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EFFECTS OF SELECTED PROPERTIES OF WOODCHAR AND BONECHAR ON LEAD AND CADMIUM ADSORPTION

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ABSTRACT

The choice of materials used for clean-up of contaminated soils is mostly based the adsorption capacities of such materials. Biochar, a pyrolysed product of organic materials was employed in Lead (Pb) and Cadmium (Cd) sorption studies. Fourier transform-infrared (FT-IR) spectrometer was employed to determine the presence of functional groups in the biochar samples that may likely influence the sorption of the heavy metals. Biochar samples were subjected to electronic scanning to reveal the micro-structures of the biochar particles using a scanning electron microscope. Batch experiments were carried out to determine the adsorption isotherm that best fits Cd and Pb ions. FT-IR spectroscopy performed on the biochars detected the characteristic peak values and the functional groups contained by the biochars. The spectroscopy revealed that the functional groups were dominated by C-H, O-H, S=O, C=C and C-O groups of alkane, alcohol, carboxylic, sulphate, alkene and vinyl ether. Electronic scanning of the biochar samples revealed uneven surfaces for bonechar and well developed mesopores for woodchar. The Langmuir isotherm gave maximum adsorption values of 6.39 and 0.17 for Pb ions onto woodchar and bonechar; 0.05 and 0.042 mg g^{-1} for Cd ions onto woodchar and bonechar respectively. Langmuir adsorption isotherm model was best fit with high R^2 values (0.97 and 0.99) and were obtained from woodchar and bonechar sorption of Pb. Woodchar was observed to have significantly ($p<0.05$) higher sorption capacity for Pb than Cd when compared to bonechar. The n values obtained from the Freundlich adsorption isotherm indicated that the adsorption process was a chemical phenomenon. This study showed that biochar especially those made from plant sources can be used as a promising adsorbent for remediating Pb contaminated soils.

Keywords: Adsorption, Isotherms, Biochar, Lead, Cadmium

INTRODUCTION

The need to cleanup heavy metal contaminated soils has led to the development of materials with high sorption capacities. The use of these materials is based on their adsorption capacities. Materials such as biochar though mostly used as amendments, are continually being tested in order to determine their capacity to reduce heavy metal contents in soils through the phenomenon known as sorption. Biochars made from agricultural residues, animal wastes and woody materials have been tested for their capacity to sorb various heavy metals, including lead (Pb), copper (Cu), nickel (Ni), and cadmium (Cd) (Cao *et al*. 2009; Uchimiya *et al*. 2011).

Biochar is defined as the carbonaceous product obtained when plant or animal biomass is subjected to heat treatment in an oxygen-limited environment and applied to soil as an amendment (Lehmann and Joseph, 2009). It is a solid material obtained from the carbonization of biomass. Biochar is a carbon-rich product produced by the slow thermo-chemical pyrolysis of biomass materials (Shih-Hao and Chieng-Sheng, 2013). Biochar can be produced from different organic sources. Organic wastes, such as livestock manures, bones, sewage sludge, crop residues, woodchips, rice husk, cereal stubbles and composts are converted to biochar and then applied to soils as an amendment (Jien and Wang, 2013). Previous studies have shown that physical and chemical properties of biochar, such as pH, surface potential and surface area are important factors controlling their environmental applications (Inyang *et al.,* 2010). Therefore the aim of this study was to evaluate woodchar and bonechar capacity and properties that may influence the sorption of Pb and Cd in the soils.

MATERIALS AND METHODS

Biochar preparation and Analysis

Biochars used for this study were produced and analyzed by the processes described by Onokebhagbe *et al.* (2018). The experiment was conducted at the Soil Science Department laboratory, Ahmadu Bello University, Zaria. Fourier transform-infrared spectrometer was employed to determine the presence of functional groups in the biochar samples that may likely influence the sorption of the heavy metals. The spectra recorded for biochars were between 650 to 4000 cm^{-1} (30 scans, 8 cm^{-1} resolution) and were obtained using a Cary 630 FT-IR spectrometer (Agilent Technologies). The biochar samples were also subjected to electronic scanning to reveal the micro-structures of the biochar particles using a scanning electron microscope (Jeol, Japan).

