Copper (II), Cadmium (II) and Lead (II) Adsorption Kinetics from Aqueous Metal Solutions Using Chemically Modified and Unmodified Cocoa Pod Husk (*Theobroma cacao*) Waste Biomass

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Abstract: The use of thiolated and unmodified cocoa pod husk for the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} ions from aqueous solution was studied in this study with respect to adsorption capacity and kinetic studies. Adsorption capacity was rapid as appreciable level of metal ions uptake was achieved at contact time of 10 min and increase in adsorption capacity occurred between 10 and 60 min. Results further showed maximum adsorption capacity of the adsorbents as 97.6057 mg g^{-1} (Cu^{2+}), 98.8860 mg g^{-1} (Cd^{2+}) and 99.9454 mg g^{-1} (Pb^{2+}) by the Unmodified Cocoa Pod Husk (UCPH). The trend of the sorption capacity was found to be $Pb^{2+}>Cd^{2+}>Cu^{2+}$ for both unmodified and modified adsorbents. Thiolation modification decreased the adsorption capacity of the adsorbent. Pseudo second-order kinetic model favoured the adsorption process with $R^2 = 1$ thus giving a better fit than the Pseudo first-order model. Intraparticle diffusion model by Weber and Morris gave a better fit with highest R^2 value of 0.9724 and confirmed particle diffusion as the predominant mechanism for the sorption process.

Key words: Adsorption, kinetics, heavy metal, cocoa pod husk, aqueous solution, modified

INTRODUCTION

Heavy metal pollution in the environment has become a serious threat today. Heavy metals are among the conservative pollutants that are not subject to bacterial attack or other breakdown or degradation process and are permanent additions to the aquatic environment (El-Nady and Atta, 1996). As a result of this their concentrations often exceed the permissible levels normally found in soil, water ways and sediments. Hence, they find their way up the food chain. When they accumulate in the environment and in food chains, they can profoundly disrupt biological processes.

Heavy metals such as copper, cadmium and lead are toxic even at low concentrations (United States Environmental Protection Agency, 1997). Copper has been reported as one of the most widely used heavy metal in electrical and electroplating industries (Igwe and Abia, 2006). Since copper is an essential metal in a number of enzymes for all forms of life, problems arise when it is deficient or in excess (Ho *et al.*, 2002). Excess copper accumulates in the liver, brain, skin, pancreas and myocardium (Davis *et al.*, 2000) and most toxic form of

copper is thought to be Cu^{2+}. The sources of human exposure to cadmium include atmospheric, terrestrial and aquatic routes (Wolnik *et al.*, 1985; Lopez *et al.*, 1994). The most severe form of cadmium toxicity in human is itai-itai, a disease characterized by excruciating pain in bone (Kasuya *et al.*, 1992; Yasuda *et al.*, 1995). Other health implications of Cd in humans include kidney malfunction, hepatic damage and hypertension (Klaassen, 2001).

Lead is a heavy metal poison which forms complexes with oxo-groups in enzymes to affect virtually all steps in the process of haemoglobin synthesis and porphyrin metabolism (Ademoroti, 1996). Toxic levels of lead in man have been associated with encephalopathy, seizures and mental retardation (Schumann, 1990). The removal and recovery of these metals have become very important because of these detrimental effects on the environment.

Conventional methods for removing these heavy metal ions from solution include chemical precipitation, electrolytic recovery, ion exchange/chelation and solvent extraction/liquid membrane separation (Rorrer, 1998). Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of the residual metal sludge. In recent years considerable

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attention has been devoted to the study of removal of heavy metal ions from solution by adsorption using agricultural by-products. Research in the use of agricultural by-products has included metal binding studies with cotton seed halls, rice straw and sugarcane bagasse (Marshall and Champagne, 1995) shea butter seed husk (Eromosele and Abare, 1998) cassava fibre (Egila and Okorie, 2002) wild cocoyam biomass (Horsfall and Spiff, 2005), maize cob and husk (Igwe *et al.*, 2005) sawdust, rice husk (Abdel-Ghani *et al.*, 2007), coconut fibre (Igwe *et al.*, 2005) to mention but a few. However, the use of these agricultural by-products has continued to attract more attention in recent years because they are cheap, simple, sludge free and involve small initial cost and land investment (Horsfall *et al.*, 2004). The present study undertakes on the kinetics of copper (II), cadmium (II) and lead (II) removal from aqueous metal solutions using unmodified and chemically modified cocoa pod husk (*Theobroma cacao*) waste biomass.

