

Adsorption Isotherm Studies of Cd(II) and Pb(II) ions from Aqueous Solutions by Bamboo-Based Activated Charcoal and Bamboo Dust.

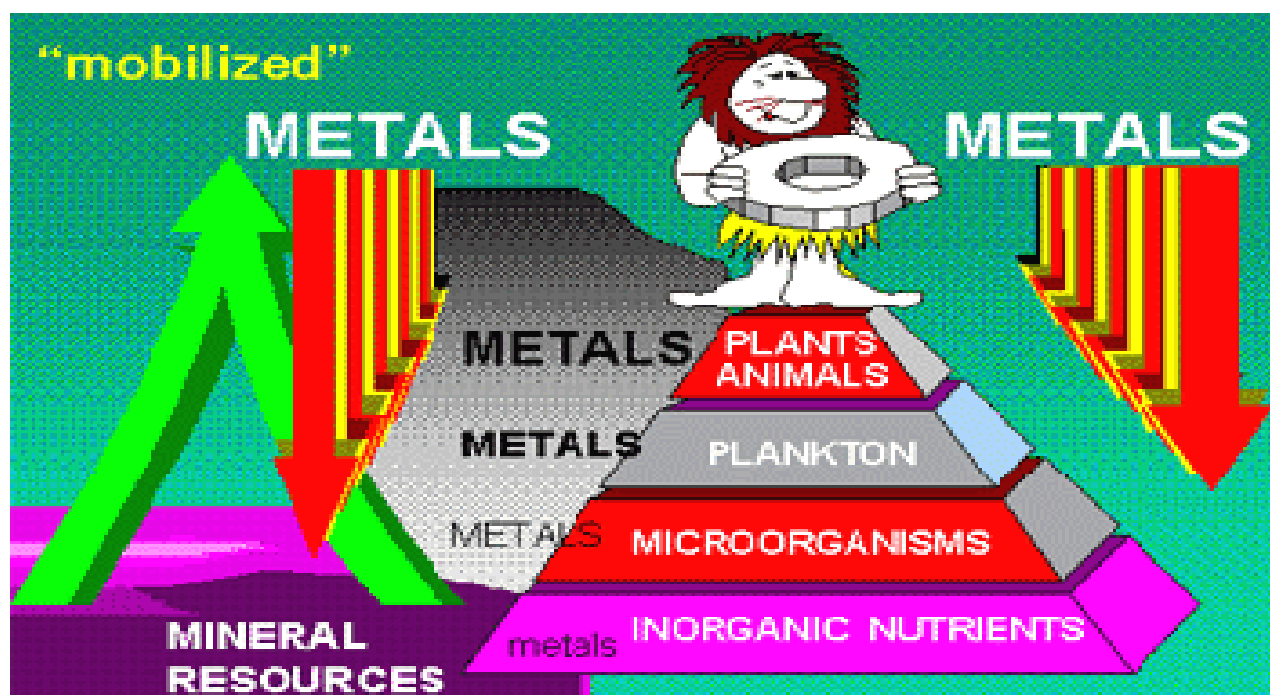
Abstract

This study investigates a comparative assessment of two adsorbents: Bamboo-based Activated Charcoal (BBAC) and Bamboo dust (BD) in the removal of lead(II) and cadmium(II) ions from aqueous solutions. Maximum Pb(II) and Cd(II) removal was observed at pH 6.0. The Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models were applied to the adsorption data. The coefficients of determination of the four models were high with Freundlich model providing the best description for the experimental adsorption data. The fitting of the adsorption data into Freundlich model shows that the mode of adsorption of the metal ions by both adsorbents follows physisorption. Investigation into the maximum adsorption capacity showed that Pb(II) was better adsorbed than Cd(II) on both adsorbents. Maximum adsorption capacities corresponding to monolayer coverage, obtained from the Langmuir plots were 4.792 mg g⁻¹ and 4.594 mg g⁻¹ respectively for Pb(II) and Cd(II) ions onto the BBAC and 4.771 mg g⁻¹ and 4.400 mg g⁻¹ for their adsorption onto BD. The Langmuir adsorption coefficient, K_L which is related to the affinity of the adsorbents for the metal ions were 0.699 and 0.271 respectively for adsorption of Pb(II) and Cd(II) ions onto BBAC and 0.299 and 0.226 for adsorption onto BD following the initial order. The carbonized bamboo based adsorbent was generally found to have an increased adsorption capacity for the metal ions than bamboo dust.

Keywords- Adsorption, bamboo-based activated charcoal, bamboo dust, biosorbents, adsorption isotherms.

Introduction

It is a well known fact that dissolved heavy metals escaping into the environment pose serious health hazards to humans and other animals. They accumulate in living tissues throughout the food chain, which has humans at its top and hence there is the need for controlling heavy metal emissions into the environment. Awareness of the environmental problems are now focussed on: Regulations for metal discharges, which are now strictly enforced in industrialized nations; identification of the toxic and carcinogenic nature of these heavy metals and their dangerous impacts on the environment; investigations into the current technologies for removal of heavy metals from industrial effluents, which often create secondary problems with metal-bearing sludges (Tchuifon *et al.*, 2014; Song *et al.*, 2014; Hossain and Rahman, 2012; Veglio and Beolchini, 1997). The figure below shows the route through which these heavy metals accumulate in living organisms.



The food-chain pyramid receives metals through man's activities and on top of the pyramid, man receives pre-concentrated metal toxicity.

The methods commonly used to remove toxic heavy metals from municipal and industrial wastewater are based on the adsorption of ions onto insoluble compounds and the separation of the sediments formed. Physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies have been widely employed to remove heavy metal ions from industrial effluents. These conventional methods in use have several disadvantages such as unpredictable metal ion removal, high reagent requirements and formation of sludge and its disposal, in addition to high installation and operational costs (Kehinde *et al.* 2009; Deepa *et al.*, 2006; Argun and Dursun, 2006). Adsorption has advantages over these other methods because of its simple design, sludge-free and low investment in terms of initial cost (Viraraghavan and Dronamraju, 1993). Activated carbon has been recognized as a highly effective adsorbent for the removal of heavy metals in wastewater (Reed and Arunachalam, 1994). However, it is relatively expensive to produce and there is increasing research interest in sourcing for alternative low-cost adsorbents. The search for cheaper and readily available adsorbents for removal of these toxic metals from wastewaters has directed attention to biosorption involving materials of natural origin. This is based on the various chemical functional groups present in the various biological materials. Biosorption in its simplest meaning is the ability of biological materials such as plant biomass, microorganisms (alive or dead) or their derivatives to accumulate or sequester heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. The transfer of metal ions from aqueous to solid biosorbent phase is through either passive, facilitated or active transport while mechanisms of uptake could be physical adsorption, chemical complexation with microbial cell surface groups or bioaccumulation (Muraleedharan *et al.*, 1991). Algae, bacteria, fungi and yeasts have all been studied and proven to be potential metal biosorbents (Volesky, 1994; Vasudevan *et al.*, 2002; Hussein *et al.*, 2004; Cordero *et al.*, 2004; Khani *et al.*, 2006). A number of agricultural products and by-products have also been

assessed as potent biosorbents for metal removal (Okieimen *et al.*, 1991; Abia, *et al.*, 2003; Argun and Dursun, 2006; Sajidu *et al.*, 2006; Ong *et al.*, 2007; Argun *et al.*, 2007; Bansal *et al.*, 2009). The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency or competitive performance, metal selectivity, minimisation of chemical and/ or biological sludge, known process equipment, possibility of regeneration of biosorbent and recovery of metal (Onwu and Ogah, 2010).