Batch Experiments

Sorption studies were conducted using the batch technique as described by Arias *et al.*(2006) and Mulu (2013). Batch experiments were carried out to determine the adsorption isotherm that best fits Cd and Pb ions onto the adsorbents in 250 ml flask. Five grams of biochar samples were equilibrated with five different concentrations of Cd and Pb: 5, 10, 15, 30, 60 mg kg^{-1} Cd and 27, 49, 83, 90, 100 mg kg^{-1}Pb using nitrate salts of Cd and Pb. The flasks were agitated at a constant rate, to allow sufficient time for adsorption equilibrium at various time intervals (0.5, 1, 2, 5, 10 and 24 hrs.). Filtered suspension was analysed with the atomic absorption spectrophotometer to determine the equilibrium concentrations of Cd and Pb in the suspension. The pH of the solutions was determined in the course of the batch experiment. Adsorbed Cd and Pb were calculated as the difference between the initial concentration and the equilibrium concentration in solution. The metal ions sorbed by the biochars were calculated based on the following relationship as proposed by Mulu (2013).

$$Q_e = V_i \ (C_i - C_e)/M \quad \text{................(1)}$$

Q_e = Quantity of adsorbed metal ions; V_i = Volume of solution; C_i = Initial metal concentration; C_e = Equilibrium metal concentration; M = Mass of adsorbent (Biochar); Percentage metal ion removed from solution will be calculated as follows:

$$\%MR = (C_i - C_e) \times 100 \div C_i \quad \text{.....(2)}$$

Adsorption Isotherms

The batch adsorption data were fitted into the adsorption isotherms to determine which isotherm fits best. To establish equilibrium modelling, the adsorption isotherms used in the study were as follows: Langmuir and Freundlich models. The linearized Langmuir adsorption isotherm model as shown by Mulu (2013) is presented below:

$$C_e/Q_e = 1/bq_{max} + C_e/q_{max} \quad \text{....... (3)}$$

Where Q_e = the amount of metal x sorbed per unit weight of biochar (mg g^{-1}), C_e = equilibrium metal concentration (mg l^{-1}), q_{max} = metal adsorption maxima (mg g^{-1}), bq_{max} = distribution coefficient (l g^{-1}) and b = coefficient relating to bonding energy (l mg^{-1}) (Langmuir 2017, 2018). The Freundlich adsorption isotherm (Freundlich, 1907) is as shown below:

$$Q_e = K_f C_e^{1/n} \quad \text{.................. (4)}$$

Where K_f and n are the Freundlich constants characteristic of the system involved; K_f and n are indicators of adsorption capacity of biochar and adsorption intensity, respectively. The equation was linearized and the constants K_f and n found by linear regression as given by Mulu (2013):

$$\ln Q_e = \ln K_f - 1/n \ln C_e \quad \text{......... (5)}$$

RESULTS

FT-IRspectra of biochar

Results of the determined properties of the biochars are outlined in Table 1. The FT-IR spectra of the biochars are shown in Figures 1 and 2. The outcome of the FT-IR analysis revealed the most common functional groups the biochars contain. The various functional groups obtained in the two biochars revealed the presence of alcohol, amino-acid groups, amines, nitro-containing compounds, sulphate, isothionate and aromatic compounds. These surface functional groups exhibited by the biochars have the ability to influence heavy metal sorption by the biochars.

Table 1: Properties of Woodchar and Bonechar

Property	Woodchar	Bonechar
pH_{H2O}	9.4	7.3
pH_{CaCl2}	7.9	7.3
Total Nitrogen (%)	1.00	3.00
Total P (g kg^{-1})	1.60	63.2
Specific surface area (10^{-3} km^2 kg^{-1})	16.45	16.65

A broad band at about 3183 cm^{-1} and a strong peak at 1379 cm^{-1} were obtained from woodchar as shown in Fig 1. The broad band at 3183 cm^{-1} is associated with–OH stretching vibration of hydroxyl functional groups while the weak peak at 1379 cm^{-1} is evidenced by the presence of C-H group from alkane. As compared to woodchar, bonechar showed the peaks corresponding to O-H alcohol group (3671 cm^{-1}), O-H carboxylic acid group (3287 cm^{-1}), C-H alkane group (2922 cm^{-1}), S=O sulfate group (medium peak of 1409 cm^{-1}) and C=C alkene group (872 cm^{-1}) while a strong sharp peak of 1013 cm^{-1} indicated the presence of C-O vinyl ether group. These functional groups have the capacity of associating and dissociating into potential determining ions, hence with a possible influence on Pb and Cd sorption.

