed high-density polyethylene (HDPE) bottles and stored at a temperature of ≤ 4 °C.

3.1 Biochar preparation

Figure 4 shows the biochar preparation flow chart whereby the rice and corn husks were cleaned by washing with tap water and rinsed with distilled water for the eliminate exogenous impurities after which was dried in an oven at a temperature of 110 °C for 48 hours. The dried materials were ground and then sieved through a mesh size of 0.15 mm. The ground and sieved materials were then pyrolysed in a tube furnace (CTF 12/65/550) at a different temperature, i.e. 500 °C, 600 °C and 700 °C for 2 hours under a constant flow of nitrogen gas. The pyrolysis temperatures of 500 °C, 600 °C, and 700 °C were adapted as the highest adsorption capacity is achieved within the temperature range of 500 °C to 700 °C (Mohan *et al.*, 2014). The heating rate was kept unchanged at 10 °C/min until the desired temperature was achieved. Highly carbonaceous materials were obtained from this process where volatile organic compounds were released and ultimately influencing the yield and porosity (Ronsse *et al.*, 2015). The obtained biochar was kept in a clean container as RHX and CHX; where the prefixes “RH” and “CH” are the abbreviations for rice husks and corn husks and the postscript is the pyrolysis temperature.

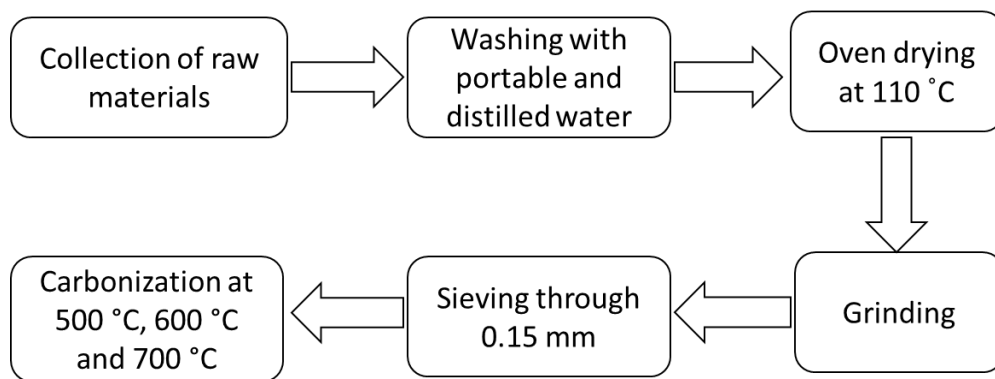


Figure 4. Materials preparation flowchart.

3.2 Activation of biochar

KOH was selected as it provides materials with the best performance, highest yield, highest adsorption capacity, and well-defined micropore size distribution, as well as the ultrahigh specific surface area under lowest activation temperature (Wang *et al.*, 2012; Yang *et al.*, 2017). A mixture of KOH and biochar in the mass ratio of 1:1 was mixed with distilled water (100 mL) in a beaker (250 mL) placed on a hot plate and stirred for 2 hours at 90 °C for complete mixing. The mixture was then dried in an oven at a temperature of 110 °C for 24 hours followed by grinding and sieving through 0.15 mm sieves to obtain uniform material which was then activated at a temperature of 500 °C for 2 hours.

After the desired time was reached, the mixture was allowed to cool at room temperature followed by washing with 0.1 M HCl and distilled water until the neutral pH was obtained. The final materials were kept in a clean plastic container as ARH and ACH for activated rice husk and activated corn husk, respectively.

3.3 Biochar characterization

The characterisation of the carbonised and activated biochar was done by Nitrogen adsorption-desorption isotherms measured at 77 K using Nova 4200e Quantachrome porosimeter at a relative pressure, P/P_0 (the range of 0 to 1), to obtain the porosity. The Brunauer Emmett Teller (BET) and Barrett–Joyner–Halenda (BJH) procedures were used to evaluate the surface area and pore size distribution, respectively (Ahmad *et al.*, 2017).

Fourier Transforms Infrared spectroscopy (FT-IR) was used to identify different functional groups in both the carbonised and activated biochar and the organic elemental analyser (Flash 2000) was used for the identification of the elemental composition of the biochar.

3.4 Metal ion removal experiments

A series of batch experiments for the removal of Pb, Cr, and Fe from industrial wastewater were carried out in the laboratory. The initial metal ion concentrations in wastewater for Cr, Fe and Pb were measured with atomic adsorption spectrophotometer (AAS) while the pH of the individual aliquots was determined by a portable pH meter (GMH 3500 Series). The initial wastewater ion concentrations were 1.82 mg/L (Cr), 9.28 mg/L (Fe), and 1.59 mg/L (Pb). The wastewater pH was measured at 7.37. The experiment was set by changing the contact time between the biochar and the adsorbate at room temperature, subjected to agitation using a shaking incubator (Stuart SI500) at 150 r.p.m. Agitation time intervals were 5, 15, 30, 60, 90, and 120 min, after which the sample was withdrawn from the shaker and was centrifuged (Eppendorf Centrifuge 5810/5810 R) at 2000 rpm for 15 minutes and was filtered through a 0.45 μm cartridge in a vacuum filtration unit. The solution obtained was kept in a clean tube pre-soaked in a 5% HNO_3 solution overnight and rinsed with the milli-Q deionised water.

3.5 Preparations for metal uptake analyses

Wastewater sample was prepared according to the EPA SW 846 Method for the analysis of heavy metals by using AAS instrument whereby a mixture of HNO_3 and HCl was added into the sample for digestion (Rice *et al.*, 2012). Heating blocks (DR 200 HACH) were used at a temperature of 150 $^\circ\text{C}$ for 2 hours which was then allowed to cool and was filled up to the initial volume mark with deionised water. The digested, solution was taken to the AAS machine for the analysis of pollutant levels. The wavelength of 357.9 nm, 248.3 nm and 283.3 nm were used for the analysis of Cr, Pb, and Fe, respectively, using the AAS machine.

Metal ion uptake (q_e) by adsorbates was calculated by using Equation (1) as described by El-Said *et al.* (2018).

$$q_e = \frac{(C_i - C_e)V}{W} \quad (1)$$

where C_i and, C_e is the initial and final metal concentrations in mg/L, V is the volume in L of the solution used in the experiment and W is the mass of the adsorbent in g.

The removal efficiency was calculated by using the following Equation (2).

$$\text{Removal efficiency (\%)} = \frac{(C_i - C_e) \times 100}{C_i} \quad (2)$$

where C_i (mg/L) and C_e (mg/L) is the initial and final metal concentration.