This present study compares the potential of two adsorbents: Bamboo-based activated charcoal and Bamboo dust in the removal of two metal ions; Cd(II) and Pb(II) from aqueous solutions. The effect of metal ion concentration was investigated and the overall representation of maximum adsorption capacity of these metal ions by the different adsorbents is presented using different equilibrium adsorption isotherm models.

Materials and methods

The source of the adsorbents, which is a bamboo tree, was gotten from a building site at Umudike near the Michael Okpara University of Agriculture in Abia State. The waste bamboo materials were cut into small pieces, washed severally to remove external waste particles and then dried under the sun. It was divided into two parts; one part was ground to produce bamboo dust while the second part was carbonized.

Preparation of Activated Bamboo Dust

The bamboo dust (BD) was produced by crushing the waste bamboo material into small particle sizes using a manual blender and then performing sieve analysis using the sieve screen to obtain a sample size of 0.3 mm. Thereafter, 40 g of the sample size was soaked in excess of 0.5 M HNO₃ solution in a beaker, stirred for 30 min at a temperature of 30°C and then left undisturbed for 24 h. It was then filtered through a whatman filter paper and rinsed copiously with deionised water until a pH 7 was obtained. The adsorbent was finally dried in the oven at 105°C for 6 h. The essence of treatment of the adsorbent with 0.5 M HNO₃ solution was to remove any debris or soluble biomolecules that might interact with the metal ions during the adsorption process and to open-up the micropores of the adsorbent in readiness for the adsorption process. This is referred to as the chemical activation of the bamboo dust.

Carbonization and Activation of the waste Bamboo

The bamboo-based activated charcoal (BBAC) was first carbonized by heating to a temperature of 200 °C for 2 h in a Gallen Kamp muffle furnace and after which the charred product was allowed to cool to room temperature. The charred sample was ground and sieved and 40 g of the sample was activated by the activating agent HNO₃. This was carried out by mixing 50 mL of 0.5M HNO₃ with 40 g of the charred bamboo product in a 250 mL beaker for 30 min and then activated for 2 h at a temperature of 350°C. The activated sample was then cooled at room temperature, washed copiously with distilled-deionised water until a pH of 6.8 was obtained. Both adsorbents, bamboo dusts (BD) and bamboo-based activated charcoal (BBAC) were finally stored in different airtight plastic vessels and carefully labeled in readiness for the adsorption process.

Adsorbates Preparation

Stock solutions of 1000 mg L⁻¹ of each of the metal ions, cadmium and lead were prepared from their salts, Cd (NO₃)₂ and PbCl₂. From the stock solutions, working concentrations of 20 - 100 mg L⁻¹ of each of the metal ions were prepared by serial dilution. The effect of concentration on the adsorption of the metal ions was studied by transferring 50 mL of the different concentrations of the metal ions into different 250 mL conical flasks while maintaining the pH of the solutions at 6.0. Thereafter, 1.0 g of each of the adsorbents was weighed into the flasks, corked and labeled

and agitated in a rotary shaker for 2 h. The adsorbent mass of 1.0 g/L was chosen in accordance with previous work done by Ademiluyi and Ujile (2013) on Kinetics of batch adsorption of iron (II) ions from aqueous solution using activated carbon from Nigerian Bamboo. At the end of the adsorption process, the content of each flask was filtered, centrifuged and the residual metal ion concentrations (C_e) analyzed. The concentrations of the standards and the test solutions were confirmed using buck scientific Atomic Absorption Spectrophotometer (AAS) model 969 502369 v5.66. The pH of the adsorbate solutions was kept at 6.0 using JENWAY pH meter model 3310. The amount of the metal ions adsorbed was calculated by difference. The analysis was carried out in triplicates and mean residual concentration analyzed. The amount of metal ions adsorbed at equilibrium, q_e (mg/g) was determined using equation (1).

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (1)$$

The percentage of metal ions adsorbed (% R) was also computed using the expression:

$$\text{Percent adsorption: } \% R = \frac{C_0 - C_e}{100} \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/L), V is the volume of solution (L) and m the dry weight of the adsorbent (g).

Results and Discussion

Fourier transform infrared spectroscopy (FTIR) analysis

The FT-IR spectra of the two adsorbents BBAC and BD were performed in order to explore the surface characteristics of the biosorbents (Figures 1a and 1b). The spectra display a number of absorption peaks, indicating the possible functional groups present on these biosorbents that may be responsible for the removal of the two metal ions from aqueous solutions. The peak positions were observed at 3461.38, 1640.51, 1192.05 for BBAC and 3440.16, 1435. 1376.26, 1093.67, 1038.70, 930.68 and 1637.62 cm^{-1} for BD. The bands at 3461.38 cm^{-1} and 3440.16 cm^{-1} are due to N-H stretch (mainly primary and secondary amines) present on the adsorbents. The band observed at 1640.51 cm^{-1} is assigned to C = C bond (from alkenes), the bands at 1093.67 and 1192.05 cm^{-1} are assigned to C-O stretch (alcohols, ethers, acids, esters), 1637.63 cm^{-1} corresponds to N-H bend of amines and amides, 1038.70 cm^{-1} is due to C – H bend of $\text{CH}_2=\text{CH}_2$ - from vinyl groups. These peaks which correspond to different functional groups are possible sites for adsorption of these metal ions by the adsorbents. The peak intensities indicate that especially the OH groups, the C- O stretch of either alcohols, ethers, carboxylic acids or esters, the N – H stretch of the primary or secondary amines, N – H bend of the amine or amides and the C=C stretch of the alkenes may play a major role in the adsorption of Pb(II) and the Cd(II) ions from the aqueous solutions. These functional groups contain either π -electron which is electron-rich or lone pairs on nitrogen or oxygen, with which they can coordinate with the metal ions leading to their adsorption. Comparing Figs. 1a and 1b, we can conclude that some of these peaks are either absent or new ones detected. This may be due to surface variation resulting from the carbonization of the bamboo waste.

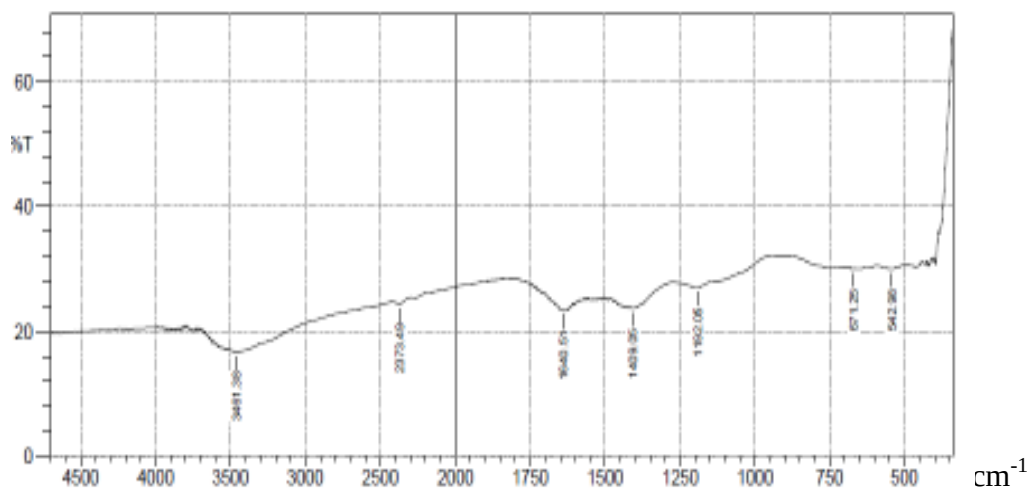


Fig. 1a. FT-IR spectrum of Bamboo-Based Activated Charcoal (BBAC)