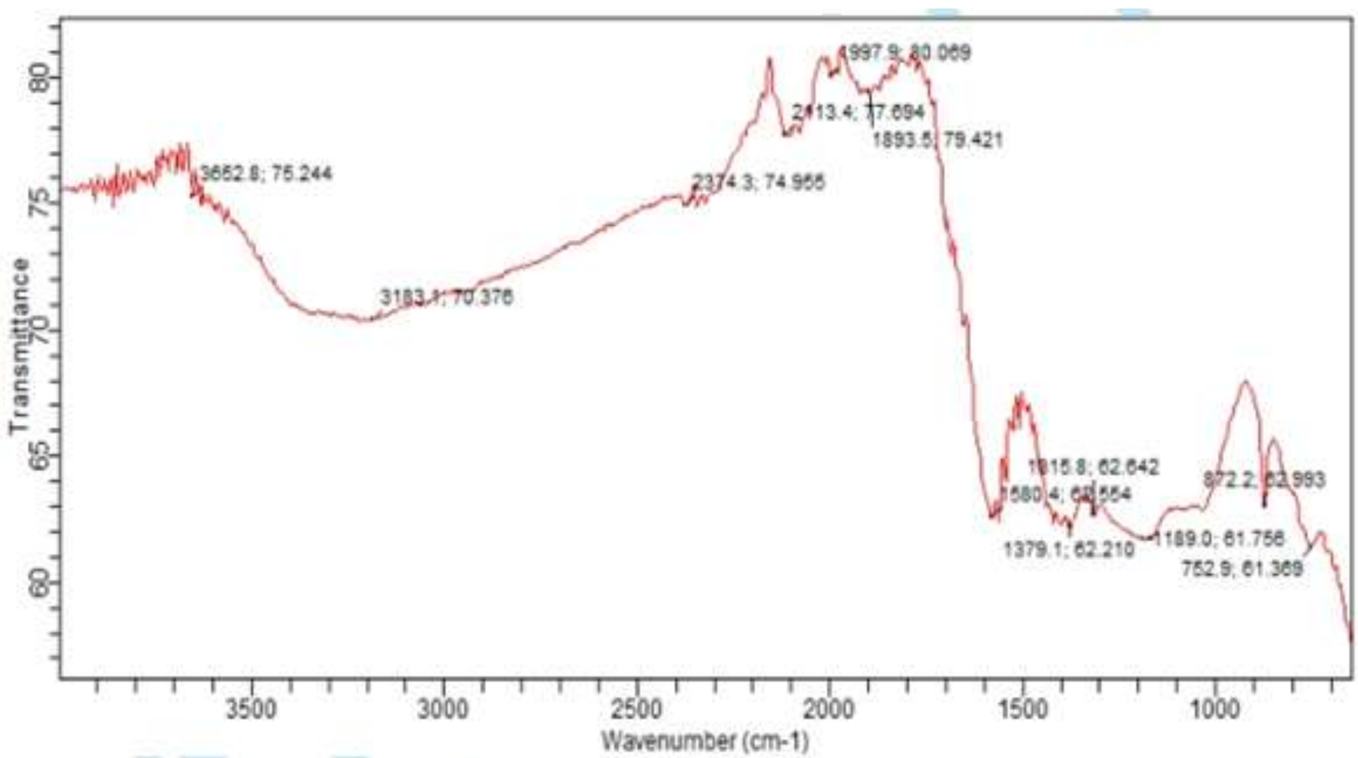


Figure 1: **FTIR Spectrum of Woodchar**

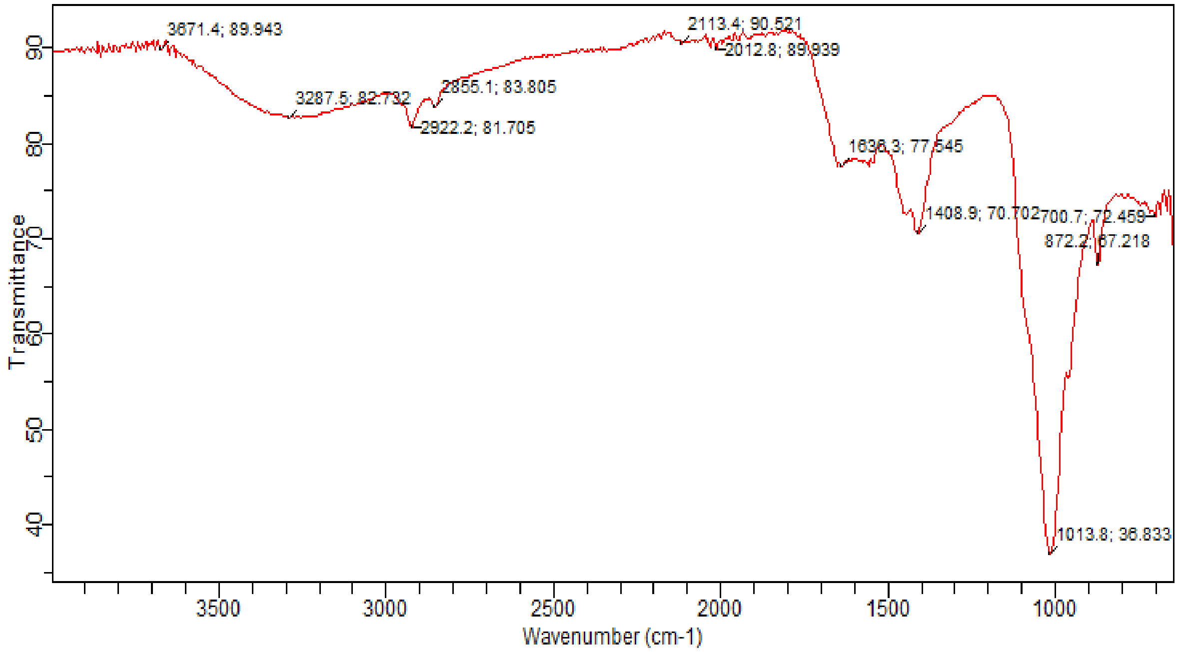
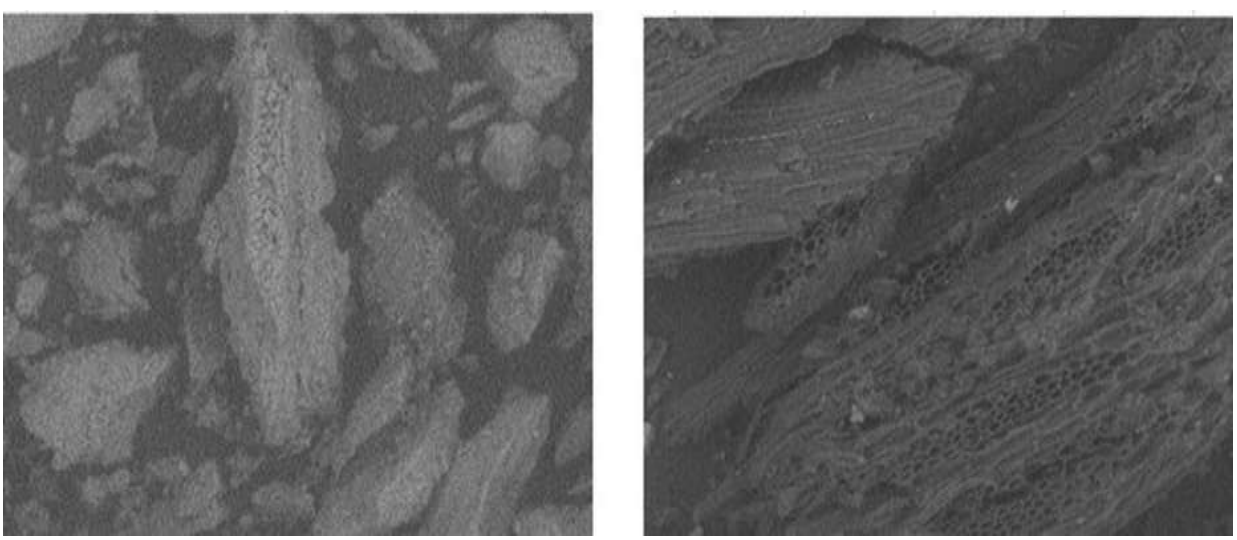


Figure 2: FTIR Spectrum of Bonechar

Microstructure of biochar

The microstructural data obtained from scanning electron microscope (SEM) section are semi-quantitative. Typical SEM microstructure of the woodchar and bonechar is shown in Plate I. The biochar morphology showed the irregular mass structures and uneven surfaces for bonechar and prolonged slit pores for the woodchar. Furthermore, the SEM results showed that woodchar appeared to have a well-developed mesopores when viewed under a magnification of 500 and 1000 of the order of 80 µm than bonechar. Using the 80 µm, most of the pores of the woodchar were within the range of 20-40 µm. The microscope resolution did not reveal the micro-pores of the biochars.



1 2

Plate I: Electron microscope scans of bonechar (1) and woodchar (2) Magnification of 1000 of the order of 80 µm.

Adsorption of Pb and Cd from Aqueous Solution by Woodchar and Bonechar

The heavy metals adsorption isotherms by biochars produced from wood-dust and bones are shown in Figures 3 to 10. The distribution of the ions between the liquid phase and the solid phase in this study were described by the Langmuir and Freundlich isotherm models. These isotherms describe the connection between the amounts of absorbate on the adsorbent. The adsorption isotherms graphs obtained, exhibited different curves. Langmuir and Freundlich isotherms showing the adsorption of Pb and Cd ions by the woodchar and bonechar were characterized by the S-curve as shown in Figures 3, 4, 6 and 8. H–curve was obtained from Figures 5 and 7 while L–curve was exhibited by Figures 9 and 10. This shows that the woodchar and bonechar adsorbed Pb and Cd ions differently. The S-curve is sigmoidal and is characterized by a small slope at low surface coverage that increases with adsorbate concentrations. The L-curved isotherm is characterized by a decreasing slope as concentration of the adsorbate increases with a corresponding decrease in vacant adsorption sites of the biochar as the adsorbent becomes covered.

