



Comparative Studies in the Removal of Pb^{2+} and Cd^{2+} from Aqueous Solutions using Corn Cobs and Cassava Peels Biochar

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Abstract The adsorption capacity of four different biochar adsorbents prepared from corn cobs and cassava peels at 350 and 450°C for the removal of cadmium and lead ions from their aqueous solutions were investigated. The biochars were characterized in terms of physico-chemical properties, functional groups, surface characteristics and thermal behaviour. The effects of adsorption process variables on the adsorption capacity of the biochars for the removal of cadmium and lead ions were evaluated using the one factor at a time method. The adsorption process variables considered and their range of values are initial metal concentration of 20 to 100 mg/l, biochar dosage of 0.2 to 1.0 g, contact time of 20 to 100 mins, and pH of 2 - 11. The characterization of the biochars revealed that all biochars had similar microporous distribution, thermal behaviour and functional groups, close surface area values and slightly different physicochemical properties. Maximum removal efficiencies of the biochars were achieved using an initial metal concentration of 20 mg/l, biochar dosage of 1.0 g, contact time of 100 mins and pH of 11. It was observed that Pb^{2+} ion was generally more adsorbed in all the adsorption experiments by the different biochar adsorbents than Cd^{2+} . The high values of the removal efficiencies obtained showed that all biochars were effective in treating aqueous solutions laden with cadmium and lead ions.

Keywords Aqueous Solutions, Corn Cobs, Cassava Peels, Biochar and Characterization

Introduction

Metals are important because they persist in the environment. Half of the metals that are categorized as toxic are released into the environment in proportions that are harmful to human health, and at least 20 metals are poisonous (Amuda et al., 2007). However, numerous trace elements have a role in a water body's capacity to support aquatic life as well as its usefulness for other purposes. Technology and industrialization have led to the rising uses of heavy metals which have resulted to massive pollution of our environment (Patra et al., 2017). Industrial and agricultural effluents are mostly toxic due to presence of heavy metals. The natural constituents of the earth's crust are heavy metals (Jadia and Fulekar, 2008; Kumar et al., 2011). The disposal of heavy metals has increase water pollution worldwide. Their presence in lakes, sand, stream has been responsible for serious health problems for plants, animals, and human beings (Patra et al., 2017). Toxic metal compounds arising from the earth's surface not only



contaminate earth's water but also causes ground water contamination in trace amounts through leakage from the soil after rain. Therefore, the earth's water may reserve various toxic metals. They mainly act as environmental pollutants and cause severe threat to animal and human health by their long-term perseverance in the environment (Subhashini and Swamy, 2013).

In recent years, biochar has gained increasing attention due to its multi-functionality including carbon sequestration and enhancement of soil fertility (Keiluweit and Kleber, 2009), production of bio-energy (Field et al., 2013) and environmental remediation (Kołodyn'ska, 2012). Use of biochar and its production produce renewable energy and release greenhouse gases from soils and waste decomposition (Patra et al., 2017). Biochars are used for the production of activated carbons which are applied as adsorbents for adsorption processes.

Tailoring the physicochemical properties of adsorbents for water treatment and purification is relevant from an economical and technical point of view (Dastgheib et al., 2004). Process efficacy and operational costs of the adsorption process highly depends on the characteristics of the adsorbent, especially its porous structure, and surface chemistry (Rojas-Mayorga et al., 2016). The synthesis conditions have a significant impact on the physicochemical properties of the adsorbent and a key issue is to identify the best route for the desired application. However, this is not an easy task because several variables are involved in the synthesis (Rivera-Utrilla et al., 2011). To date, several routes have been reported for the preparation of tailored adsorbents for the removal of both inorganic and organic pollutants, but these studies have mainly focused on activated carbons obtained from lignocellulosic precursors (Bhatnagar et al., 2013; Hokkanen et al., 2016; Rivera-Utrilla et al., 2011). The assessment of alternative materials obtained from other sources and the analysis of their surface characteristics seem mandatory to identify promising adsorbents.