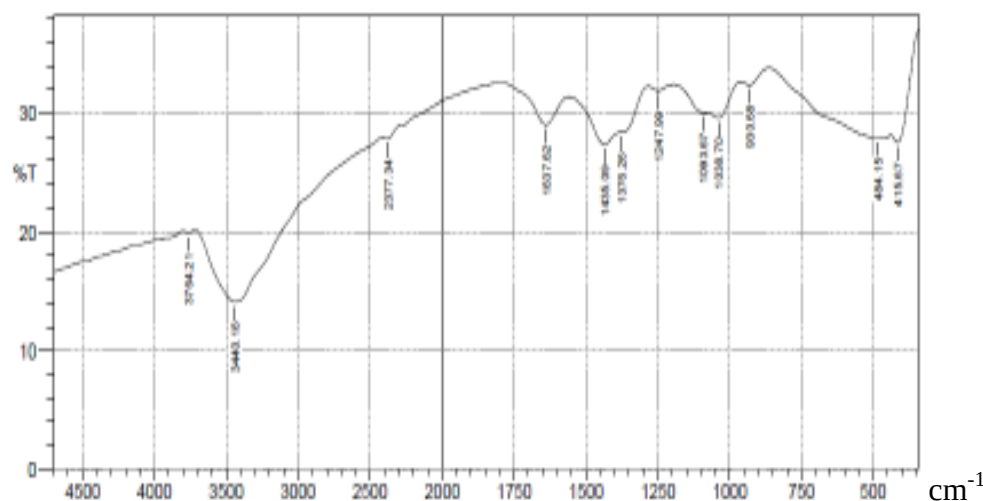


Fig. 1b. FT-IR spectrum of Bamboo Dust (BD)

Effect of pH

The influence of pH is of paramount importance in metal adsorption from aqueous solutions. The pH of a solution affects both adsorbent surface binding sites and the metal chemistry in solution. In this study, the influence of pH on the adsorption of Pb(II) and Cd(II) ions by both adsorbents was carried out in the pH range of 2.0-6.0 and the plots shown in Figures 2 and 3. No further studies were carried out beyond pH 6.0 to avoid precipitation of Cd(II) and Pb(II) as hydroxides. Results obtained revealed that maximum adsorption of Pb(II) and Cd(II) on both adsorbents occurred at pH 6.0. It can be inferred that at low pH values, the metal ions and the hydroxonium ions compete for active sites on the adsorbent surface which results in lower uptake of the metals. Previous researchers had suggested that at highly acidic condition, the adsorbent surface ligands would be closely associated with oxonium (H_3O^+) ions which may hinder the access of the metal ions to the ligands as a result of repulsive forces (Bansal *et al.*, 2009; Oformaja *et al.*, 2005; Low *et al.*, 1995). It could therefore be explained in this case that with increase in pH values, more and more ligands would be exposed which will result in attraction of positively charged metal ions.

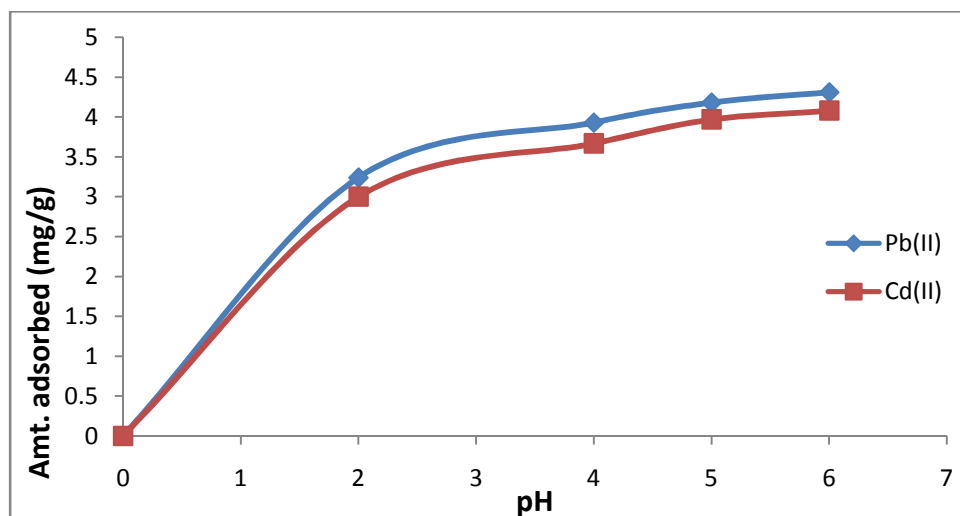


Figure 2 Effect of pH on Pb(II) and Cd(II) adsorption onto BBAC

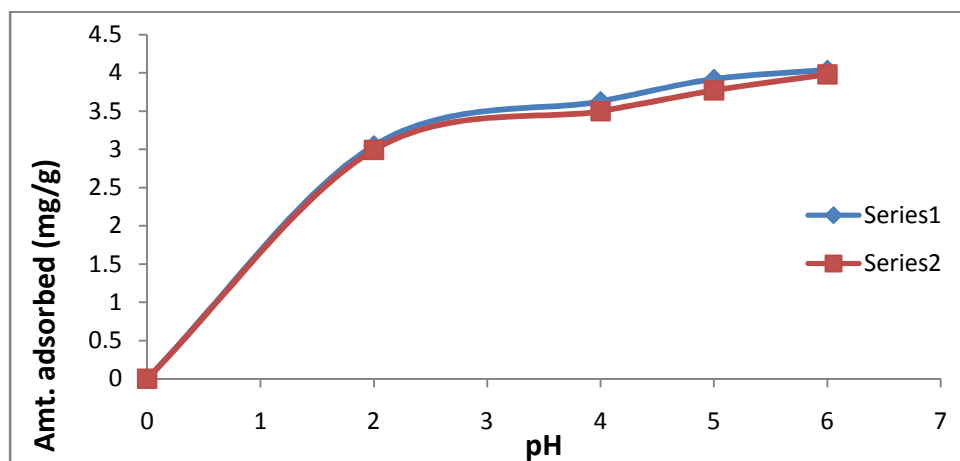


Figure 3 Effect of pH on Pb(II) and Cd(II) adsorption onto BD.

Effect of initial metal ion concentrations

Figures 4 and 5 show that the adsorption of the metal ions increased with increase in metal ion concentration. Assessment of level of metal ion uptake shows that Pb(II) ions were slightly better adsorbed than Cd(II) ions on both adsorbents. The non-flattening of the curves at the highest initial concentration of 100 mg L^{-1} employed in our study shows the incomplete coverage of the available adsorption sites on the adsorbents by the metal ions. The increased adsorption with increasing initial concentration is further confirmed by the distribution coefficients (Table 1), which expresses the concentration of the metal ions in the adsorbent phase divided by the concentration in the continuous phase. It expresses the relative effectiveness of the adsorbents in binding the metal ions. It is observed from Table 1, that for the initial metal ion concentrations used, the distribution coefficients were all greater than unity showing an uptake of more than 50%. The distribution coefficient generally decreased as the initial concentration of metal ions increased.