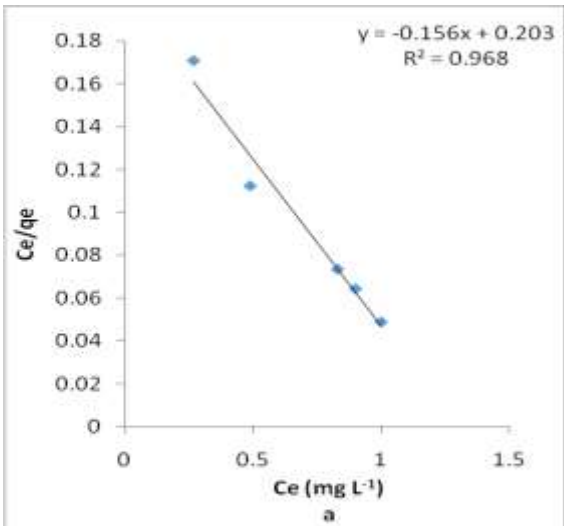


Figure 3: Langmuir isotherm showing the variation of adsorption C_e/q_e against the equilibrium concentration C_e for adsorption of Pb ions onto woodchar.

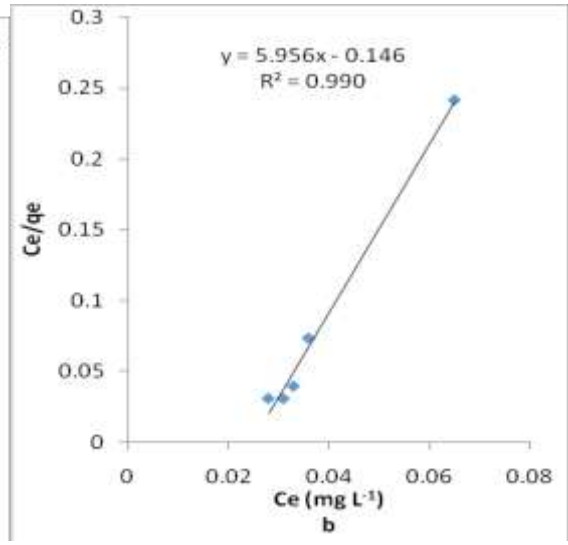


Figure 4: Langmuir isotherm showing the variation of adsorption C_e/q_e against the equilibrium concentration C_e for adsorption of Pb ions onto bonechar.

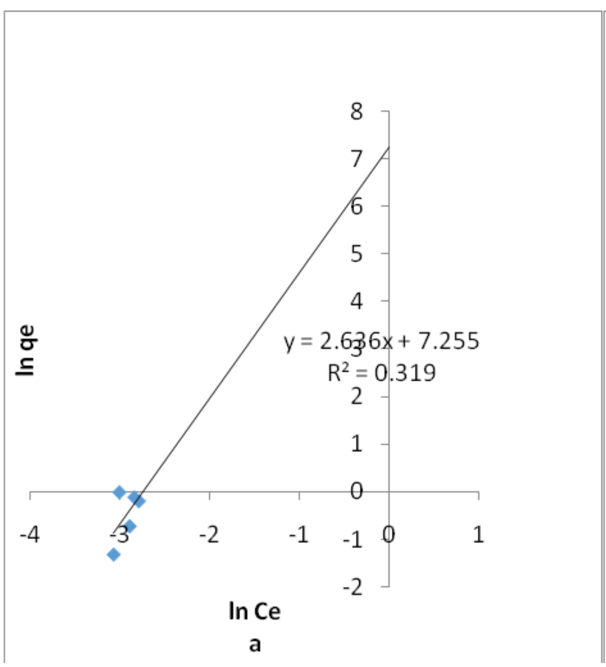


Figure 5: Freundlich isotherm showing the variation of $\ln q_e$ with respect to $\ln C_e$ for adsorption of Pb ions onto woodchar.

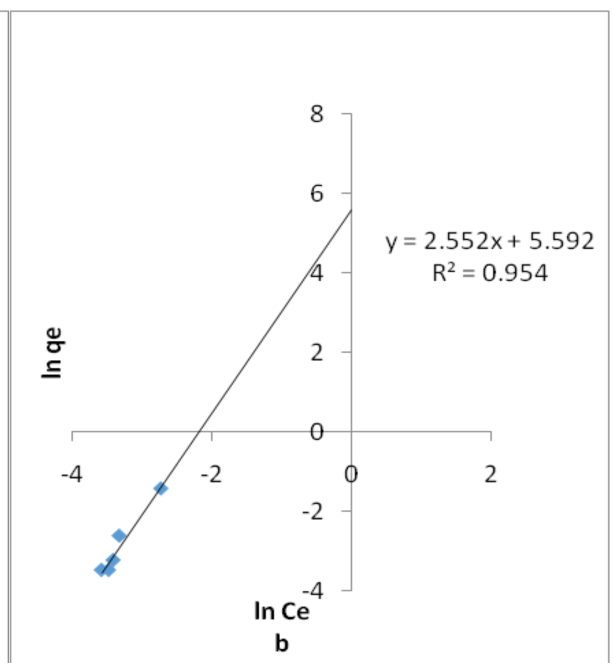


Figure 6: Freundlich isotherm showing the variation of $\ln q_e$ with respect to $\ln C_e$ for adsorption of Pb ions onto bonechar.