MATERIALS AND METHODS

All the reagents used were of analytical reagent grade and were used without further purification. Doubly distilled and deionized water was used in the preparation of all sample solutions. About 1000 mg L^{-1} stock solutions of copper (II) from Cu $(NO_3)_2$. About $6H_2O$, cadmium (II) from $CdCl_2$ and lead (II) from Pb $(NO_3)_2$ were prepared. From the stock solutions, working solutions of initial concentration (100 mg L^{-1}) of each metal were prepared by serial dilution.

Adsorbent preparation: The cocoa pod husks were obtained from a waste disposal site at the Cocoa Research Institute of Nigeria, Ibeku sub-station off Bende road, Umuahia, Abia State, Nigeria. The pod husks were cut into small pieces, air-dried and crushed/grounded into powdery forms using a manually-operated grinder. The meal obtained was dried further in the oven at 50°C. It was then removed after 12 h from the oven and screened or passed through a test-sieve shaker where different particle sizes of the adsorbent were obtained. The meal retained on 250 μm mesh was however used for the adsorption studies.

Activation of adsorbent: The screened (or sieved) cocoa pod husk (s) adsorbent (about 200 g) was further soaked in dilute nitric acid solution (HNO_3) of 2% V/V overnight (24 h) at room temperature. After 24 h duration the meal was then filtered through a Whatman No. 41 filter paper and rinsed with deionized water. The rinsed adsorbent was later air dried for about 12 h. The adsorbent was again dried in the oven at 105°C for about 6 h. The

adsorbent was then removed from the oven (after 6 h) and stored in an air-tight plastic vessel/container. This represented the unmodified adsorbent (UCPH) used for the adsorption studies. The treatment of the adsorbent with 2% V/V dilute HNO_3 solution aids the removal of any debris or soluble biomolecules that might interact with metal ions during sorption. This process is called chemical activation of the cocoa pod husk.

Chemical modification of adsorbent: About 100 g portion of the activated cocoa pod husk was weighed out of the 200 g activated adsorbent and was called Unmodified Cocoa Pod Husk (UCPH). The other 100 g portion was modified chemically by thiolation using the method reported by Okieimen and Okundaye thus was labeled MCPH i.e., Modified Cocoa Pod Husk. Specifically, the 100 g was dissolved or soaked in 1000 mL of 0.3 mol (0.3 M) thioglycollic acid for 24 h at 29°C. After 24 h duration, the mixture labeled MCPH (thiolated adsorbent) was filtered off using Whatman No. 41 filter paper washed and rinsed with distilled deionized water and then with methanol. It was rinsed again with deionized water and dried at 50°C for 12 h. The adsorbent (MCPH) was then stored in an air-tight plastic vessel/container.

Sorption studies: Sorption studies for copper (II), cadmium (II) and lead (II) were carried for each adsorbent (UCPH and MCPH) at pH 7.5, temperature 30°C, initial concentration 100 mg L^{-1}. About 50 mL of standard solutions of each metal was transferred into various 250 cm^3 Erlenmeyer flask corked and labeled. Then 1 g of each adsorbent was weighed into the different flasks and agitated in a shaker for the different contact times (10, 30, 60, 90 and 120 min).

After each agitation time, the content of each flask was then filtered using Whatman No. 41 filter paper and filtrates collected into various labeled sample bottles. The residual (equilibrium) concentration of the filtrate of each metal solution was analyzed using UNICAM 969 solar Atomic Absorption Spectrophotometer (AAS).