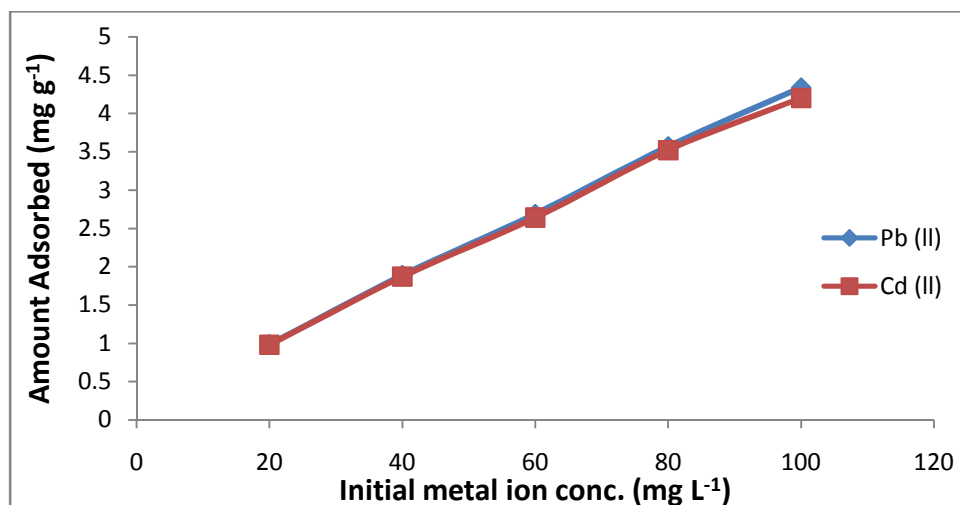


Fig.4 Plot of sorption capacity vs initial concentration for adsorption of the metal ions onto Bamboo-based activated charcoal

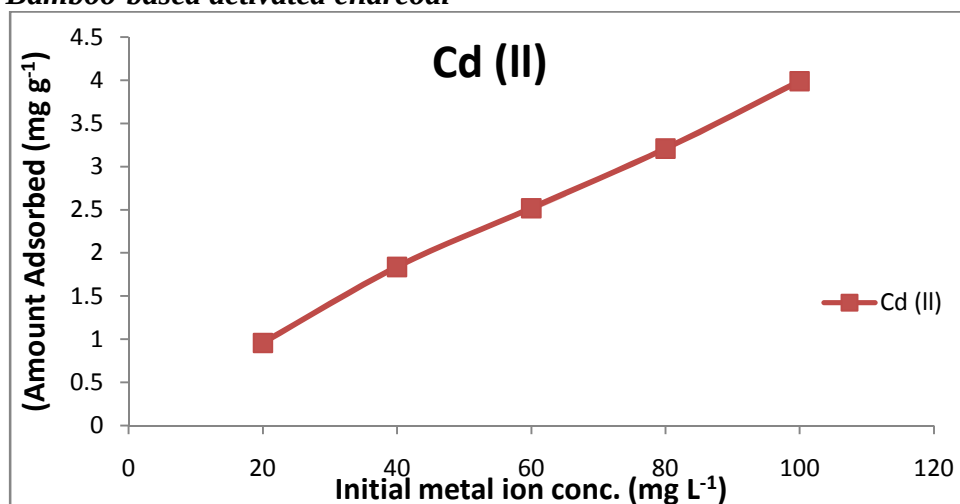


Fig.5 Plot of sorption capacity vs initial concentration for adsorption of the metal ions onto Bamboo dust

Table 1 Distribution coefficients for adsorption of the metal ions

Initial Conc. (C_0) (mg L ⁻¹)	BBAC		BD	
	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺
20	89.91	51.63	43.44	26.78
40	17.96	14.94	12.61	11.38
60	8.80	7.38	6.71	5.26
80	8.30	7.30	5.90	4.04
100	6.62	5.23	4.26	3.95

Again, it is observed that Pb(II), which has a larger density and a higher ionic radius (Table 2) was better adsorbed than Cd(II). This trend may be explained by the fact that metal ions form

aquo complexes when dissolved in water (Abia et al., 2002). The aquo complex is of the form $[M(H_2O)_x]^{n+}$, where M denotes the metal ion, n^+ the net charge on the complex and x the coordination number. The relative uptake levels of the two metal ions are nearly inversely dependent on their hydration energies (values shown in Table 2). Cd^{2+} with ionic radius of 0.097nm has hydration energy of $-1806 \text{ kJ mol}^{-1}$ while Pb^{2+} with ionic radius of 0.12nm has hydration energy of $-1480 \text{ kJ mol}^{-1}$. Since the displacement of water molecules from the aquo ion is the basis of adsorption dynamics, the stability of the aquo ion is expected to play a major role in the adsorption process. The aquo ion stability, as can be observed from the hydration energies of the metal ions is found to be dependent on the size of the ion. It is observed here that an ion with a relatively large size (and low hydration energy) will attach less strongly to the water molecules than an ion with a smaller size (and of course relatively higher hydration energy). This suggests that an ion with a large size will interact better with the adsorbents than that with small size since it is easier for them to discharge the water molecules formed in the aquo complex. This may have contributed to the greater adsorption of Pb(II) ions than Cd(II) ions.

Table 2: Some Physical and Chemical properties of these metal ions

Element	^a Stable oxidation states	^a Density g/cm^3 (25 ^o C)	^a Ionic radii (Å)	^b Hydration energy (ΔH) kJmol^{-1}	^b 1 st hydrolysis constant pka
Cadmium	+2	8.65	0.97	-1806	10.0
Lead	+2, +4	11.34	1.20	-1480	7.7

(^aLiptrot, 1983; ^bGreenwood and Earnshaw, 1993)

However, the actual percentage adsorption of the metal ions from solution was observed to decrease with increase in initial metal ion concentration for both adsorbents (Figures 6 and 7). This is as a result of the fact that at lower metal ion concentrations, almost all the metal ions were adsorbed but at higher initial concentrations, it is expected that the ratio of amounts of the metal ions to the available surface active sites is high; hence fractional adsorption becomes strongly dependent on initial concentration. At a given dose (mass) of the adsorbents, the total available adsorption sites are limited thereby adsorbing almost the same amount of metal ions, resulting in a decrease in removal efficiencies of the metal ions by the adsorbents.

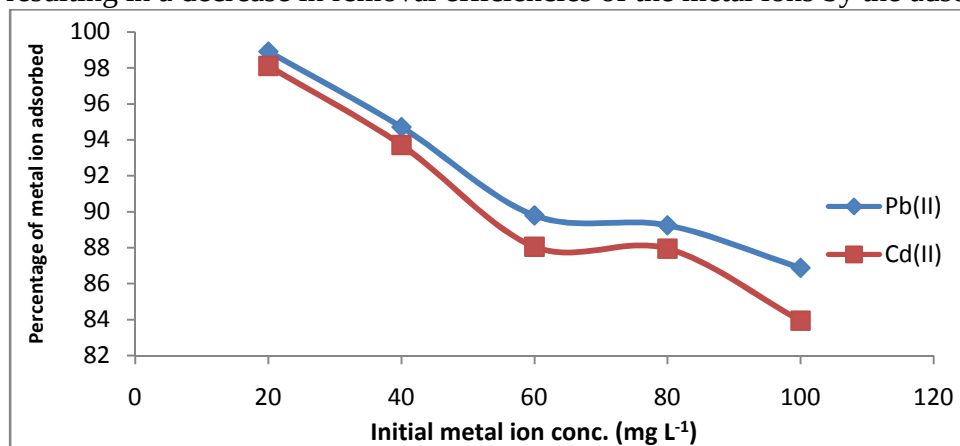


Fig. 6 Plot of percentage metal adsorbed vs initial conc. for adsorption of the metal ions on BBAC