A. Statement of Problem

Contaminated water risks both the physical and social health of all people. It does not only demolish the environment, but it also can pose a severe effect on the human health. According to the severe environmental protection legislation and public environmental concerns of lead and other toxic heavy metals like zinc, cadmium, nickel, chromium, silver, copper and arsenic, these heavy metals can be removed from wastewater by conventional techniques such as chemical precipitation, membrane filtration, reverse osmosis, electro-coagulation, chelation and ion exchange. Recently, biosorption of contaminants by sorbents of natural origin has gained important reliability because of its good capability and low cost of these complexing materials. Due to high uptake capacity and very cost effective source of raw materials, biosorption is a progression towards a perspective method. In this study, the potential advantages of the use of corn cob and cassava peels (low cost adsorbents) are: (i) abundant availability, (ii) low cost, (iii) good adsorption capacity, (iv) easy for chemical modification, (v) easy renewal and (vi) less disposal problem after adsorption.

B. Relevance of study

Research and development on different materials and techniques has revealed several promising avenues in this regard. Wastewater contaminants, especially heavy metals, can be removed from wastewater using a number of well-established techniques. These include adsorption, nanofiltration, reverse osmosis, solvent extraction, chemical precipitation, flotation, coagulation and flocculation, membrane filtration, ion exchange, etc.

Agricultural wastes provide low cost and environmental friendly alternative to commercial adsorbents for water treatment and they are readily available. Agricultural wastes like corn cobs and cassava peels can be chemically modified and applied as adsorbent rather than be burnt or disposed uncontrollably to the detriment of the environment. This study will provide information and data on the potentials of corn cob and cassava peels for water treatment.

C. Aim and Objectives

The main aim of this study is to evaluate of adsorption capacity of bone char adsorbent prepared from corn cobs and cassava peels for the removal of lead and cadmium ions from their aqueous solutions. The objectives of this study are to:

- [1]. Prepare and characterize biochar adsorbent from corn cob and cassava peels.
- [2]. Preparations of aqueous water systems that contain heavy metals (lead and cadmium ions).
- [3]. Adsorption of the heavy metals from their aqueous solutions considering adsorption process variables such as initial concentration of the metals, adsorbent dosage, pH of adsorbate solution and contact time of uptake process.
- [4]. Subject the data obtained to isotherm studies such as Freundlich and Langmuir isotherm of the adsorption process will be carried out to determine the best model for the adsorption process.

D. Scope of study



- [1]. Corn cobs and cassava peels will be sourced locally, pretreated, pyrolyzed, and characterized employing suitable techniques.
- [2]. The adsorbent will be used for the uptake of lead and cadmium from their aqueous solutions considering the impact of adsorption process variables such as adsorbent dosage, pH and contact time at room temperature.
- [3]. The adsorption capacity (using amount of metals adsorbed) of the adsorbents will be analyzed.
- [4]. Isotherm studies will be carried out to determine the model best fit for the biochar adsorption process

Materials and Methods

Corn cobs and cassava peels used for this study were sourced locally in Benin City, Edo State. All chemicals used for this study was of analytical grade and was purchased and used without further purification. The chemicals/reagents used are listed below.

- [1]. Distilled water
- [2]. Deionized water
- [3]. Sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)
- [4]. Sodium carbonate
- [5]. Iodine solution
- [6]. Potassium iodide (KI)
- [7]. Starch
- [8]. Potassium iodate (KIO_3), Primary standard
- [9]. Starch indicator

A. Preparation of Reagents/Solutions

Adsorbate Preparation

Lead (Pb^{2+}) and cadmium (Cd^{2+}) ion solutions were prepared from their salt of lead nitrate $\text{Pb}(\text{NO}_3)_2$ and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ respectively. 1.6g of $\text{Pb}(\text{NO}_3)_2$ and 2.6g of $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ were weighed and dissolved in 1000 ml volumetric flasks separately and then diluted with distilled water to the mark which gave a concentration of 1000 ppm. This is the stock solution.

B. Preparation of Buffer 4 and 7 Solutions

Solutions of buffer 4 and 7 were prepared by dissolving the tablets in a 100 ml of distilled water. These solutions were used for pH determination.

C. Preparation of Iodine Solution

A 0.05 g of iodine solution was prepared by dissolving 20 g of free potassium iodide into 40 ml of water in a glass-stopper 1L volumetric flask. After that, 12.7 g of iodine was transferred by a means of a small dry funnel into the flask and stirred in cold water until all the iodine dissolved. The solution was allowed to acquire room temperature and then diluted up to the 1L mark with distilled water.

D. Preparation of Sodium Thiosulphate Solution

Sodium thiosulphate crystals ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) of 25 g was dissolve in boiled distilled water and made up to 1L in a graduated flask.