3.6 Adsorption isotherms

The adsorption processes were studied through fitting the experimental data into the Langmuir (Equation (3)) and Freundlich (Equation (5)) models as described in Ayawei *et al.* (2017).

$$\frac{C_{eq}}{q_e} = \left(\frac{1}{q_m}\right)C_{eq} + \frac{1}{k_L q_m} \quad (3)$$

$$R_L = \frac{1}{1 + k_L C_i} \quad (4)$$

where q_e (mg/g) is the metal concentration adsorbed at equilibrium, q_m (mg/g) is the maximum adsorption capacity, C_{eq} (mg/L) is the concentration at equilibrium, C_i (mg/L) is the initial metal concentration and k_L (L/mg) is the Langmuir equilibrium constant. R_L (Equation (4)) is the Langmuir separation factor.

$$q_e = k_f \cdot C_e^{1/n} \quad (5)$$

where q_e (mg/g) is the metal concentration adsorbed at equilibrium, C_{eq} (mg/L) is the concentration at equilibrium, k_f (mg/g) is the Freundlich capacity coefficient and $1/n$ is the measure of adsorption intensity.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.0 Effects of temperature on biochar yield

Biochar yield refers to the size of materials rich in carbon produced at different pyrolysis temperatures under the constant flow of nitrogen gas (Crombie *et al.*, 2013). Table 2 shows the yield amount in the percentage of the rice husk and corn husk biochar attained at various pyrolysis temperatures. With the increase in pyrolysis temperature, the yield of both materials decreases. The pyrolytic temperature negatively but differentially affected the biochar yield. Usually, as the pyrolysis temperature increases, there is a removal of the volatile matter from the biomass, causing the biochar yield to decrease (Yadav *et al.*, 2019). However, corn husks were more negatively affected compared to rice husks at the same temperature.

Table 2. Biochars yields obtained for rice husk (RH) and corn husk (CH) at different pyrolysis temperatures.

Biochar	RH500	RH600	RH700	CH500	CH600	CH700
Yield (%)	38.63	29.79	23.26	24.58	22.25	19.16

4.1 Biochar characterization

4.1.1 Elemental content

The carbon content was analysed by using the organic elemental analyser (Flash 2000). The results are as shown in Table 3. Rice husks indicated no significant difference in the carbon content at various pyrolysis temperatures. In previous studies by Nuamah *et al.* (2012), it was stated that rice husk contains about 30 to 50% organic carbon and is mainly composed of silica. The highest content of carbon was observed with the corn husk increasing from 64.5% (at 600 °C) to 75.3% (at 500 °C). Generally, a higher pyrolysis temperature regime favoured higher C-content for rice husk; whereas a lower pyrolysis temperature regime favoured more C-content for corn husk. Hydrogen and oxygen decrease as the pyrolysis temperature is increased and may be attributed to the breakage and cleavage of weak bonds within the biochar structure (Rafiq *et al.*, 2016). The

H/C ratio indicated the biochar aromaticity, whereas the smaller the H/C value, the aromaticity becomes stronger, and the biochar structure. Thus, for both rice and corn husks, high pyrolysis temperatures resulted in the high aromaticity of the adsorbents. The decrease in O/C or (O+N)/C ratios show the increase in hydrophobicity and the reduction of polar groups (Zhang *et al.*, 2011).

The C/N ratio is a vital biosorption parameter. Biomaterials with a low C/N ratio are usually rich in protein in their extracellular polymeric substance (EPS); whereas biomaterial with a high C/N ratio is usually rich in carbohydrates in their EPS (Yuncu *et al.*, 2006). The dominant functional groups in proteins are mainly carboxylic and amines, whereas for carbohydrates, the dominant functional groups are mainly carboxylic. Thus, by studying the C/N ratios, we may gain some insights into the mechanisms of adsorption (Jia *et al.*, 2018). For the present study, the C/N ratio attained a maximum value at the highest pyrolysis temperature (700 °C) (Table 3). The maximum cornhusk biochar's C/N ratio was more than twice that of the maximum C/N ratio attained in the rice husk biochar.

Table 3. Carbon content in the biochar as analyzed by the organic elemental analyzer (Flash 2000).

Carbonization temperature (°C)	Elemental content (%)				Atomic ratio			
	N	C	H	O	H/C	O/C	(O + N)/C	C/N
RH500	0.27	36.89	1.79	3.9	0.05	0.11	0.11	136.63
RH600	0.28	42.84	1.26	1.00	0.03	0.02	0.03	153.00
RH700	0.10	39.8	0.78	1.29	0.02	0.03	0.03	398.00
CH500	0.28	75.34	2.60	1.55	0.03	0.02	0.02	269.07
CH600	0.21	64.52	2.57	1.47	0.04	0.02	0.03	307.24
CH700	0.07	68.44	1.55	1.44	0.02	0.02	0.02	977.71

4.1.2 Functional groups

The FT-IR spectra of activated biochars at different carbonisation temperatures were obtained in a wavenumber between 4000 cm⁻¹ and 400 cm⁻¹, as shown in Figure 5. Stretching of the hydroxyl groups in the raw rice and corn husk at around 3179.76 cm⁻¹ and 3334.56 cm⁻¹ for the RH and CH

have been indicated and could be the results of the adsorbed water on the biochar. The band intensities (-OH stretching vibration) significantly weakened, signifying the dehydration of cellulosic and ligneous components as the pyrolysis temperature increased (Zhang *et al.*, 2011). The decrease of functional groups containing oxygen in the biochars agreed with the reduction of the O/C ratio. The intensities of bands at around 751.32 cm^{-1} to 879.66 cm^{-1} were improved with the rise in pyrolytic temperature and is supported by the decrease of H/C ratio for both the rice husk biochar and corn husk biochar.

The spectra in Figure 5 indicate prominent peaks in the region from 1370 to 750 cm^{-1} . This region include the following functional groups: acyl (R-C=O) C-O group of esters; symmetric nitro (N=O); acyl C-O associated with lignin; aromatic C-O; aromatic C=C; alkoxy (C-O); meta/para disubstituted aromatics; unsaturated groups' and C-H trisubstituted alkene (C=C) (Rwiza *et al.*, 2018). This is per the observation made in the elemental content analysis above; where smaller H/C ratio values indicated high aromaticity and high C/N ratio values indicated the dominance of carboxyl groups.