Data analysis: The amount of Cu^{2+}, Cd^{2+} and Pb^{2+} adsorbed (q_e) in mg g^{-1} from each metal solution by the various adsorbents at contact time t was computed by using the following simplified mass balance equation expressed as:

$$q_e = C_o - C_e \qquad (1)$$

Where:
q_e = Amount adsorbed (mg g^{-1}) by the adsorbent at equilibrium or metal concentration on adsorbent at equilibrium
C_e = Metal ion concentration (mg L^{-1}) of the filtrate at equilibrium
C_o = The initial metal ion concentration (mg L^{-1}) used

RESULTS AND DISCUSSION

Sorption capacity: The values of amount of Cu^{2+}, Cd^{2+} and Pb^{2+} ions adsorbed by the Unmodified and Modified Cocoa Pod Husk (UCPH and MCPH) calculated through Eq. 1 have been used to plot Fig. 1 and 2. Figure 1 shows the plot of amount adsorbed versus contact time for adsorption of Cu^{2+}, Cd^{2+} and Pb^{2+} by the Unmodified Cocoa Pod Husk (UCPH). From the plot it can be seen that the amount adsorbed increased with contact time for Unmodified Cocoa Pod Husk (UCPH). However, there was a slight drop in the amount adsorbed from 90-120 min for the three metal ions hence the trend of sorption capacities remained fairly constant and almost close to each other as time increased.

Figure 2 shows the plot of amount adsorbed versus contact time by the Modified Cocoa Pod Husk (MCPH). From Fig. 2 there was significant drop in sorption capacity of Cu^{2+} ions by modified cocoa pod husk at 30 min. Subsequently, a slight increase was noticed from contact time 60-90 min and a slight drop at 120 min.

Amount of Cd^{2+} adsorbed by the MCPH maintained regular increase from 10-90 min but dropped slightly at 120 min. Amount of Pb^{2+} ions adsorbed by the MCPH increased slightly from 10-90 min and dropped slightly at 120 min.

Generally, optimum adsorption capacity was exhibited by the adsorbents at the least contact time of 10 min. This means that it was possible for an appreciable level of metal ions uptake to be achieved by the adsorbents (UCPH and MCPH) at the lowest time contact. This suggests that the intrinsic property or the functional groups of the adsorbents become easily active and bound to the metal ions from solutions of Cu^{2+}, Cd^{2+} and Pb^{2+} at constant initial concentration of 100 mg L^{-1}.

However, at 120 min, precipitation of metal ions adsorbed likely occurred leading to a slight drop of amount adsorbed by the adsorbents. Nevertheless, the functional groups from the modification, -SH (thiol) groups was not favourable with cocoa pod husk due to the original nature or composition of the adsorbent. Nonetheless, maximum equilibrium sorption capacity of the metal ions was achieved by the adsorbents at shorter contact time for both UCPH and MCPH.

Sorption kinetics and intraparticle diffusion models: The kinetics of Cu^{2+}, Cd^{2+} and Pb^{2+} adsorption on unmodified and modified cocoa pod husk were analysed using Pseudo-first order, Pseudo-second order (Ho *et al.*, 2000), Intraparticle diffusion (McKay and Poots, 1980; Srivastava *et al.*, 1989; Weber and Morris, 1963) kinetic
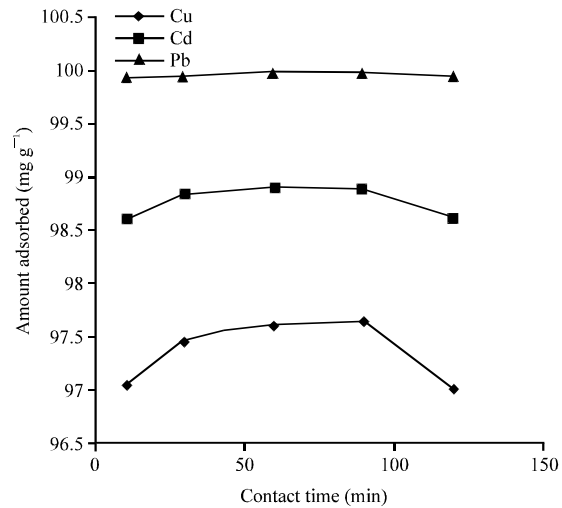

Fig. 1: Variation of amount adsorbed versus contact time for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Unmodified Cocoa Pod Husk (UCPH)
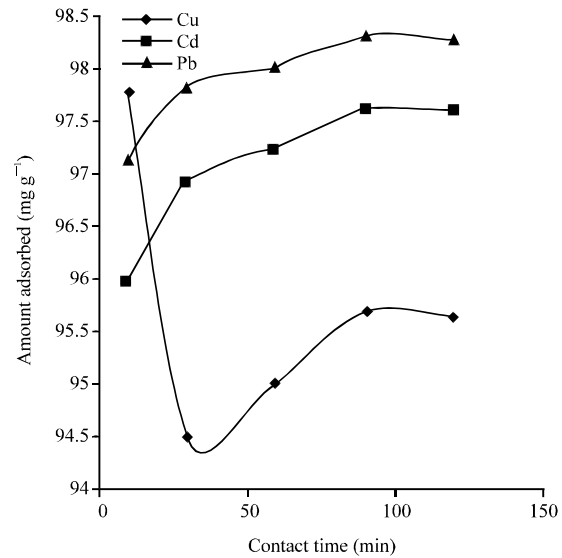