E. Preparation of Cassava Peel Carbon (Carbonization)

Cassava peels were washed and sun dried for 7 days followed by moisture content determination. This was followed by grinding of the cassava peel with an electric grinding machine to reduce the size. The moisture free cassava peels were loaded into different clean silica crucibles and then into the muffle furnace and allowed to carbonize at a temperature of 350°C for a period of 25 minutes. Then the cassava peel was allowed to cool overnight thereby yielding the base carbon material (Gimba and Bahago, 2004; Omeiza et al., 2011). Thereafter, the carbonized cassava peel was sieved using a $250 \mu\text{m}$ sieve to obtain cassava peel carbon of uniform size. The filtrates were then washed thoroughly to remove the unwanted matter and impurities introduced during the crushing process.

F. Preparation of Corn Cob Carbon

Corn cob char was prepared using method by Arunkumar et, al., (2014). Corn cob was washed with distilled water and allowed to dry. The collected sample was then oven dried at 80°C for 8 hours, then pulverized and sieved using various size sieves. Finally 250 micron size particles were used for further experiments.

G. Determination of Moisture Content

The moisture content of the corn cob and cassava peel char adsorbent was determined by thinly spreading 2 g each of the fresh bio-solids in petri dishes. They were dried in an air-circulating oven at 105°C for 24 hrs. The dried samples were then cooled in a dessicator for 30 mins and then reweighed (Itodo et al., 2010). The process was repeated at 1 hr intervals and the percentage moisture content (% loss in weight) was calculated using Equation (1).



$$\text{Moisture content (\%)} = \frac{\text{loss in weight (g)}}{\text{initial weight (g)}} \times 100\% \quad (1)$$

H. Determination of Surface Area

The surface area of the corn cob and cassava peel chars sorbent was determined using iodine adsorption method. The amount of iodine adsorbed from aqueous solution was estimated by titrating a blank with standard thiosulphate solution and compared by titrating against iodine containing the sample. Surface area was calculated using the expression in Equation (2).

$$\text{surface area} = \frac{B-S}{B} \times \frac{VM}{W} \times 126.91 \quad (2)$$

I. Determination of Ash Content

Corn cob and cassava peel char sorbents of 5 g each was weighed into a crucible. The crucible containing the sample was placed in a muffle furnace and was allowed to ash at 550°C. The sample was then removed from the furnace and allowed to cool in a desiccator then weighed immediately (Abdulsalam et al., 2018). The weight of the residual ash was then calculated as percentage ash content as follows;

$$\text{Percentage ash content} = \frac{\text{weight of ash}}{\text{weight of sample}} \times 100\% \quad (3)$$

J. Determination of Bulk Density

A mass of 2 g each of corn cob and cassava peel biochars were inserted into the measuring cylinder and allowed to fill the empty spaces by tapping the bench until a constant volume was achieved. This constant volume was recorded and used to calculate the bulk density by applying the Equation (4).

$$\text{Bulk density} = \frac{\text{weight of sample (g)}}{\text{volume (m}^3\text{)}} \quad (4)$$

K. Determination of Pore Density

A 100 mL beaker was weighed and labelled W1. 5 g each of both biochar was turned into the beaker and bumped for about 20 - 30 minutes until all the pores were filled thereby leaving space above the sample contained in the beaker. The sample was then filled and bumped continuously until it reached the 100 mL mark of the beaker. The weight of the sample after bumping plus that of the beaker was weighed and recorded as W3 while the volume of the beaker was recorded as W2 (Evbomwan and Alalibo, 2017). The Pore density then was calculated using the formula.

$$\text{Pore density} = \frac{W_3 - W_1}{W_2} \quad (5)$$

Porosity: The Porosity of samples of KOH impregnated biochars were calculated using the formula in Equation (6).

$$\text{Porosity (\%)} = \frac{\text{Bulk Density}}{\text{Pore Density}} \times 100\% \quad (6)$$

L. Langmuir Isotherm Model

The essential characteristics of Langmuir isotherm model can be expressed by a dimensional constant called equilibrium parameter, RL (Pattabhi et al., 2008) which is defined by equation below;

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

Where b = Langmuir constant at m³/kg

C_e = initial concentration in mg/dm³

The Langmuir isotherm modeling equation is given below

$$q = \frac{abC_e}{bC_e + 1} \quad (8)$$

Analytical isotherm equation such as Langmuir isotherm is widely used for modeling adsorption data. This equation can be rearranged to yield the following linear expression

- Where q is the amount of metal adsorbed per unit mass of set (g)
- [a] and [b] are the Langmuir constants and are indicative of adsorption capacity mg/g and energy of adsorption (1/mg) respectively and
- C_e is the equilibrium concentration of adsorbate in waste water sample after adsorption (mg/l). The Langmuir constants [a] and [b] were obtained from the intercept and slope of the plot of (C_e/q) against (C_e).