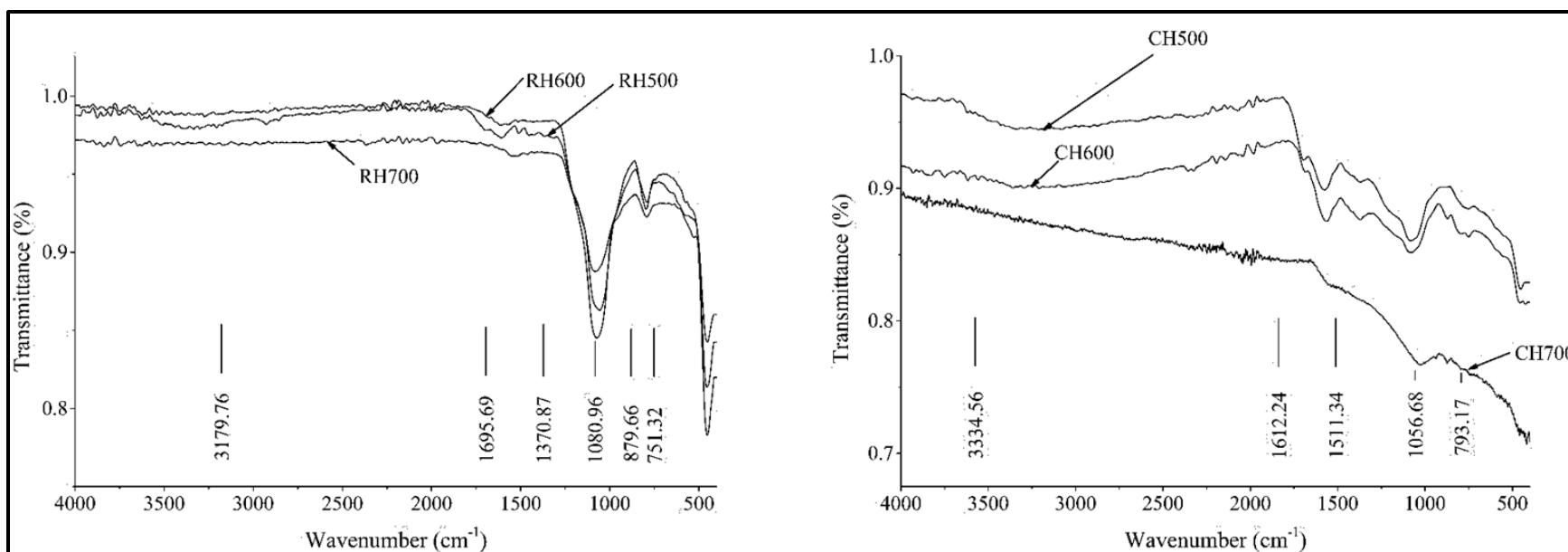


Figure 5. FTIR spectra for the biochars at different carbonization temperatures. The left-hand side spectra are for rice husk (RH) biochars at 500, 600, and 700 °C. The right-hand side spectra are for corn husk (CH) biochars at 500, 600, and 700 °C.

4.1.3 Surface area and pore volume

Table 4 shows the micropores' surface area and pore volume of the biochar prepared at different pyrolysis temperatures of the activated biochar. The pyrolysis temperature accelerates thermal degradation and the volatilisation process of the biomass which leads to increases in the surface area and pore volume development and hence improves the adsorption capacity (Kumar *et al.*, 2015). The data in Table 4 indicate that the pore volume increased from 0.584 to 0.652 cm³/g for the pyrolysis temperature of 500 °C to 700 °C for the rice husk (RH500 to RH700) and from 0.514 cm³/g to 0.561 cm³/g respectively for the pyrolysis temperature of 500 °C to 700 °C for the corn husk biochar (CH500 and CH700). The surface area increased from 645.835 to 919.829 m²/g at pyrolysis temperatures from 500 to 700 °C, respectively, for rice husk biochar. For corn husk biochar, the surface area increased from 549.559 to 659.375 at pyrolysis temperatures from 500 to 700 °C, respectively. Generally, rice husk biochar indicated higher pore volume and surface area features. This means that activated rice husk biochar may be more effective in removing pollutants from the solution than the activated corn husk biochar.

Table 4. The Brunauer Emmett Teller (BET) surface area and pore volume characterization results.

	Pore volume (cm ³ /g)	Surface area (m ² /g)	Constant (C)
Rice husk biochar			
RH500	0.584	645.835	2.725
RH600	0.619	635.792	6.41
RH700	0.652	919.829	49.447
Corn husk biochar			
CH500	0.514	549.559	3.701
CH600	0.531	575.809	14.866
CH700	0.561	659.375	2.647

4.1.4 Metal ion removal efficiency

The removal efficiencies of the activated biochars are as shown in Figure 6 (a). Adsorption efficiencies did not follow any clear pattern or order. Adsorption of Cr onto rice husk biochar had the best performance with pyrolysis temperature of 600 °C followed by pyrolysis at 700 °C. Pyrolysis of rice husk at 500 °C attained the poorest performance in Cr removal. Thus, adsorption of Cr onto rice husk biochars followed the following trend:

$$\text{RH600} > \text{RH700} > \text{RH500}$$

whereas for corn husk biochars (Figure 6 (b)), Cr adsorption followed the following trend:

$$\text{CH600} > \text{CH500} > \text{CH700}$$

It is important to note that Cr adsorption efficiency onto rice husk biochars at different pyrolysis temperatures ranged approx. Between 50 and 65%.

On the other hand, Cr adsorption onto corn husk biochars at different pyrolysis temperatures ranged approx. Between 20 and 40%. In this case, rice husk biochars performed better than corn husk biochars.

The adsorption of Fe onto rice husk biochars was also clearly affected by pyrolysis temperatures. It is seen in Figure 6 (c) that pyrolysis at 600 °C achieved the best Fe removal efficiency. It was followed by biochar carbonised at 500 °C and carbonisation at 700 °C resulted in the least performance. Thus, the trend of Fe adsorption onto rice husk biochars was as follows:

$$\text{RH600} > \text{RH700} > \text{RH500}$$

whereas for corn husk biochars (Figure 6 (d)), Fe adsorption followed the following sequence:

$$\text{CH600} > \text{CH500} > \text{CH700}$$

Note that for both Cr and Fe, adsorption onto corn husk biochars followed a similar trend; also, that biosorption onto rice husk biochar for both Cr and Fe ions followed a similar trend. However, when compared to Cr removal efficiencies; both rice and corn husk-based biosorbents performed better in removing Fe from wastewater, with efficiencies ranging from 70 to 90%.

The adsorption of Pb from wastewater onto rice husk biochars was almost 90% regardless of the pyrolysis temperature. As Figure 6 (e) shows, there was no significant difference in Pb removal efficiencies by rice husk biochars carbonized at different pyrolysis temperatures. Only by excessively zooming-in Figure 6 (e) does it become apparent that the adsorption of Pb onto rice husk biochar slightly follows the following pattern:

$$\text{RH600} > \text{RH500} > \text{RH700}$$

Interestingly, the rice husk biochars when adsorbing Pb, followed the trend of corn husk biochars adsorption efficiencies for Cr and Fe. The adsorption efficiency trend for Pb on corn husk biochars is shown in Figure 6 (f) and seems to go with the following pattern:

$$\text{CH500} > \text{CH700} > \text{CH600}$$

Maximum Pb adsorption efficiencies onto corn husk biochars range between approx. 35 and 50%. It seems that for corn husk biochars to reach higher Pb adsorption efficiencies, a pyrolysis temperature regime < 500 °C would be favourable. This is further corroborated by the FT-IR spectra for corn husk biochar in Figure 5. At a pyrolysis temperature of 700 °C, corn husk biochars lost almost all their functional groups.