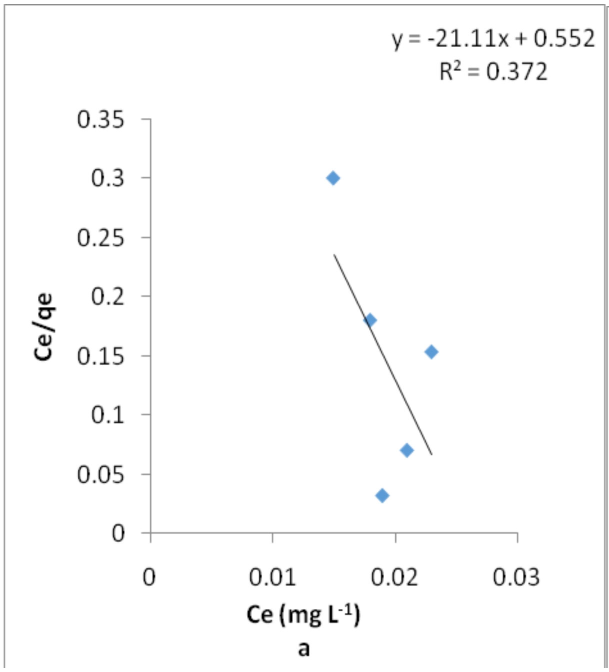


Figure 7: Langmuir isotherm showing the variation of adsorption C_e/q_e against the equilibrium concentration C_e for adsorptionof Cd ions onto woodchar.

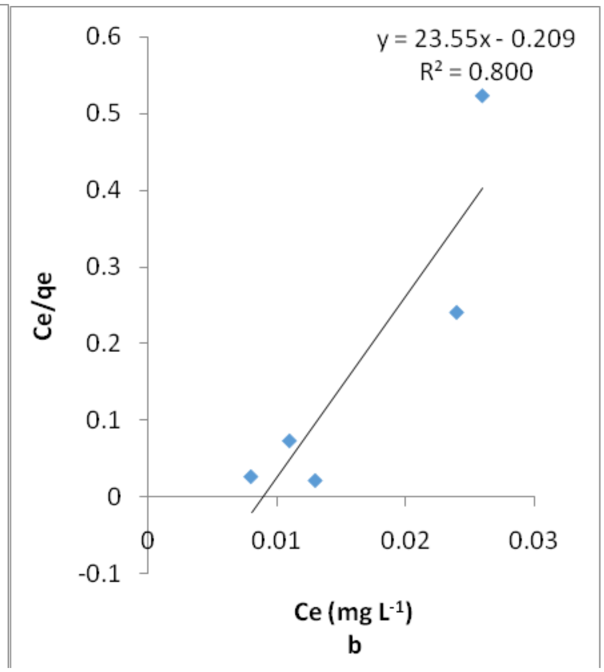


Figure 8: Langmuir isotherm showing the variation of adsorption C_e/q_e against the equilibrium concentration C_e for adsorptionof Cd ions onto bonechar.

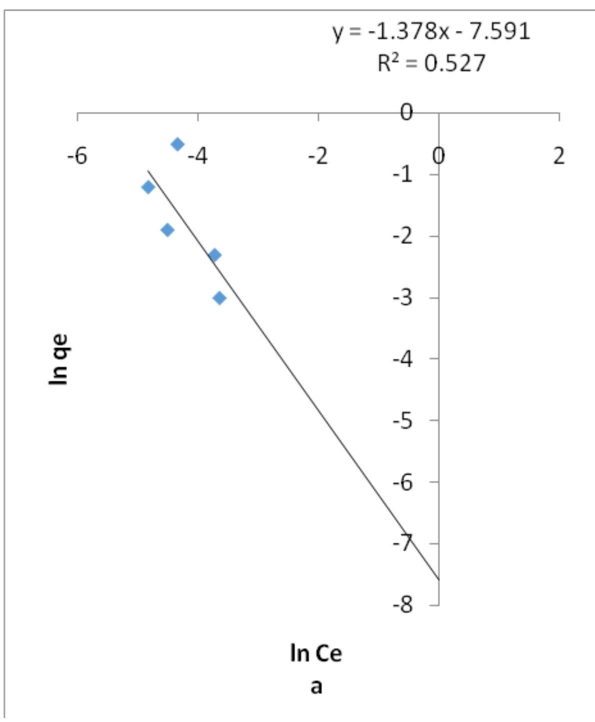


Figure 9:Freundlich isotherm representing variation of $\ln q_e$ with respect to $\ln C_e$ for adsorption of Cd ions onto woodchar.