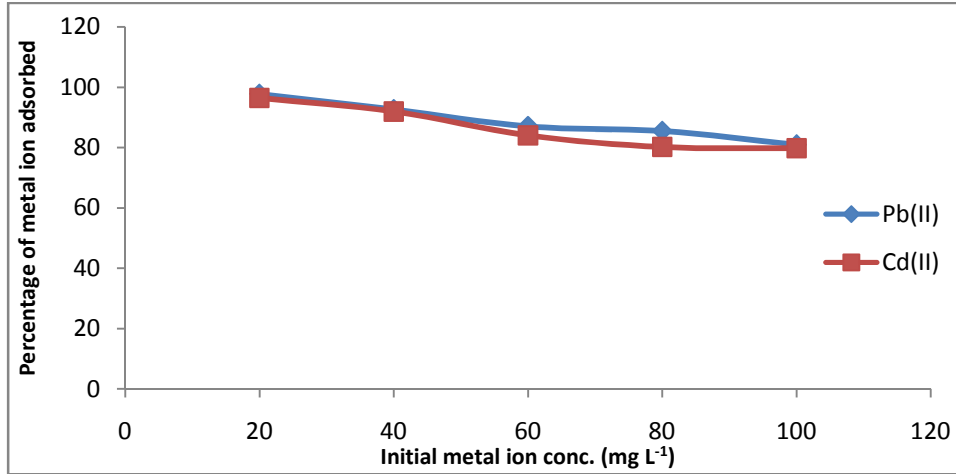


Fig. 7 Plot of percentage metal adsorbed vs initial conc. for adsorption of the metal ions on BD

Adsorption Isotherms

The adsorption equilibrium is usually assessed by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent, at a fixed temperature and pH (Ho *et al.*, 2002).

Adsorption equilibrium is established when the concentration a metal ion in a bulk solution (C_e) is in dynamic balance with that at the interface. The metal ion uptake capacities in our study were evaluated using the Langmuir, Freundlich, Temkin and Dubinin – Radushkevich isotherm models and are hereby stated.

The Equilibrium Langmuir Isotherm

The Langmuir isotherm represents the equilibrium distribution of metal ions between the solid and liquid phases.

The Langmuir isotherm is based on the following assumptions:

- * Metal ions are chemically adsorbed at a fixed number of well-defined sites;
- * each site can hold only one ion (restricted to only monolayer coverage).
- * all sites are thermodynamically equivalent and
- * there is no lateral interaction between the adsorbed metal ions.

The linearized Langmuir isotherm equation allows for the evaluation of the maximum adsorption capacity ($q_{\max}$) corresponding to monolayer coverage and the Langmuir constant K_L , which expresses the intensity of the adsorption process and is given as (Song *et al.*, 2014):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (3)$$

Where C_e is the equilibrium or residual concentration after adsorption (mg L⁻¹), q_e is the equilibrium adsorption capacity (mg g⁻¹), $q_{\max}$ is the maximum adsorption capacity (mg g⁻¹) corresponding to monolayer coverage, K_L is the Langmuir adsorption constant. The linear plots of C_e/q_e vs C_e showed that adsorption process follows the Langmuir adsorption isotherm (Figures 8 and 9).

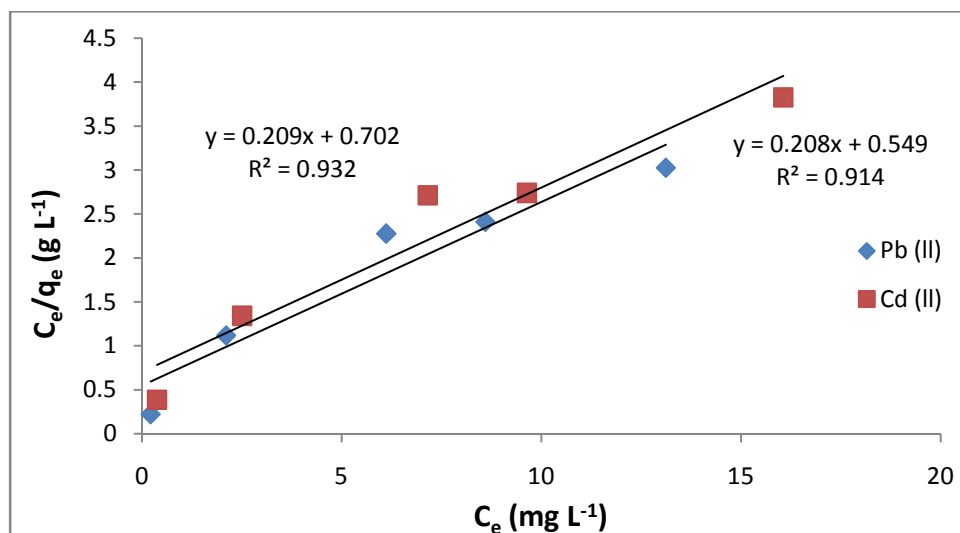


Fig. 8 Langmuir isotherm plot of C_e/q_e vs C_e for adsorption of the metal ions on the Bamboo-Based Activated Charcoal

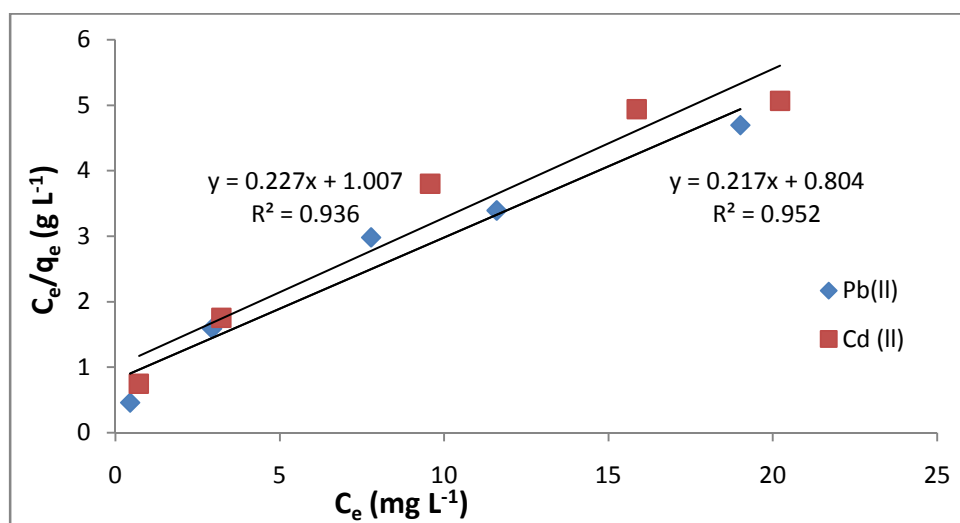


Fig. 9 Langmuir isotherm plot of C_e/q_e vs C_e for adsorption of the metal ions on the Bamboo Dust

The Langmuir constants K_L and $q_{\max}$, and R^2 values are shown in Table 3. The correlation coefficients (R^2 values) > 0.90 for all the metal ions showed that the Langmuir Isotherm gave a good interpretation for the adsorption data. The Langmuir constants, $q_{\max}$ and K_L were determined from the slope and intercept of the linear plots. The Langmuir capacity corresponding to monolayer coverage, $q_{\max}$ is normally used to compare the efficiencies of adsorbents with other materials, which have been tested as biosorbents for the metal ions in the chemical literature. Table 4 is a summary of heavy metal adsorption capacities (mg g^{-1}) of some common adsorbents in comparison with the bamboo dust and its activated form used in our study. The differences in the adsorption capacities of the different adsorbents could result from the type of functional groups present on the biosorbents, which may have different affinities for metal ions and the variations in the particle size of the adsorbents which usually affect their surface area as well as the porosity of the adsorbents. The adsorption capacities (mg g^{-1}) of 4.42

and 4.16 for Pb^{2+} and Cd^{2+} by the bamboo dust and 4.67 and 4.57 respectively for the metal ions by the bamboo-based activated charcoal in our study in comparison with some other adsorbents presented in the literature as shown in Table 4, shows that the bamboo wastes are good adsorbents for the removal of these metal ions from aqueous solutions. The results from our study further show that Pb^{2+} was better adsorbed than Cd^{2+} on both surfaces.