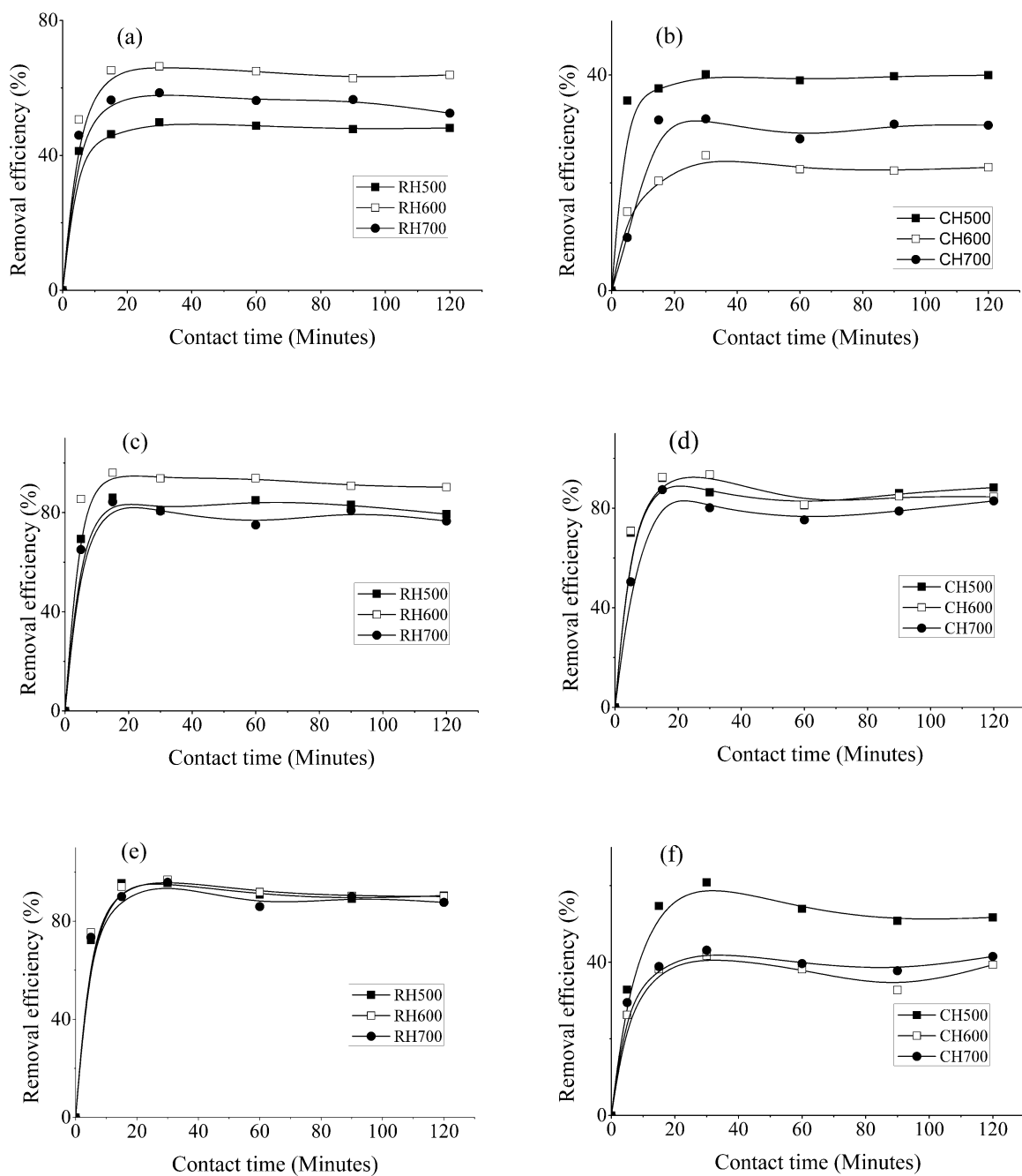


Figure 6. Wastewater pollutant removal efficiencies from wastewater at different pyrolysis temperatures for (a) Cr removal by rice husk biochars, (b) Cr removal by corn husk biochar (c) Fe removal by rice husk biochar (d) Fe removal by corn husk biochar (e) Pb removal by rice husk biochar, and (f) Pb removal by corn husk biochar.

For all the biosorbents and pyrolysis temperature regimes, the maximum removal efficiencies were attained in the first 20 min, after which there was no change in removal efficiencies. This is an

essential industrial application aspect because, for industrial use, high efficiencies at shorter contact times are desirable.

4.2 Adsorption capacities for Cr, Fe, and Pb

Figure 7 (a), (b) and (c) indicate adsorption capacities for Cr, Fe, Pb, respectively. In Figure 7 (a) it is shown that rice husk biochar carbonised at a pyrolysis temperature of 600 °C performed better than the rest of the biosorbents in removing Cr from wastewater. It was followed by rice husk biochar carbonised at 700 °C whereas corn husk pyrolysis at 600 °C produced the worst Cr removal results. Overall, the removal of Cr from wastewater followed the following trend:

$$\text{RH600} > \text{RH700} > \text{RH500} > \text{CH500} > \text{CH700} > \text{CH600}$$

In Figure 7 (b), the trend is slightly different; but still, rice husks carbonised at 600 °C produced the best Fe ion removal capacity followed by corn husks biochar at a carbonisation temperature of 600 °C. The overall trend in the removal capacities of Fe by the different biochars followed the following sequence:

$$\text{RH600} > \text{CH700} > \text{CH500} > \text{RH500} > \text{RH700} > \text{CH700}$$

For Pb ions (Figure 7 (c)), the removal capacities were in the following order:

$$\text{RH600} > \text{RH500} > \text{RH700} > \text{CH500} > \text{CH700} > \text{CH600}$$

By looking at the removal capacity trends, it is evident that rice husk biochars were more efficient than corn husk biochars. The results also indicate that rice husk biochars produced at 600 °C were the best adsorbents for the removal of Cr, Fe, and Pb ions from wastewater. Results from elemental analysis and FT-IR analysis indicate that corn husk biochars were rich in stable aromatic hydrocarbons and hydroxyl functional groups with substituted and unsaturated -C=C- and -C-H groups. These may have contributed to high removal efficiencies and high removal capacities for the rice husk biochars.