Fig. 2: Variation of amount adsorbed versus contact time for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Modified Cocoa Pod Husk (MCPH)

models. The conformity between experimental data and the model predicts values that expressed by correlation coefficients (R^2 values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of the adsorption process.

Pseudo first-order kinetic model: The Pseudo-first order equation is generally expressed as follows:
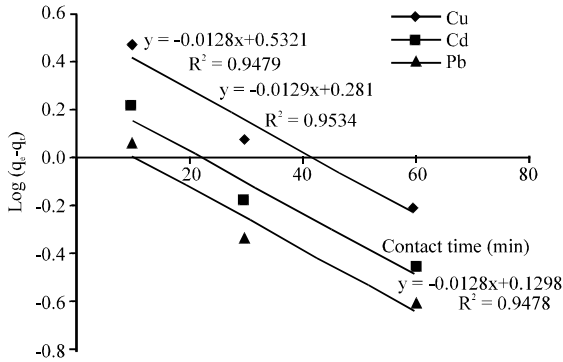
$$dq_t/d_t = K_1 (q_e-q_t) \qquad (2)$$

Fig. 3: Pseudo first-order plot for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Modified Cocoa Pod Husk (MCPH)

Table 1: Kinetic parameters (constants) and correlation coefficients (R^2 values) for Pseudo-first model for sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} onto Modified Cocoa Pod Husk (MCPH)

| Constants (units)	Modified Cocoa Pod Husk (MCPH)		
	Cu^{2+}	Cd^{2+}	Pb^{2+}
K_1 (min^{-1})	0.0295	0.0297	0.0295
q_e (mg g^{-1})	3.4049	1.9099	1.3483
Correlation coefficients (R^2)			
R^2	0.9479	0.9534	0.9478

where, q_e and q_t are adsorption capacity at equilibrium and at time t, respectively (mg g^{-1}), K_1 is the rate constant of Pseudo first-order adsorption (L min^{-1}). After integration and applying boundary conditions t = 0 to t = t and q_t = 0 to $q_t = q_t$, the integrated form of Eq. 2 becomes:

$$\log (q_e-q_t) = \log (q_e)-K_1 \, t/2.303 \qquad (3)$$

When the values of log (q_e-q_t) are linearly correlated with t and a plot of log (q_e-q_t) versus gives a straight line then researchers have a good fit for the Pseudo first-order kinetic model. K_1 and q_e are determined from the slope and intercept of the plots, respectively. The plot of log (q_e-q_t) versus t for the metal ions (Cu^{2+}, Cd^{2+} and Pb^{2+}) using Modified Cocoa Pod Husk (MCPH) is shown in Fig. 3. However, there was no plot for the unmodified adsorbent (UCPH) this is as a result of disagreement between the experimental data generated and parameters of the Pseudo first-order model.

The constants for Pseudo first-order (K_1 and q_e) and the correlation coefficient (R^2) are shown in Table 1. From Table 1 the K_1 values for MCPH was higher for Cd^{2+} than Cu^{2+} and Pb^{2+} that have the same K_1 value. It is important to note that the higher the K_1 values the greater the adsorption. For q_e values the trend is as follows, $Cu^{2+}>Cd^{2+}>Pb^{2+}$ for modified cocoa pod husk.

Generally, the lower the q_e values the greater the adsorption which conforms to the trend of adsorption in the fashion:

$$Pb^{2+}>Cd^{2+}>Pb^{2+}$$
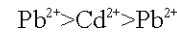
Furthermore, the least R^2 value from Table 1 above for the MCPH adsorbent is 0.9478 on Pb^{2+} ions and the highest is 0.9534 on Cd^{2+} ions. However, a relatively set of high R^2 values was achieved by the adsorbent MCPH which indicates that the Pseudo first-order model successfully describes the kinetics of the adsorption of MCPH for the metal ions. As mentioned earlier, Unmodified Cocoa Pod Husk (UCPH) did not agree with the Pseudo first-order model hence was not modeled as a result of erroneous values of the parameters for Pseudo first-order got from the experimental data of UCPH. Other researchers have reported this with other adsorbents (Igwe and Abia, 2007).