M. Freundlich Isotherm Modeling

A fairly satisfactory empirical isotherm, which can be applied to adsorption of gases with considerable success but has been used principally for adsorption from solution, has been discussed by Freundlich.

The Freundlich equation has general formula



$$q = K_F C_e^{\frac{1}{n}} \tag{9}$$

By taking logarithms of both sides, we have

$$\log_{10} q = \log_{10} K + \frac{1}{n} \log_{10} C_e \tag{10}$$

Where q is the amount of adsorbate adsorbed per unit weigh adsorbent,

- K_F is Freundlich constant measuring adsorption capacity,
- C_e is the equilibrium concentration of the adsorbate in solution,
- n is a constant related to adsorption efficiency and energy of adsorption or adsorption intensity of the adsorbent.

Results and Discussions

A. Characterization of Biochar

The physico-chemical properties, functional groups and surface characteristics (surface morphology, surface area, pore volume and pore size distribution) of the corn cob biochars at 350 and 450 °C (CCBC350 and CCBC450) and cassava peel biochars at 350 and 450 °C (CPBC350 and CPBC450) as obtained from analysis are discussed in this section.

B. Physico-Chemical Properties of Biochars

The physico-chemical properties of the biochars; CCBC350, CCBC450, CPBC350 and CPBC450 obtained after characterization is given in Table 1.

Table 1: Physico-Chemical Properties of Biochars

Properties	CCBC350	CCBC450	CPBC350	CPBC450
Bulk density (g/cm ³)	0.32	0.37	0.45	0.41
pH	6.86	7.42	6.07	7.49
Surface charge (MMol [H ⁺])	4.80	15.20	8.39	6.90
Ash content (%)	12.80	15.90	15.10	26.90
Volatile matter (%)	87.20	84.60	84.80	73.04