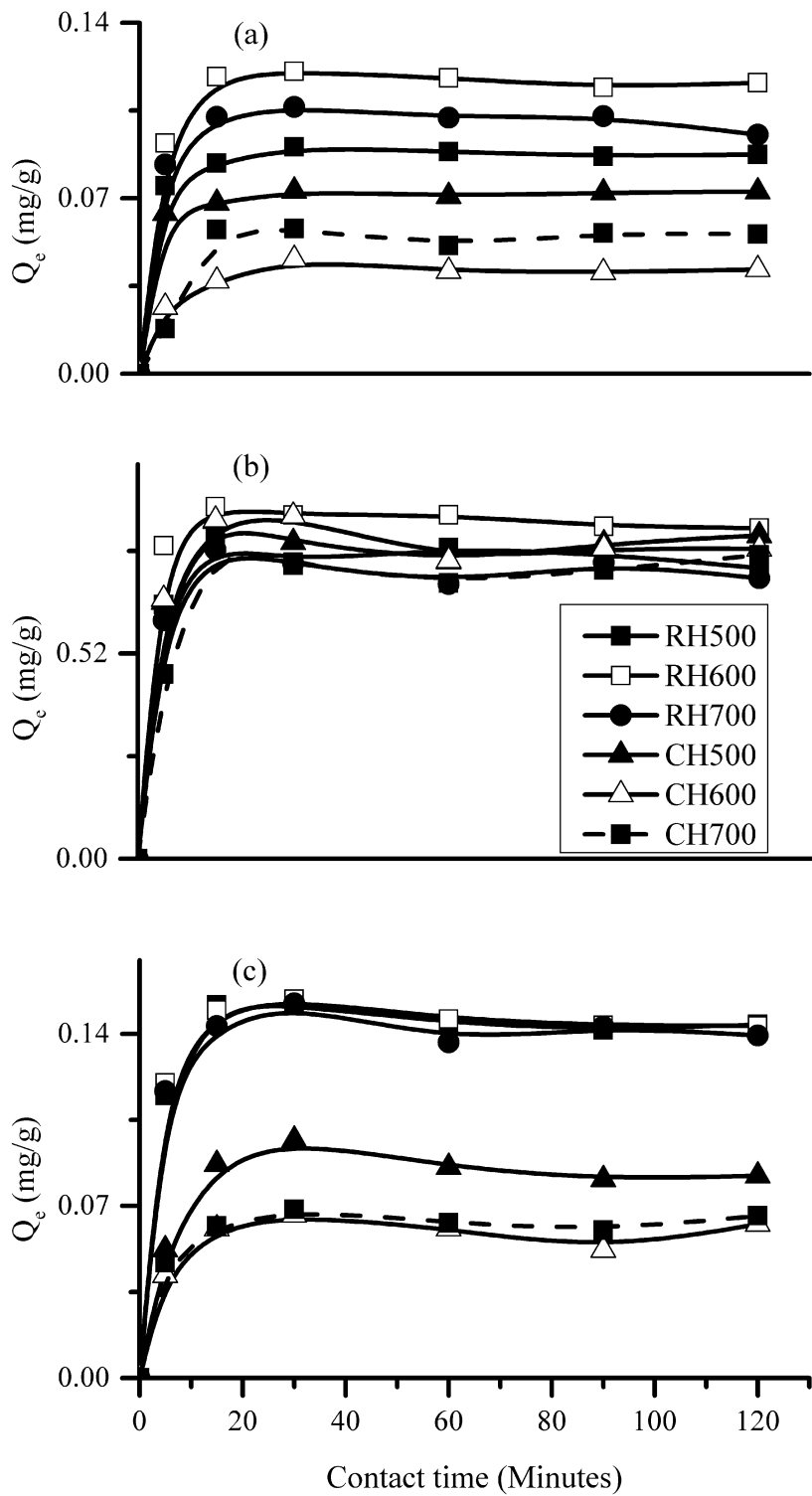


Figure 7. Adsorption capacities of (a) Cr, (b) Fe, and (c) Pb from industrial wastewater by rice husk (RH) and corn husk (CH) biochars carbonized at different pyrolysis temperatures.

4.3 Adsorption isotherm studies

Langmuir isotherm model was tested for Cr removal to find conformity with the experimental results (Figure 8). The results fitted well in the model with the R^2 ranging between 0.82 and 0.99 for both the carbonised rice husk and corn husks biochars. The R^2 value was higher for RH600 and CH500 indicating that the experimental results correlated well with one another at a carbonisation temperature of 600 °C and 500 °C for rice husks and corn husks, respectively.

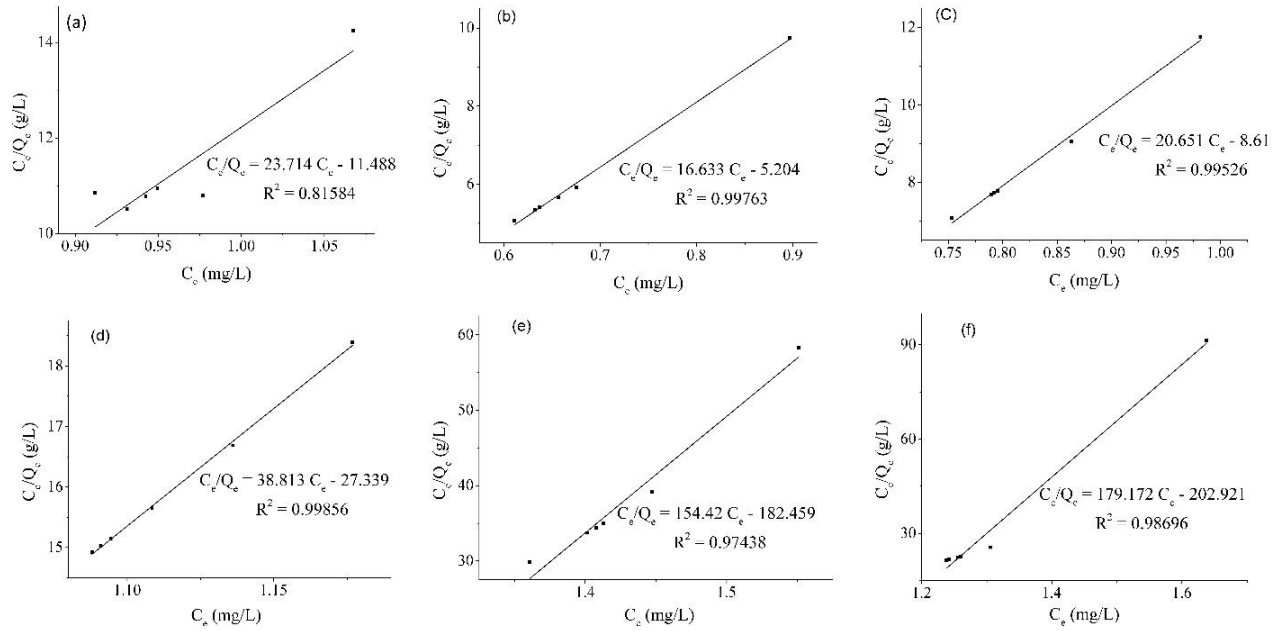


Figure 8. Langmuir adsorption isotherms for Cr onto a) RH500, b) RH600, c) RH700, d) CH500, e) CH600, and f) CH700. Initial Cr concentration in the industrial wastewater was 1.82 mg/L.