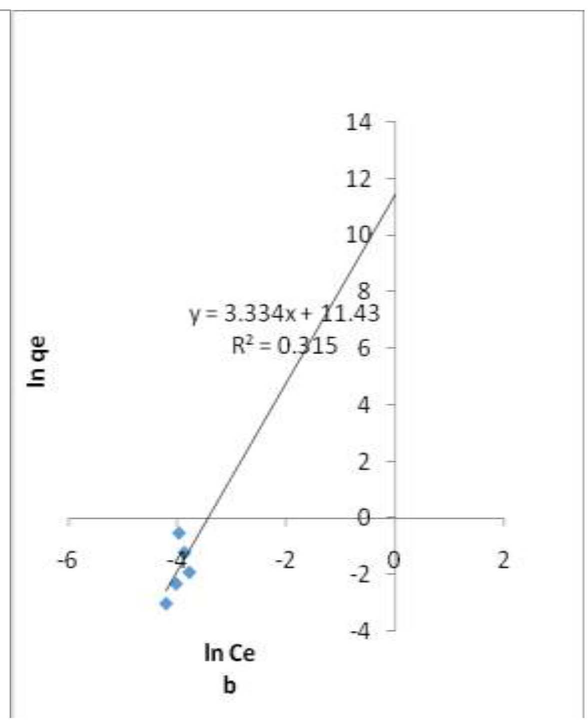


Figure 10: Freundlich isotherm representing variation of $\ln q_e$ with respect to $\ln C_e$ for adsorption of Cd ions onto bonechar.
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Langmuir and Freundlich adsorption constants and the regression coefficients (R^2) calculated are presented in Tables 2 and 3. The results revealed that Langmuir adsorption isotherm was the best fit model for Pb ions onto woodchar and bonechar with R^2 of 0.97 and 0.99 respectively. The value of the regression coefficient R^2 for Freundlich was only suitable for describing the adsorption of Pb ions onto bonechar (0.96). From the Tables, Pb ions fitted the adsorption models better than Cd ions.

Table 2: Langmuir isotherm parameters for adsorption of metal ions onto biochar

		Estimated isotherm parameters		
Biochar	**Metal ion**	q_{max} **(mg/g)**	*b* **(l/mg)**	R^2
Woodchar	Pb	6.39	0.77	0.97
	Cd	0.05	36.19	0.37
Bonechar	Pb	0.17	40.13	0.99
	Cd	0.04	2.64	0.80

Table 3: Freundlich isotherm parameters for adsorption of metal ions onto biochar

Biochar	**Metal ion**	Estimated isotherm parameters		
		n	K_f	R^2
Woodchar	Pb	0.38	4.86	0.32
	Cd	0.30	1.96	0.32
Bonechar	Pb	0.39	7.28	0.96
	Cd	0.73	2.89	0.53

The Cd adsorption data obtained from sorption of the metal ions on bonechar was better fitted by Langmuir adsorption isotherm (R^2 = 0.80) than by Freundlich equation (0.32 and 0.53) and onto woodchar (0.37) as shown in Tables 2 and 3. Langmuir parameters which include the boundary energy (*b*) at the surface of the biochars, which is a measure of the affinity of Pb and Cd ions for the biochars; the maximum adsorption capacity ($q_{\max}$); calculated from the data plotted on Figures 3, 4, 7 and 8 are presented in Table 2. The Langmuir equation gave maximum adsorption values of 6.39 and 0.17 for Pb ions onto woodchar and bonechar; 0.05 and 0.04 mg g^{-1} for Cd ions onto woodchar and bonechar respectively. The boundary energy (*b*) obtained for Pb ions onto woodchar and bonechar was 0.77 and 40.13; 36.19 and 2.64 l mg^{-1} for Cd ions onto the woodchar and bonechar as shown in Table 2.

The parameters obtained from the linear regression equation for the Freundlich adsorption isotherm are shown on Table 3. The table shows the values of the adsorption capacity (*Kf*) and adsorption intensity (*n*) calculated from the intercepts and slopes of the Freundlich plots respectively. The *n* values which indicates the degree of nonlinearity between the solution concentration and adsorption {if 1 $<n<1$, if $n = 1$, adsorption in linear; if $n< 1$, then adsorption is a chemical process; if $n> 1$, then adsorption is a physical process (Mulu, 2013)}; were found to be less than 1. This therefore indicates that Pb and Cd adsorption by the biochars were due to chemical processes such as complexation and co-precipitation as influenced by the presence of –OH, -COOH, -NH_2 and PO_4^{-3} functional groups on the surfaces of the woodchar and bonechar, as revealed by the FT-IR analysis.