SEM Analysis

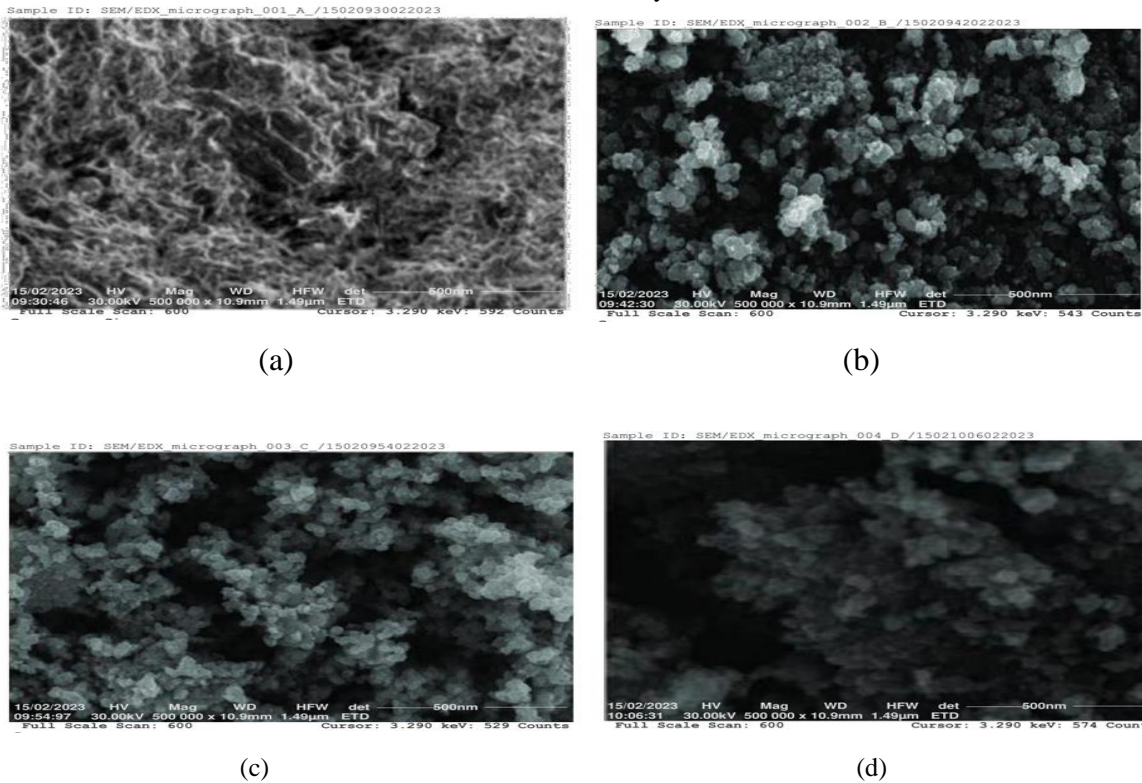


Figure 1: SEM micrograph of (a) CCBC350, (b) CCBC450, (c) CPBC350 and (d) CPBC450 at 600 resolution.

It can be seen from the micrograph of Figure 1 (a) that CCBC350 had spherical and irregular appearance of pores with clustered shape of the surface. From Figure 1 (b), it can be observed that CCBC450 appeared like a polyhedral for the most part and some are spherical in shape with interconnected macropores. The micrograph in Figure 1 (c) of CPBC350 indicate the particles of biochar are spherical in shape with agglomerated micro-spheres or granules with smooth surfaces. The particles of the CPBC450 were found to be spherical in shape, with a smooth surface and a high degree of regularity as shown in Figure 1 (d). It can be concluded that CCBC350 had a better pore surface structure which indicate the presence of more active sites for chemical reaction to take place.

C. FTIR Analysis

The functional groups of the biochars: CCBC350, CCBC450, CPBC350 and CPBC450 are given in Tables 2, 3, 4 and 5 respectively.

Table 2: Functional Group of CCBC350

S/N	Wavelength (cm ⁻¹)	Transmittance (%)	Assignment	Functional group
1	3450.70	44.16	O-H stretching vibration, which indicates the presence of alcohol and phenol	Hydroxyl
2	2918.53	65.80	O-H and C-H aldehydic stretching vibrations	Aldehyde
3	2861.32	72.54	C=C stretching vibration in unconjugated ketone, carbonyl and ester groups	Carbonyl, alkenes and ester
4	1516.38	40.00	C=O stretching vibration in carboxyl or C=N bending in the amide	Carboxylic acid and/or amide
5	1400.63	64.21	C-O stretching vibration (amide) and C-C stretching from phenyl groups	Amide
6	1350.82	72.08	Stretching vibration of (NH) C=O group in primary amines and amides	Amine
7	1252.61	76.30	C-O-C stretching vibrations	Carboxyl
8	1125.64	80.00	C-H stretching of alkane	Alkanes
9	902.55	26.85	Aliphatic C-N stretching vibration	Carboxyl/ amines
10	650.73	72.66	C-Cl, C-Br, and C-I stretching vibration	Alkyl halide

Table 3: Functional Group of CCBC450

S/N	Wavelength (cm ⁻¹)	Transmittance (%)	Assignment	Functional group
1	3618.53	27.50	O-H stretching vibration of hydroxyl functional group in alcohols and phenolic compounds	Hydroxyl
2	3300.28	60.85	N-H stretching in primary amines and amides	Amine
3	2175.46	40.32	C=C stretching vibration in unconjugated ketone, carbonyl and ester groups	carbonyl, Alkenes and ester
4	1832.36	53.18	C=O stretching vibration in carboxyl or C=N bending in the amide	Carboxylic acid and/or Amide
5	1641.05	85.26	Stretching vibration of (NH) C=O group in primary amines and amides	Amine
6	1461.43	80.16	C-O stretching vibration (amide) and C-C stretching from phenyl groups	Amide
7	1398.23	80.07	N-O symmetry stretching typical of the nitro compound.	Amines
8	1125.64	85.78	C-H stretching of alkane	Alkanes
9	900.50	72.54	C-N stretching vibration	Amide
10	650.73	68.51	C-Cl, C-Br, and C-I stretching vibration	Alkyl halide

Table 4: Functional Group of CPBC350

S/N	Wavelength (cm ⁻¹)	Transmittance (%)	Assignment	Functional group
1	3446.80	32.49	O-H stretching vibration, which indicates the presence of alcohol and phenol	Hydroxyl group
2	2950.16	56.24	Symmetric and asymmetric stretching vibrations of	Alkyl group