Pseudo second-order kinetic model: The Pseudo-second order adsorption kinetic rate equation is expressed as (Ho *et al.*, 2000):

$$dq_t/dt = K_2(q_e-q_t)^2 \qquad (4)$$

where, K_2 is the rate constant of Pseudo-second order adsorption (g/mg/min or g/mg/min). For the boundary conditions t = 0 to t = t and q_t = 0 to $q_t = q_t$, the integrated form of Eq. 4 becomes:

$$1/(q_e-q_t) = 1/q_e+Kt \qquad (5)$$

This is the integrated rate law for a Pseudo-second order reaction. Equation 5 can be rearranged to obtain Eq. 6 which has a linear from:

$$tq_t = 1/(K_2 \, q_e^2)+t/q_e \qquad (6)$$

If the initial adsorption rate, h (mg/g/min) is:

$$h_0 = K_2 q_e^2 \qquad (7)$$

Then Eq. 6 and 7 will combine to show:

$$t/q_t = 1/h_0+t/q_e \qquad (8)$$

The plot of t/q_t versus t (contact time) using Eq. 6 should give a linear relationship from which q_e and K_2 are determined from the slope and intercept of the plots, respectively. The Pseudo second-order plots for unmodified adsorbent (UCPH) and the modified adsorbent

Table 2: Kinetic parameters (constants) and correlation coefficients (R^2 values) for Pseudo second-order models for sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} onto Unmodified and Modified Cocoa Pod Husk (UCPH and MCPH)

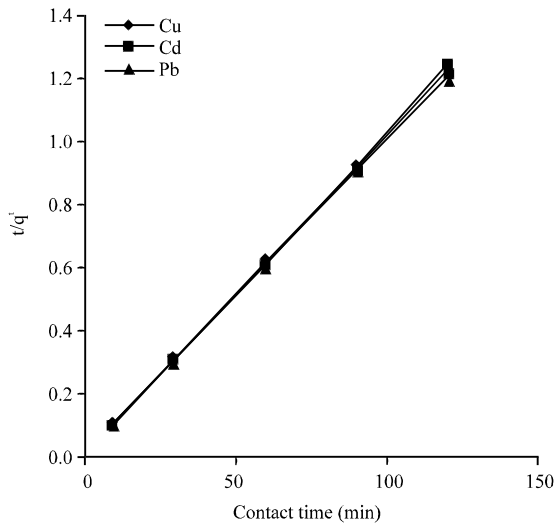|	Unmodified and modified cocoa pod husk					
	UCPH			MCPH		
Constants (units)	Cu^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}
q_e (mg g^{-1})	97.0900	99.0100	100.000	96.1500	98.0400	98.04000
h_o (mg g^{-1})	-769.2300	-1666.6700	-20000.000	217.3900	400.0000	588.24000
K_2 (g/mg/min)	-0.0816	-0.1700	-2.000	0.0235	0.0416	0.06120
Correlation coefficients (R^2)						
R^2	1.0000	1.0000	1.000	1.0000	1.0000	1.00000

Fig. 4: Pseudo second-order plot for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Unmodified Cocoa Pod Husk (UCPH)
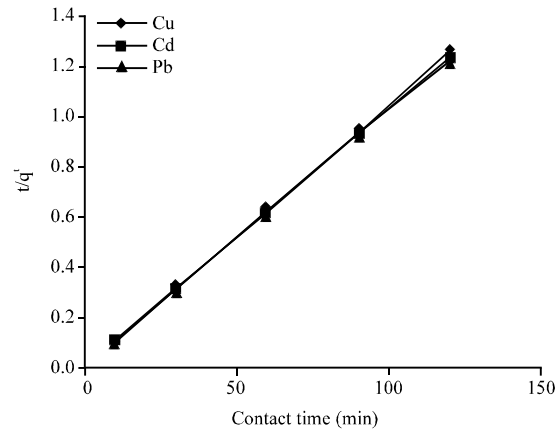