Langmuir isotherm model was tested for Fe removal to find conformity with the experimental results (Figure 9). The results fitted well in the model with the R^2 ranging between 0.98 and 0.99 for both the carbonised rice husk and corn husks biochars. The R^2 value was higher for RH600 and CH500 indicating that the experimental results correlated well with one another at a carbonisation temperature of 600 °C and 500 °C for rice husks and corn husks, respectively.

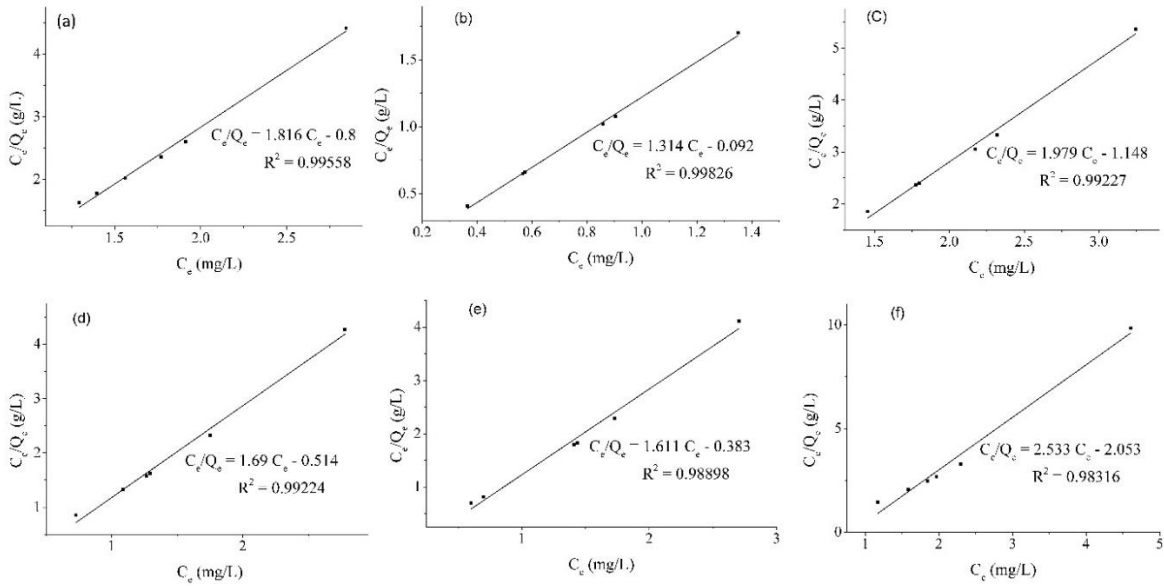


Figure 9. Langmuir adsorption isotherms for Fe onto a) RH500, b) RH600, c) RH700, d) CH500, e) CH600, and f) CH700. The initial concentration of Fe in industrial wastewater was 9.28 mg/L.

Langmuir isotherm model was tested for Pb removal to find conformity with the experimental results (Figure 10). The results fitted well in the model with the R^2 ranging between 0.97 and 0.99 for both the carbonised rice husk and corn husks biochars. The R^2 value was higher for RH600 and CH700 indicating that the experimental results correlated well with one another at a carbonisation temperature of 600 °C and 700 °C for rice husks and corn husks, respectively.

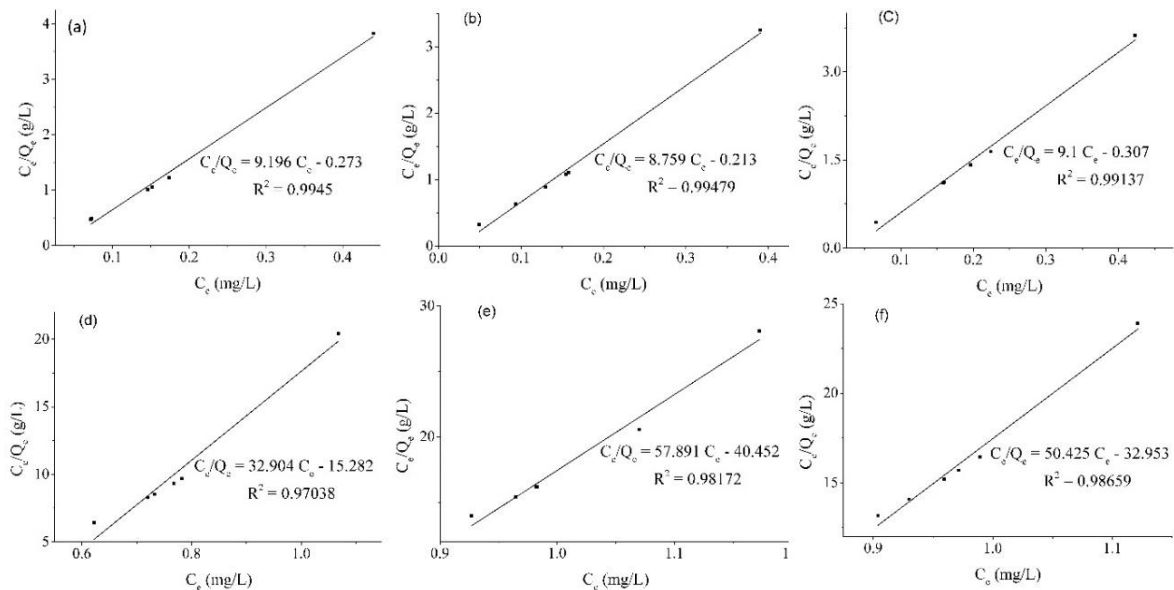


Figure 10. Langmuir adsorption isotherms for Pb onto a) RH500, b) RH600, c) RH700, d) CH500, e) CH600, and f) CH700. The initial concentration of Pb in industrial wastewater was 1.59 mg/L.

Freundlich isotherm model was tested for Cr removal to find conformity with the experimental results (Figures 11). The results fitted well in the model with the R^2 ranging between 0.98 and 0.99 for both the carbonised rice husk and corn husks biochars. The R^2 value was higher for RH500 and CH500 indicating that the experimental results correlated well with one another at a carbonisation temperature of 500 °C and 500 °C for rice husks and corn husks, respectively.