			-CH ₂ - group stretches	
3	1591.04	48.03	-OH in-plane bending modes, the presence of water and carbonyl (C = O) and other common alkane and oxygenated hydrocarbon functional groups	Hydroxyl/ carbonyl group
4	1347.11	60.17	O-CH deformation vibrations	Alkenes
5	1286.50	64.80	C-O stretching vibration	Carbonyl group
6	1074.62	76.11	C-O-C asymmetric stretching vibration	Ether group
7	650.06	78.25	C-Cl, C-Br, and C-I stretching vibration	Alkyl halide

Table 5: Functional Group of CPBC450

S/N	Wavelength (cm ⁻¹)	Transmittance (%)	Assignment	Functional group
1	3451.38	25.21	O-H stretching vibration which can be associated with the water content within system	Hydroxyl group
2	2950.16	64.38	C-H stretching vibrations specific to CH ₃ and CH ₂	Alkanes
3	2384.02	68.70	C-O stretching vibrations	Carbonyl
4	1654.09	60.82	N-H stretching vibration of amines	Amine
5	1421.38	54.25	C-N stretching of aromatic amine groups	Amine
6	1357.55	54.01	C-H stretching in symmetric planes	Alkane
7	1246.17	53.65	C-O stretching vibration	Carbonyl group
8	1100.97	47.08	C-H stretching of alkane	Alkanes
9	1000.62	60.99	C-O stretching vibration of alcohols, ester, or carboxylic acid	Alcohols, ester
10	650.00	64.53	C-Cl, C-Br, and C-I stretching vibration	Alkyl halide

Oxygen containing surface functional groups plays important role in influencing the surface properties and adsorption behavior of adsorbents (Dawood and Sen, 2014). These groups can be formed during carbonization process or are introduced by oxidation. The FTIR spectra obtained for CCBC350, CCBC450, CPBC350 and CPBC450 are given in Table 2, 3, 4 and 5 respectively. The adsorbents showed several and similar absorption bands indicating the presence of similar functional groups in adsorbents. Hydroxyl, amine, alkyl group, aldehyde, amides, alkane, esters, alcohols, alkyl halides are the functional groups present in all adsorbents.

D. BET Analysis

The results of the BET analysis (surface area, pore volume and pore diameter) of CCBC350, CCBC450, CPBC350 and CPBC450 are given in Table 6.

Table 6: BET analysis of CCBC and CPBC

Biochar adsorbent	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
CCBC350	88.528	0.026	0.472
CCBC450	75.063	0.033	0.205
CPBC350	67.410	0.037	0.243
CPBC450	62.391	0.046	0.248

The BET surface area is the main indicator for the surface properties of adsorbents/catalysts as described by Chandra et al. (2009) and Kalderis et al. (2008). The BET surface area, pore volume and pore size as seen in Table 3.6 of CCBC350 as analyzed using BET machine are 88.528 m².g⁻¹, 0.026 cm³.g⁻¹ and 0.472 nm respectively. The BET surface area, pore volume and pore size of CCBC45 are 75.063 m².g⁻¹, 0.033 cm³.g⁻¹ and 0.205 nm respectively. The BET surface area, pore volume and pore size of CPBC350 are 67.410 m².g⁻¹, 0.037 cm³.g⁻¹ and 0.243 nm respectively while CPBC450 are 62.391 m².g⁻¹, 0.046 cm³.g⁻¹ and 0.248 nm respectively. According to the International Union of Pure and Applied Chemistry (IUPAC), the pore development of an adsorbent/catalyst is classified into three groups which are micropores (size < 2 nm), mesopores (2–50 nm) and macropores (size > 50 nm) (Pandolfo and Hollenkamp, 2005; Mohd Iqbalidin et al., 2013). This shows that CCBC350, CCBC450, CPBC350 and CPBC450 fall within the microporous pore size distribution. A higher surface area was observed in CCBC350 and CCBC350 than in CPBC350 and CPBC450, which indicate that reaction rate will be higher with CCBC than CPBC. Also, the surface area of the biochars decreased with increase in temperature, which is consistent with results obtained by Lillo-Rodenas et al. (2004) and Chunlan et al. (2005). Lower pore volumes were observed in CPBC than in CCBC while CCBC350 had the highest pore size making CCBC350 a better adsorbent material.



E. Thermal Behaviour of the Biochars

Thermogravimetric analysis (TGA) reveals the thermal stability of the materials while differential thermogravimetric analysis (DTA) gives the temperature of the maximum decomposition rate. The TGA and DTA curves of CCBC350, CCBC450, CPBC350 and CPBC450 are presented as Figure 3.2 (a), (b), (c) and (d) respectively.