The Langmuir adsorption coefficient K_L , for the metal ions were high and the high K_L values indicate a high affinity of the adsorbents for the metal ions and equally represents a steep beginning of the isotherm for the metal ions (Ho and McKay, 1999).

The essential characteristics of the Langmuir isotherms are also expressed in terms of a dimensionless quantity called separation factor (or equilibrium parameter) R_L , defined as: (Webber and Chakravarti, 1974; Gupta and Bhattacharyya, 2006)).

$$R_L = \frac{1}{(1 + K_L C_o)}. \quad (4)$$

Where C_o is the initial metal ion concentration and K_L , the Langmuir constant. According to McKay *et al.* (1982) and Horsfall *et al.* (2004), the separation factor (R_L value) indicates the shapes of the isotherm, *i.e.*, $R_L > 1$ unfavourable isotherm, $R_L = 1$ linear isotherm, $R_L = 0$ irreversible isotherm and $0 < R_L < 1$ favourable Isotherm

The values of R_L obtained for the two metal ions, Cd (II) and Pb (II) on both adsorbents at initial concentration of 100 mg L^{-1} are all less than unity showing that the isotherm was favourable under the condition of our study and also indicated that the adsorbents could be good substrates for the metal ion removal.

Table 3. Langmuir Isotherm Constants

Constants	BBAC		BD	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
$q_{\max} (\text{mg g}^{-1})$	4.792	4.594	4.771	4.400
$K_L (\text{L mg}^{-1})$	0.699	0.271	0.299	0.226
R_L	0.026	0.036	0.032	0.042
R^2	0.9147	0.9520	0.9324	0.9363

Table 4. Comparison of heavy metal removal capacities (mg/g) by different adsorbents.

Adsorbent	Sources		
	Pb(II)	Cd(II)	
Unmodified rice husk and modified rice husk	-	8.82 11.03	Ong <i>et al.</i> , 2007
African white star apple shell	8.40	10.59	Anusiem <i>et al.</i> , 2010

Sphagnum moss peat	12.30	-	Ho and Mckay, 2000
Maple sawdust	3.19	-	Yu <i>et al.</i> , 2001
Activated carbon Sigma C-3014)	-	1.51	Ücer <i>et al.</i> , 2006.

Equilibrium Freundlich Isotherm

The Freundlich model was used to assess the adsorption intensity of the adsorbates (metal ions) towards the adsorbents. The linearized form of Freundlich adsorption isotherm is represented as (Malkoc and Nuhoglu, 2007):

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (5)$$

Where K_F and n are Freundlich constants describing both the intensity and capacity of the adsorption process, respectively. Figures 10 and 11 are linear plots of $\ln q_e$ vs $\ln C_e$ according to Freundlich isotherm equation. The Freundlich parameters, K_F and $1/n$ were calculated from the intercept and slope of the linear plots and are presented in Table 5. K_F values show the ease of adsorption and separation of the heavy metals from aqueous solutions. The values of the exponent, n , which explain the distribution of bonded metal ions on the adsorbent surfaces, gives an indication of the favourability and capacity of the adsorption process. Anusiem *et al.* (2010) had reported that 'n' values between 1 and 10 represent favourable adsorption conditions. In all cases reported here, the range of the exponent was between 2.486 and 2.843, showing beneficial adsorption for the system. According to Anusiem *et al.* (2010), the fit of experimental adsorption data to Freundlich model indicates that the forces of adsorption by the adsorbents are governed by physisorption. The R^2 values are high for adsorption of the metal ions on the sorbents and this shows that the isotherm gives a good interpretation of the adsorption behaviour of the metal ions.

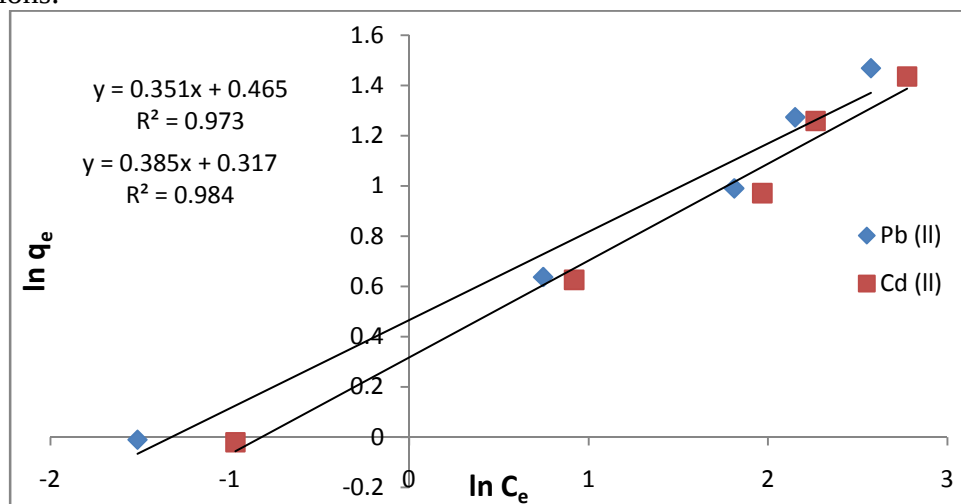


Fig. 10 Freundlich isotherm plot of $\ln q_e$ vs $\ln C_e$ for adsorption of the metal ions onto Bamboo-Based Activated Charcoal

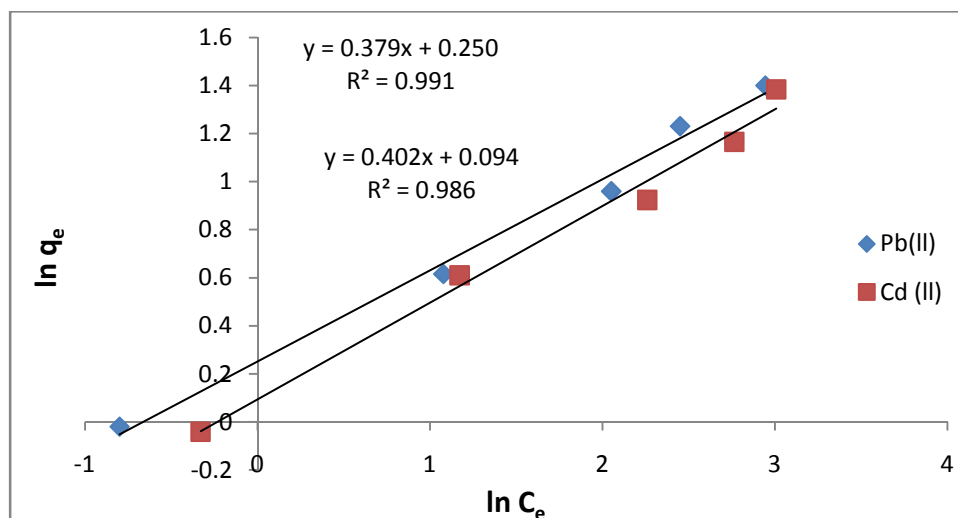


Fig. 11 Freundlich isotherm plot of $\ln q_e$ vs $\ln C_e$ for adsorption of the metal ions onto Bamboo Dust

Table 5: Freundlich Isotherm Constants

Constants	BBAC		BD	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
K_F	1.593	1.285	1.373	1.099
$1/n$	0.352	0.379	0.386	0.402
n	2.843	2.638	2.593	2.486
R^2	0.9734	0.9910	0.9840	0.9868