Fig. 5: Pseudo second-order plot for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Modified Cocoa Pod Husk (MCPH)

(MCPH) are shown in Fig. 4 and 5, respectively. The plots gave good linear plots or very good straight lines were obtained from these figures. Therefore, the plots gave a very good fit to the experimental data. This means that the sorption process can be best described by a pseudo-second order rate equation hence q_e (the adsorption capacity at equilibrium), h_o (the initial adsorption rate and K_2 (the pseudo second-order rate constant) were calculated for the three metal ions and are shown in Table 2. R^2 (correlation coefficient) values for the Pseudo second-order equation model plots are also shown in Table 2.

The values of R^2 show that the Pseudo second-order model equation gave a better fit to the sorption process than the Pseudo first-order. The R^2 values are almost of the same value for all three metal ions and the two adsorbents (both unmodified and modified) with a value of 1. From Table 2, the value of initial rate of sorption (h_o) for the modified adsorbent (MCPH) was highest on Pb^{2+} ions followed by Cd^{2+} and then Cu^{2+} ions (i.e.,

$Pb^{2+}>Cd^{2+}>Cu$). For the unmodified adsorbent (UCPH) the h_o value was highest for Cu^{2+} ions but a negative value and is in the order: $Cu^{2+}>Cd^{2+}>Pb^{2+}$. Also from the K_2 values in Table 2, Pb^{2+} ions had the highest K_2 values for the modified adsorbent (MCPH) confirming Pb^{2+} ions as having higher sorption rate than Cd^{2+} and Cu^{2+}. On the other hand the unmodified adsorbent (UCPH) had Cu^{2+} ions as the highest for K_2 value though with a negative value. These results are similar to previous researches by some researchers with other adsorbents/biosorbents and metal ions (Demirbas *et al.*, 2004; Horsfall *et al.*, 2004).

However, the rate constant K_2 gives a measure of how fast the reaction proceeds. The higher values of K_2 observed (for Pb^{2+} and Cu^{2+}) gives higher reaction rates hence, higher adsorption rate for MCPH and UCPH, respectively.

Intraparticle diffusion models: The mechanism of sorption is either film diffusion controlled or particle diffusion controlled. Before adsorption takes place, several diffusion processes known to affect the adsorption process takes place. The sorbate will have to diffuse through the bulk of the solution to the film
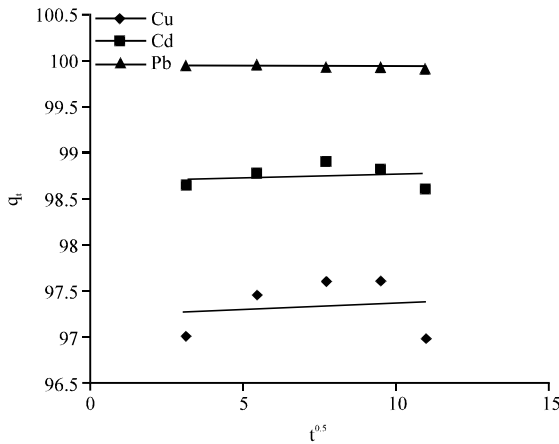
Fig. 6: McKay and Poots plot for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Unmodified Cocoa Pod Husk (UCPH)

surrounding the adsorbent and then into the micropores and macropores of the adsorbent. Several models have been developed for the studies of mechanism of sorption processes by intraparticulate diffusivity.

McKay and Poots intraparticle diffusion model: The model developed by McKay and Poots (1980) was used to establish the mechanism of the sorption process. McKay and Poots (1980) observed that the fraction of solute adsorbed can be expressed in terms of the square root of time. The McKay and Poots equation is given as:

$$q_t = X_i + K' \, t^{0.5} \qquad (9)$$

Where:
X_i = The boundary layer diffusion effects
K' = The rate constant for intraparticle diffusion $(mg/g/min^{0.5})$

From Eq. 9 a plot of fraction of solute adsorbed, q_t (amount adsorbed at each time t) versus $t^{0.5}$ (square root of time) should give a straight line thus confirming intraparticle diffusion sorption. The slope of the linear part of the curve uptake capacity (q_t) versus square root time $(t^{0.5})$ gives the initial rate of sorption controlled by intraparticle diffusion, K' $(mg/g/min^{0.5})$ (McKay and Poots, 1980). The initial curved portion of the plot is attributed to boundary layer diffusion effects (i.e., external film resistance).