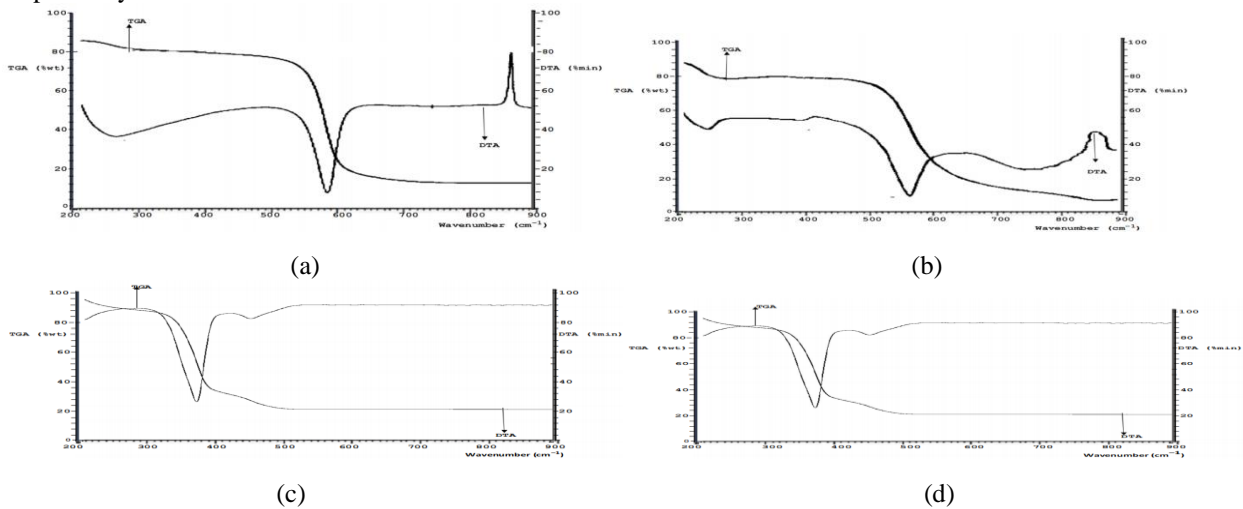


Figure 2: TGA and DTA curves of (a) CCBC350, (b) CCBC450, (c) CPBC350 and (d) CPBC450

According to the results of TGA presented in Figure 2(a-d), all biochar samples showed a similar thermal degradation profile with the weight loss proportionally increasing with the temperature of pyrolysis. The loss of weight can be attributed to the removal of weak-bonded water molecules within the materials. This indicates that the biochar adsorbents exhibited greater thermal stability which may be as a result of pyrolysis (Olasehinde and Abegunde, 2020).

Table 7: Effect of initial concentration on removal efficiency of biochars

Initial concentration (mg/l)	Removal Efficiency (%)							
	CCBC350		CPBC350		CCBC450		CPBC450	
	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺
20	70.32	77.21	81.29	85.23	79.44	82.92	89.36	90.74
40	65.45	68.97	73.43	74.29	71.90	72.16	76.86	78.42
60	62.07	58.62	69.09	67.07	66.79	64.05	72.10	70.74
80	60.51	52.88	65.67	62.66	61.82	59.86	68.27	65.43
100	57.33	50.63	60.32	56.04	57.87	54.36	61.77	60.85

As can be observed in Table 7, as the initial concentrations of the metal ions (Cd²⁺ and Pb²⁺) increased from 20 to 100 mg/l in the adsorbate solutions, the removal efficiency of all four biochar adsorbents decreased. Maximum efficiency was observed with initial concentrations of 20 mg/l why the least efficiency was observed with initial metal ion concentrations of 100 mg/l. Also in all cases, Pb²⁺ was more adsorbed by all biochar adsorbents than Cd²⁺.

F. Effects of Biochar Dosage

The effects of varying the dosage of each adsorbent at constant initial concentration of the metal ions and contact time on the adsorption capacity of CCBC350, CCBC450, CPBC350 and CPBC450 for Cd²⁺ and Pb²⁺ uptake in their aqueous solutions is given in Table 8.