The equilibrium Temkin Isotherm

The Temkin isotherm describes the characteristic adsorption potential of the adsorbents for the adsorbates. The derivation of the Temkin isotherm assumes that the fall in the heat of adsorption is linear rather than logarithmic, as implied in the Freundlich equation. The linearized form of the isotherm model is given as (Song *et al.*, 2014):

$$q_e = \frac{RT}{b_T} \ln k_T + \frac{RT}{b_T} \ln C_e \quad (6)$$

Where q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount adsorbed at equilibrium and the equilibrium concentration, respectively, T is the absolute temperature in K and R is the universal gas constant, $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$. According to Akkaya and Ozer, (2005) and Pearce *et al.* (2003), the constant b is related to the heat of adsorption. A linear plot of adsorption capacity, q_e vs $\ln C_e$ describes the isotherm for the adsorption of the metal ions (Figures 12 and 13). The Temkin constants b_T and k_T were determined from the slope and intercept of the linear plots and their values displayed in Table 6. Assessment of the values of coefficient of determination (R^2) showed that Temkin isotherm is another good model for the description of the adsorption of the

metal ions on the adsorbents. Their R^2 values are all high but lower than those of Freundlich and Langmuir isotherm models.

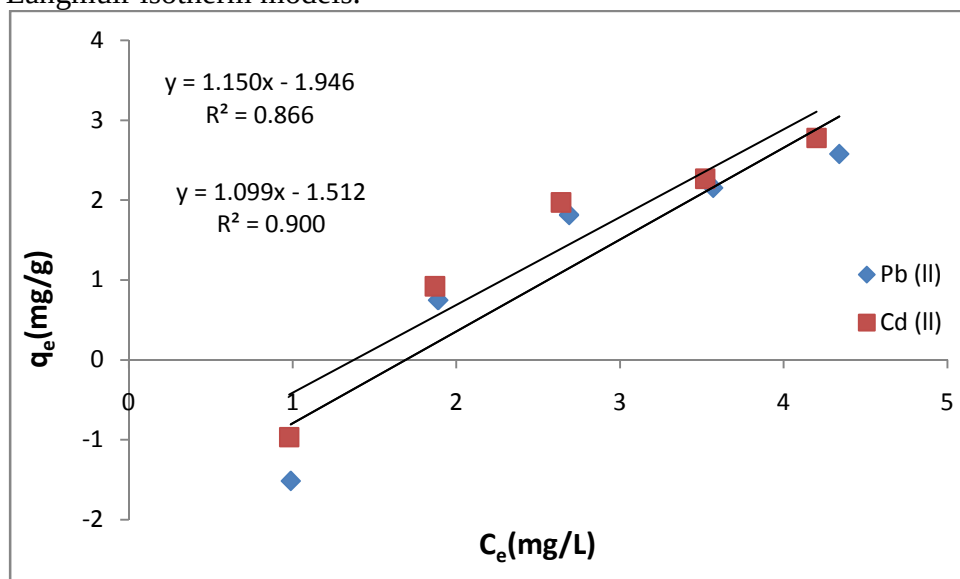


Fig. 12 Temkin isotherm plot of q_e vs $\ln C_e$ for adsorption of the metal ions onto Bamboo-Based Activated Charcoal

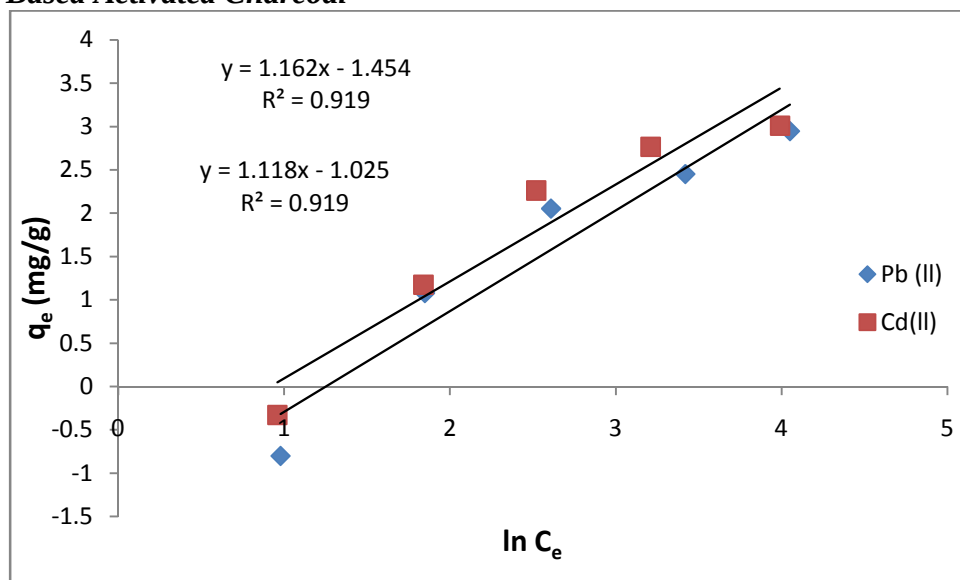


Fig. 13 Temkin isotherm plot of q_e vs $\ln C_e$ for adsorption of the metal ions onto Bamboo dust

Table 6. Temkin Isotherm Constants

Constants	BBAC		BD	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
K_T	5.435	3.498	3.956	2.502
b_T (kJ/mol)	21.63	21.41	22.62	22.25

R^2	0.8665	0.9196	0.9003	0.9196
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Dubinin-Radushkevich (D-R) Isotherm model

To predict the mode of adsorption (*i.e.*, physical or chemical), the mean free energy of adsorption was calculated by the Dubinin-Radushkevich (D-R) isotherm equation and is expressed as (Ho *et al.*, 2002):

$$\ln(q_e) = \ln Q_{DR} - K_{DR} \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2 \quad (7)$$

Where q_e (mg g⁻¹) is the amount of metal ions adsorbed, Q_{DR} is the theoretical saturation capacity (mg g⁻¹), K_{DR} (mol²/kJ²) is the Dubinin-Radushkevich isotherm constant, C_e (mg L⁻¹) is the equilibrium concentration of metal ions, R is the gas constant (8.314 J/mol K) and T (K) is absolute temperature in Kelvin. The Dubinin-Radushkevich (D-R) isotherm constant, K_{DR} , is related to the mean free energy of adsorption, E_D (kJ/mol) and can be computed using the following expression (Horsfall *et al.*, 2004):

$$E_D = \frac{1}{\sqrt{2K_{DR}}} \quad (8)$$

The linear plots obtained (Figures 14 and 15) show weak or low fitting of the isotherm to the experimental adsorption data. The Dubinin-Radushkevich (D-R) isotherm parameters, K_{DR} and Q_{DR} were calculated from the slope and intercept of the linear plots of $\ln q_e$ vs $[RT \ln (1+1/C_e)]^2$ and summarized in Table 7. Examination of the data shows that the Dubinin-Radushkevich isotherm does not provide an accurate description of the data for the metal ions over the range of concentrations studied.

As summarized in Table 7, it can be observed that the values of linear regression coefficient (R^2) are in the range of 0.5559 – 0.6085, revealing that the experimental data did not fit perfectly well into the Dubinin-Radushkevich (D-R) isotherm model.

The constant K_{DR} gives an idea of the mean energy, E_D (kJ mol⁻¹) of adsorption per mole of the adsorbate as it is transferred to the surface of the solid from infinite distance in the solution. Singha and Das (2013) and Ho *et al.* (2002) had reported that the magnitude of E_D provides an information on the nature of the adsorption process, *i.e.* whether it is chemical or physical, with values in the range $E_D = 1 - 8$ kJ mol⁻¹ indicating physical adsorption and in the range 9 – 16 kJ mol⁻¹ to chemisorption. The calculated mean free energy, E_D values were found to be less than 8 kJ mol⁻¹ as indicated by our results (Table 7), showing that the adsorption process of the metal ions in our study by the adsorbents followed physical adsorption.