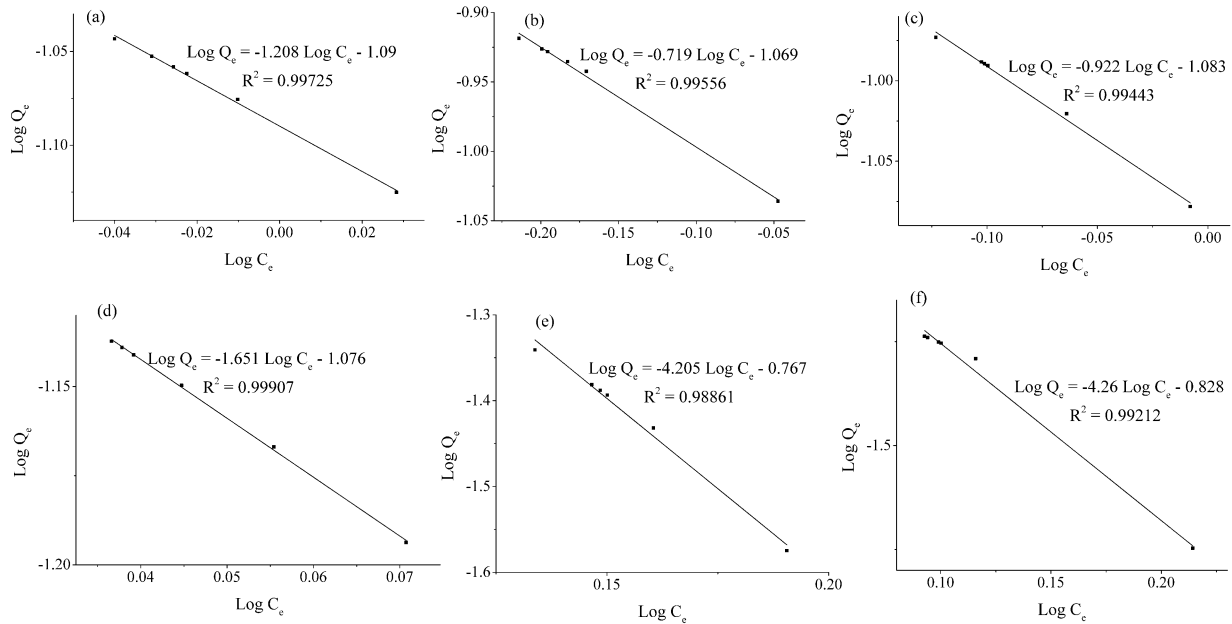


Figure 11. Freundlich adsorption isotherms for Cr onto a) RH500, b) RH600, c) RH700, d) CH500, e) CH600, and f) CH700. Initial Cr concentration in the industrial wastewater was 1.82 mg/L.

Freundlich isotherm model was tested for Fe removal to find conformity with the experimental results (Figure 12). The results fitted well in the model with the R^2 ranging between 0.90 and 0.97 for both the carbonised rice husk and corn husks biochars. The R^2 value was higher for RH500 and CH500 indicating that the experimental results correlated well with one another at a carbonisation temperature of 500 °C and 500 °C for rice husks and corn husks, respectively.

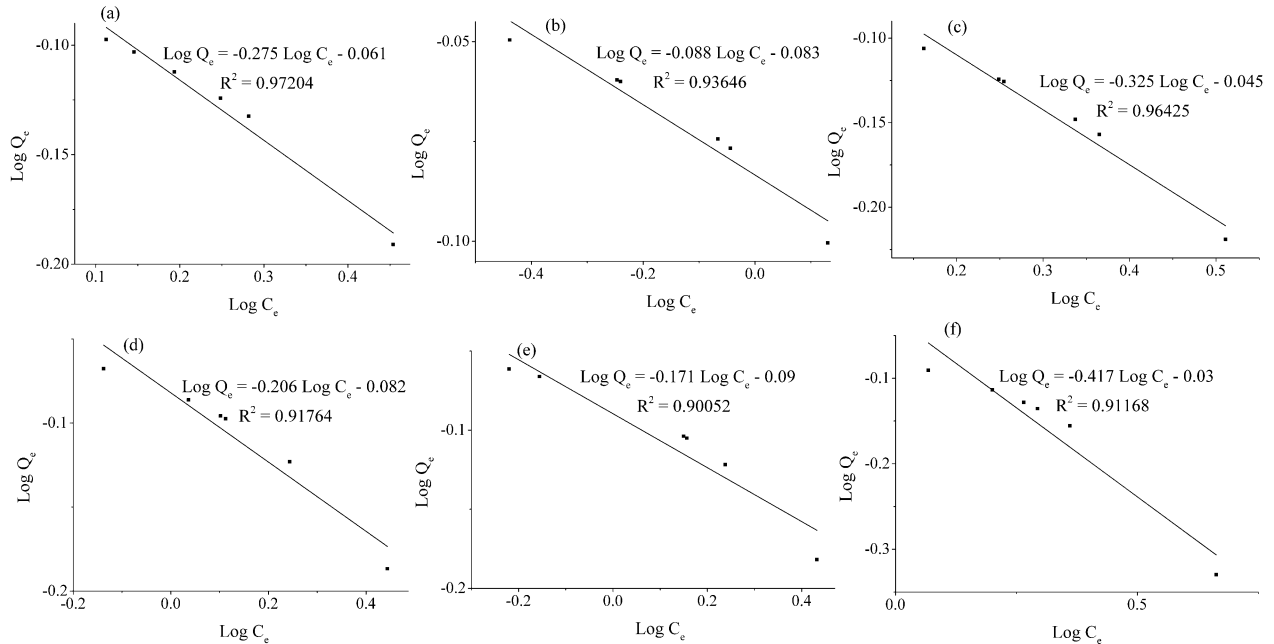


Figure 12. Freundlich adsorption isotherms for Fe onto a) RH500, b) RH600, c) RH700, d) CH500, e) CH600, and f) CH700. The initial concentration of Fe in industrial wastewater was 9.28 mg/L.

Freundlich isotherm model was tested for Cr removal to find conformity with the experimental results (Figure 11). The results fitted well in the model with the R^2 ranging between 0.82 and 0.99 for both the carbonised rice husk and corn husks biochars. The R^2 value was higher for RH500 and CH700 indicating that the experimental results correlated well with one another at a carbonisation temperature of 500 °C and 700 °C for rice husks and corn husks, respectively.