Table 8: Effects of biochar dosage on removal efficiency of biochars

Biochar dosage (mg/l)	Removal Efficiency (%)							
	CCBC350		CPBC350		CCBC450		CPBC450	
	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺
0.20	58.86	59.44	65.78	71.79	63.95	69.13	75.67	79.44
0.40	62.73	66.21	73.69	83.62	67.27	76.09	81.53	87.29
0.60	70.32	77.21	81.29	85.23	79.44	82.92	89.36	90.74
0.80	82.61	87.71	91.83	92.86	85.88	90.22	93.79	95.45
1.00	92.19	94.12	95.27	95.37	94.37	94.77	97.37	97.81

From Table 8, as each biochar dosage increased from 0.20 to 1.00 g, the removal efficiency of all four biochar adsorbents increased correspondingly. Maximum efficiencies of the biochars was observed with dosage of 1.00 g why the least efficiency was observed with dosage of 0.20 g. The removal efficiency of the biochars followed the

order with increasing biochar dosage: CPBC450 > CPBC350 > CCBC450 > CCBC350 indicating that the cassava peel biochar adsorbents were more effective than the corn cob biochar adsorbents in Cd²⁺ and Pb²⁺ uptake from their aqueous solutions.. The removal efficiency of the biochars was more pronounced with CPBC450 than other biochar adsorbents. Again in all cases, Pb²⁺ was more adsorbed by all biochar adsorbents than Cd²⁺.

G. Effects of Contact Time

The effects of varying the contact time at constant initial metal concentration and biochar dosage on the adsorption capacity of CCBC350, CCBC450, CPBC350 and CPBC450 for Cd²⁺ and Pb²⁺ ions uptake in their aqueous solutions is given in Table 9.

Table 9: Effects of contact time on removal efficiency of biochars

Contact time (mins)	Removal Efficiency (%)							
	CCBC350		CPBC350		CCBC450		CPBC450	
	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺	Pb ²⁺
20	71.89	79.21	80.64	89.42	78.38	80.88	91.23	95.43
40	89.27	87.01	93.27	93.53	89.81	89.22	95.09	96.44
60	92.19	94.12	95.27	95.37	94.37	94.77	97.37	97.81
80	94.89	95.53	97.49	96.54	95.94	96.88	98.32	98.95
100	96.86	97.45	98.42	97.92	97.32	97.81	99.44	99.48

As seen from Table 9, increase in contact time led to a corresponding increase in the removal efficiency of all four biochar adsorbents for both for Cd²⁺ and Pb²⁺ uptake from their aqueous solutions. Maximum efficiencies of the biochars were observed at contact time of 100 mins why the least efficiencies were observed at contact time of 20 mins. With increase in contact time, the removal efficiency of the biochars followed the order increasing: CPBC450 > CPBC350 > CCBC450 > CCBC350 indicating that the cassava peel biochar adsorbents were more effective than the corn cob biochar adsorbents in Cd²⁺ and Pb²⁺ uptake from their aqueous solutions. The removal efficiency of the biochars was more pronounced with CPBC450 than other biochar adsorbents and Pb²⁺ was more adsorbed by all biochar adsorbents than Cd²⁺.

It was observed that Pb²⁺ ion was generally more adsorbed in all the adsorption experiments by the different biochar adsorbents than Cd²⁺. The variations in adsorption of these heavy metal ions might be due to their differences in physical and chemical properties. It might also be due to a combination of factors such as hydrogen bonding, precipitation and formation of insoluble metal complexes (Pavasant et al., 2006; Moshen, 2007).

Conclusion

The following conclusions were deduced from the competitive adsorption of lead and cadmium metal ions from their aqueous solutions using biochars prepared from corn cob and cassava peel at different temperatures of 350 and 450°C.

- The biochar adsorbents showed similar physico-chemical properties, functional groups, with differences in surface characteristics.
- The efficiency of all biochars increased with increase in biochar dosage and contact time, pH and decreased with increase in initial metal concentration.
- The biochar adsorbents were highly efficient in both cadmium (Cd²⁺) and lead (Pb²⁺) ion uptake from their aqueous solutions with the high efficiencies recorded.
- Cassava peel biochar carbonized at 450°C was found to be more efficient in the metal ions removal while corn cob biochar carbonized at 350°C was least effective in the metal ions removal.
- It was observed that lead (Pb²⁺) ion was generally more adsorbed in all the adsorption experiments than cadmium ion (Cd²⁺) by all biochar adsorbents.

From the study it can be concluded that all biochars had similar properties and were highly efficient in cadmium and lead ion removal from their aqueous solutions.

Contribution To Knowledge

- From this study up to date information on the surface chemistry, functional groups, physico-chemical properties of corn cob and cassava peel biochars at two different temperatures have been provided.
- The applicability of the data obtained to Langmuir



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