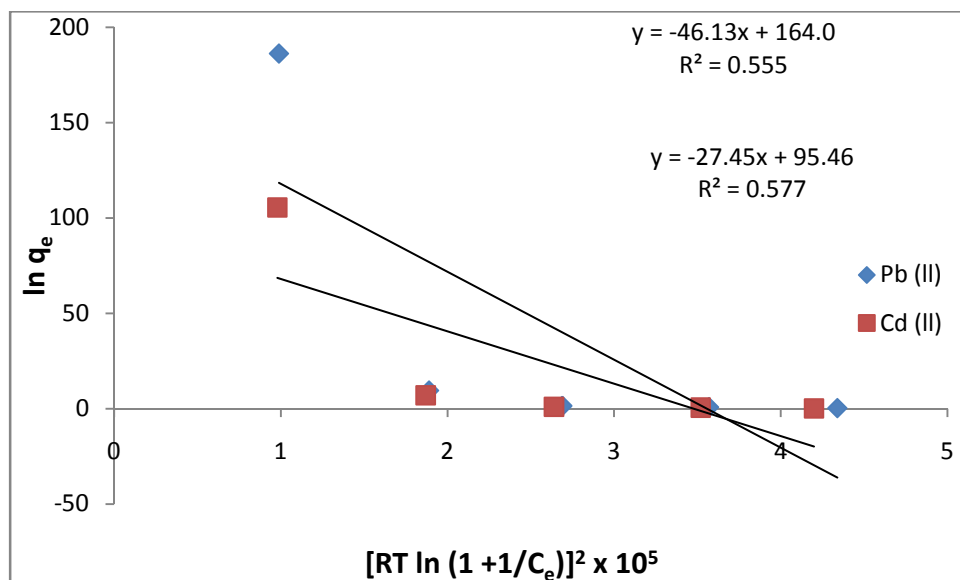


Fig. 14 Dubinin-Radushkevich isotherm plot of $\ln q_e$ vs $[RT \ln (1+1/C_e)]^2$ for adsorption of the metal ions onto Bamboo-Based Activated Charcoal

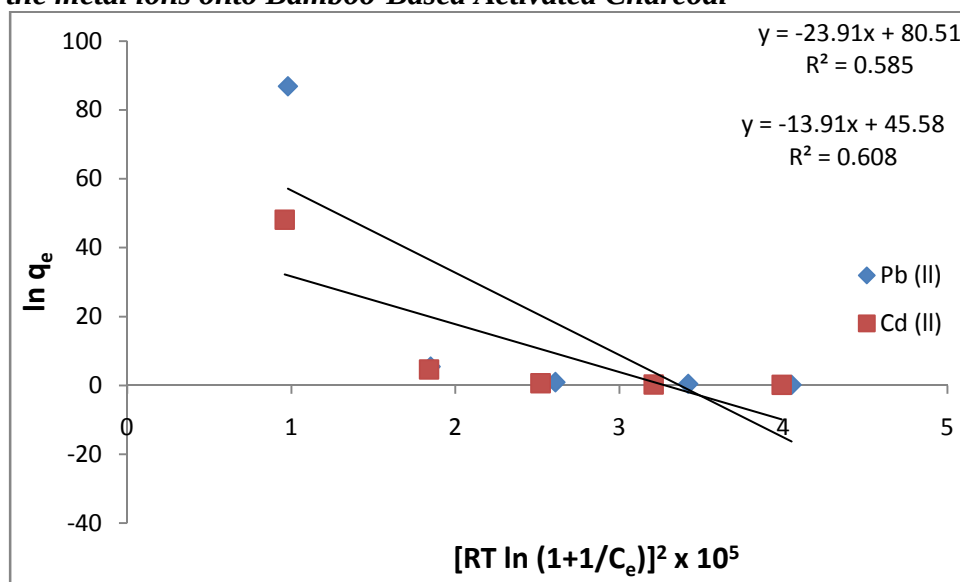


Fig. 15 Dubinin-Radushkevich isotherm plot of $\ln q_e$ vs $[RT \ln (1+1/C_e)]^2$ for adsorption of the metal ions onto Bamboo Dust

Table 7: Dubinin-Radushkevich Isotherm Constants

Constants	BBAC		BD	
	Pb(II)	Cd(II)	Pb(II)	Cd(II)
$Q_{DR} (mg g^{-1})$	1.727×10^{71}	2.886×10^{41}	9.254×10^{34}	6.271×10^{19}
$K_{DR} (mol^2 KJ^{-2})$	4.613×10^6	2.746×10^6	2.391×10^6	1.391×10^6

E (kJ mol ⁻¹)	3.292 X 10 ⁻⁴	4.267 X 10 ⁻⁴	4.573 X 10 ⁻⁴	5.995 X 10 ⁻⁴
R ²	0.5559	0.5771	0.5859	0.6085

Analysis of the adsorption data using R² values of the four isotherm models revealed that Langmuir and Freundlich isotherm models provided the best description for the adsorption data under the conditions of the study, followed by Temkin and lastly Dubinin-Radushkevich model. The fit of the data into Freundlich model suggests that the forces of adsorption follow physical mode. The energy values obtained from Dubinin-radushkevich Isotherm were all less than 8.00 kJmol⁻¹, indicating that the adsorption process was physisorption.

Analysis of Coefficient of Determination of the Isotherms

Coefficient of determination (R²) is a regression analysis that describes the relationship between the variables employed for the evaluation of the kinetic and thermodynamic parameters for an adsorption process. In this present study, the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models, which are applied for the data analysis in this work are all equations of the form $y = mx + c$ (where m is slope and c is intercept), showing that y and x values must display certain degree of linear relationship for the equations to be useful for prediction.

R² is a measure of the variation in y values that is explained by the linear relationship with x (the regression line). If R² value equals zero, it means the two variables are not related, but if R² value is one, then the variables are perfectly related, hence, R² values between zero and one were used for the assessment of the experimental data. The coefficients of determinations of the four isotherm models: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms were compared and R² values that are closest to unity were considered as the best fitting models. For this study, the Freundlich isotherm gave the best description of the adsorption process for the two metal ions followed by the Langmuir isotherm, while Temkin and Dubinin-Radushkevich gave fairly good interpretation for the adsorption process.

Conclusion

This study has shown that the adsorbents, Bamboo-based activated charcoal and Bamboo dust can adsorb Cd(II) and Pb(II) ions from aqueous solutions. In this present investigation, effects of pH and metal ion concentration on the adsorption of the metal ions was reported and results obtained showed an increase in adsorption capacity with increase in metal ion concentrations. Maximum Pb(II) and Ni(II) was observed at pH 6.0. The experimental data was analysed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The R² values of the four models were high, with Freundlich giving best fit for the experimental data, followed by Langmuir isotherm while Temkin and Dubinin-Radushkevich models gave fairly good description for the adsorption data. The adsorbents were found to have better affinity for Pb(II) than Cd(II) and BBAC showed better removal for the metal ions than BD. The adsorption process was found to be a physisorption process as seen from the apparent energy of adsorption calculated from the Dubinin-Radushkevich model. The energy values were all less than 8 kJ mol⁻¹. The conclusion from this study is that BBAC and BD could be good adsorbents for the removal of heavy metal ions from aqueous solutions and may possibly be useful for treating industrial wastewaters.

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