Further assessment of the effects of some selected properties of the biochars on Pb and Cd sorption was carried out using Pearson correlation analysis. The results of the correlation analysis conducted to identify some key properties of the biochars affecting Pb and Cd sorption are presented in Table 4. The results showed that pH in water for woodchar had a strong correlation with sorption of the two heavy metals under the tried experimental settings as shown in Table 4 while a weak correlation of pH of bonechar with sorption of the two heavy metals was obtained. The solution pH of woodchar was strongly correlated with both Pb and Cd sorption with Pearson's R^2 values of 0.93 and 0.82 respectively as shown in Table 4. This relationship was significant for pH of woodchar on Pb sorption.

Table 4: **Pearson correlation coefficients (*R*) and significance of linear relationship between q_{max} of Pb and Cd and physiochemical properties of biochar**

Qe	Correlation Relationship	Biochar Properties			
		pH_{H20}	pH_{CaCl2}	TN ($g\ kg^{-1}$)	Surface Area
			Woodchar		
Pb	R^2	0.93	-0.25	0.61	0.68
	p level	*	NS	NS	NS
Cd	R^2	0.82	0.13	0.66	0.87
	p level	NS	NS	NS	NS
			Bonechar		
Pb	R^2	-0.22	-0.45	-0.18	0.17
	p level	NS	NS	NS	NS
Cd	R^2	-0.46	-0.61	0.15	0.59
	p level	NS	NS	NS	NS

*Note: * is significance level of 0.05; NS= Not statistically significant.*

DISCUSSION

The sorption situation in this study indicated a chemical adsorption of Pb and Cd ions onto the biochar rather than physical adsorption of the ions onto the biochar. It also indicated that significant adsorption took place at high concentrations but increase in the amount adsorbed became highly significant at higher concentration (Moreno *et al.*, 2010). The S-curve obtained suggested that the affinity of the biochars for the adsorbate was less than that of the aqueous solution when the solution concentration of the adsorbate was low (Essington, 2005; Abdu and Ugbaje, 2013). While the H-curve indicated a high affinity isotherm (adsorbates exhibited a high affinity for the biochars) which is indicative of strong adsorbate–adsorbent interactions such as inner–sphere complexes (Sparks, 2003; Limousin *et al.*, 2007). The L-curve suggested a progressive saturation of the biochar adsorption sites (Limousin *et al.*, 2007). This adsorption behavior could be explained by the high affinity of the woodchar and bonechar for the adsorbate at low concentrations which then decreases as concentration increases (Sparks, 2003). As the adsorption capacity (K_F) value increased, the adsorption intensity (n) increased too. Therefore, the higher K_F for Pb ions as shown in Table 3 confirmed by this model, that the adsorption capacity of woodchar for Pb was with greater intensity than for Cd ions. Summarily, the prepared biochars exhibited preferences for Pb ions adsorption more than Cd ions adsorption. Thus there was optimal removal of Pb ions from the aqueous solutions at the studied concentrations by the biochars.

The pH for optimum heavy metal sorption varies with the metal involved as the solution pH significantly influences the metal speciation and surface charge of the biochar (Li *et al*., 2017). A higher pH of biochar with higher alkaline mineral content also suggests a more active aromatic structure, which will aid the electrostatic adsorption due to cation-π interaction (Keiluweit *et al*., 2010). This is an indication that electrostatic interaction and surface precipitation among other forms of interaction were the dominant mechanisms for the adsorption (Meena *et al*., 2008; Inyang *et al*., 2012). This also may have controlled the sorption of Pb over Cd by woodchar as pH strongly affects the sorbate ion species and surface charge of the sorbent.

The statistical correlation of 0.60 and 0.66 identified for Total Nitrogen contents of woodchar for Pb and Cd sorption respectively shows that N-groups likely impacted on biochar sorption of Pb and Cd. This also suggests the possibility of N containing functional groups such as amine as revealed by the FT-IR spectra being involved in Pb and Cd sorption process (Yantasee *et al.*, 2004).

However, unlike other parameters of biochar, functional groups such amino, carboxylic and hydroxyl groups are being controlled by pyrolysis temperature and nature of feedstock (Li *et al*., 2017). The abundance of these functional groups tends to decrease with increase in temperature (Inyang *et al*., 2012). The insignificant relationship between q_{max} and surface area of the biochars suggests that physical adsorption was not the predominant adsorption mechanism as outlined by Inyang *et al*. (2015) which is in line with the findings from this sorption and equilibrium studies.

CONCLUSION

The use of the FT-IR spectrum on the biochars confirmed the presence of functional groups such as alcohol and amine which likely influenced the sorption of Pb and Cd by the biochars. An analysis of the adsorption mechanisms revealed that woodchar adsorption efficiency of Pb and Cd was higher. This can be directly related to the well-developed mesopores contained by the woodchar. This also implies that woodchar can be successfully used as a novell and feasible adsorbent for the clean-up of Pb and Cd contaminated soils due to anthropogenic activities. The use of woodchar as an amendment is a promising technique to immobilize Pb in Pb-contaminated soils. Biochar made from plant sources should be used for effective remediation of contaminated soils.

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