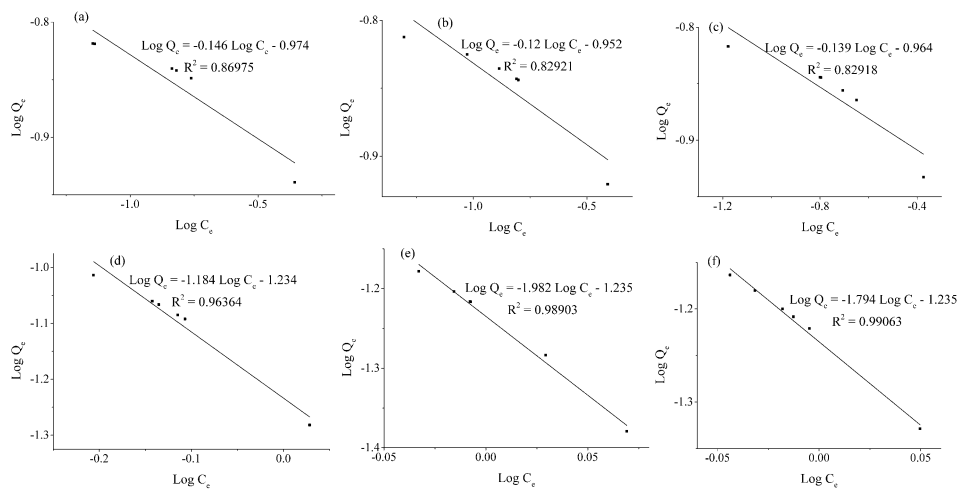


Figure 13. Freundlich adsorption isotherms for Pb onto a) RH500, b) RH600, c) RH700, d) CH500, e) CH600, and f) CH700. The initial concentration of Pb in industrial wastewater was 1.59 mg/L.

For both isotherm models (Langmuir and Freundlich), the R^2 values ranged between 0.82 and 0.99 indicating that the experimental data fitted well with these models as seen (Table 5 and Figures 8 to 13). However, the calculated Langmuir separation factor (R_L) values yield negative values indicating that the Langmuir isotherm parameters may not be suitable indicators of the biosorption processes. The negative R_L values may be due to the low initial pollutant concentrations in the used industrial wastewater (Ayawei *et al.*, 2017). The initial concentration of Cr, Fe, and Pb were 1.82, 9.28, and 1.59 mg/L, respectively. In Table 5, it is shown that the R_L values for Fe adsorption were close to zero because Fe was present in relatively higher concentrations. Most laboratory-scale studies yield non-negative R_L values because the initial spiked metal ion concentrations are usually high (Meroufel *et al.*, 2013).

Generally, the values in Table 5 indicate the superiority of rice husk biochars compared to corn husk biochars, and it agrees with the observations made earlier about the removal efficiencies and adsorption capacities. From the Freundlich parameters in Table 5, the majority of the values of n are negative. Usually, favourable sorption processes have values of n between 1 and 10, in which values of $n > 1$ indicate a monolayer sorption isotherm. Values of $n < 1$ indicate strong, almost irreversible interactions between the pollutant and the biosorbent. In cases where $n < 1$, the biosorbents are known to have high pollutant removal ability even at low initial pollutant concentrations. Thus, negative n values obtained in this study implies that the applied biosorbents can sufficiently remove the studied pollutants from wastewater.

Table 5. A summary of Langmuir and Freundlich isotherm parameter for the adsorption of Cr, Fe, and Pb onto different biosorbents.

Biosorbent	Isotherm parameters for Cr						Isotherm parameters for Fe						Isotherm parameters for Pb					
	RH500	RH600	RH700	CH500	CH600	CH700	RH500	RH600	RH700	CH500	CH600	CH700	RH500	RH600	RH700	CH500	CH600	CH700
Langmuir model																		
q_m (mg/g)	0.04	0.06	0.05	0.03	0.01	0.01	0.55	0.76	0.51	0.59	0.62	0.39	0.11	0.11	0.11	0.03	0.02	0.02
k_L (L/mg)	-2.06	-3.19	-2.39	-1.42	-0.85	-0.88	-2.27	-14.28	-1.73	-3.29	4.21	-1.23	-33.69	-41.12	-29.64	-2.15	-1.43	-1.53
R_L	-0.36	-0.21	-0.29	-0.63	-1.86	-1.66	-0.05	-0.01	-0.07	-0.03	0.03	-0.09	-0.02	-0.02	-0.02	-0.41	-0.78	-0.70
R^2	0.82	0.99	0.99	-0.99	0.97	0.99	0.99	0.99	0.99	0.99	0.99	0.98	0.82	0.82	0.82	0.82	0.82	0.82
Freundlich model																		
k_F (mg/g) (1/mg) ^{1/n}	0.34	0.34	0.89	0.34	0.46	0.44	0.94	0.92	0.96	0.92	0.91	0.97	0.39	0.39	0.38	0.29	0.29	0.29
$1/n$	-0.83	-1.39	-1.09	-0.61	-0.24	-0.24	-3.64	-11.36	-3.08	-4.85	5.85	-2.39	-6.85	-8.33	-7.19	-0.85	-0.51	-0.56
R^2	0.99	0.99	0.99	0.99	0.99	0.99	0.94	0.94	0.96	0.92	0.90	0.91	0.87	0.83	0.83	0.96	0.98	0.99

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.0 Conclusions

This study investigated the ability of rice husk and corn husk biochars in the removal of heavy metals from industrial wastewater released into a municipal waste stabilisation pond in Arusha, Tanzania. Rice and corn husk biochars were prepared at different pyrolysis temperatures, i.e. 500, 600 and 700 °C. The biochars were activated using KOH as an activating agent. The activated biochars were used to remove ions of Cr, Fe, and Pb from industrial wastewater. Rice husk biochars were more efficient than the corn husk biochars. This was probably attributable to high intensities of carboxylic groups as evidenced by the FT-IR characterisation results. Although pyrolysis temperatures increased with C/N ratios; high C/N ratios did not directly translate into high removal efficiencies, an indication that there are other features than the C/N ratio contributing to pollutant removal. The optimum pyrolysis temperature for rice husk biochars in this study was 600 °C. For the improvement of corn husk biochars, this study suggests pyrolysis temperatures between 300 and 500 °C. All the biochars used for this study indicated maximum removal efficiencies in the first 20 to 30 min. This has a favourable implication for industrial applications, as most industrial processes require high performance under relatively shorter contact times.

5.1 Recommendations

This study has shown the ability of biochars developed from rice and corn husk to treat poorly managed industrial wastewater effluents. However, further studies should be conducted to recover heavy metal ions adsorbed by the biochars as well as to conduct a study on the secondary pollution as a result of heavy metals ions removal by using rice and corn husks biochars.

Scaling of the experimental setup is an essential factor in treating poorly managed industrial wastewater, and further studies should be conducted by considering the discharge capacity of different industries.

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