The extrapolation of the linear straight lines to the time axis gives intercepts X_i which is proportional to the boundary layer thickness. The plots are shown in Fig. 6 for Unmodified Cocoa Pod Husk (UCPH) and Fig. 7 for Modified Cocoa Pod Husk (MCPH). The slope of the
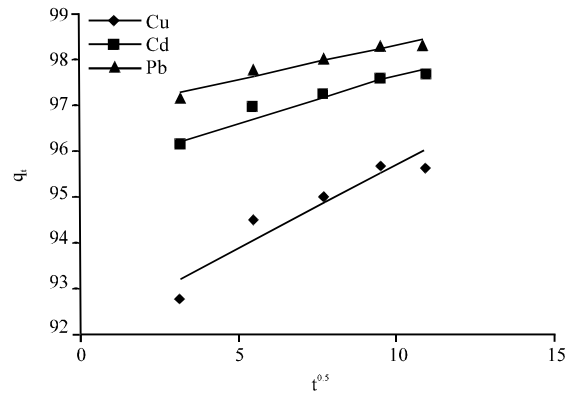

Fig. 7: McKay and Poots plot for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Modified Cocoa Pod Husk (UCPH)

Table 3: Kinetic parameters (constants) and correlation coefficients (R^2 values) for McKay and Poots intraparticle diffusion model for sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} onto unmodified and modified cocoa pod husk (UCPH and MCPH)

| | Unmodified and modified cocoa pod husk | | | | | |
| | UCPH | | | MCPH | | |
Constants (units)	Cu^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}
X_i $(mg\,g^{-1})$	97.2220	98.6880	99.9270	92.0610	95.5720	96.8560
K' $(mg/g/min^{0.5})$	0.0146	0.0079	0.0005	0.3620	0.2022	0.1434
Correlation coefficients (R^2)						
R^2	0.0229	0.0310	0.0196	0.8963	0.8995	0.8963

plots (q_t vs $t^{0.5}$) gives the initial rate of sorption controlled by intraparticle diffusion, K' $(mg/g/min^{0.5})$. The values of K' are shown in Table 3. The extrapolation of the linear straight lines to the time gives the intercepts X_i which are proportional to the boundary layer thickness. The values are also shown in Table 3. The boundary layer gives an insight into the tendency of the metal ions to adsorb to the adsorbent phase or remain in solution. Since diffusion takes place the boundary layer is looked upon as a viscous drag existing between the adsorbent surface and the metal ion solution diffusing across its surface. Therefore, higher values of X_i, i.e., boundary layer thickness as shown in Table 3, depict higher adsorption capacities.

Thus, Pb^{2+} ions had the highest X_i values signifying high adsorption capacity for Pb^{2+} ions with the adsorbents and in the order $Pb^{2+}>Cd^{2+}>Cu^{2+}$ (for both UCPH and MCPH, respectively). It has also been reported that at a high temperature, the thickness of the boundary layer decreases due to the increased tendency of the metal ions to escape from the biomass surface to the solution phase which results in a decrease in adsorption as the temperature increases. From Table 3, the boundary
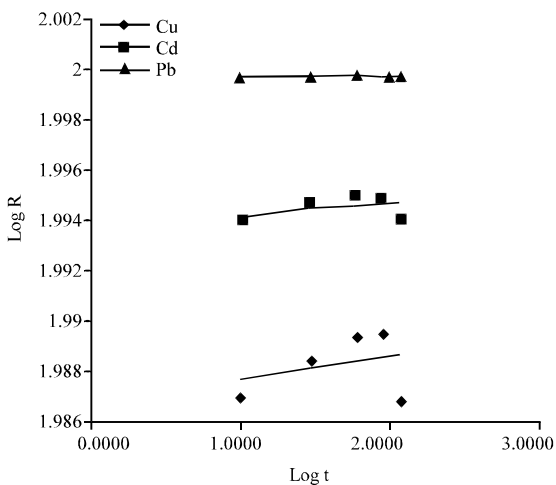
Fig. 8: Weber and Morris plot for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Unmodified Cocoa Pod Husk (UCPH)

layer thickness varies from 92.061-99.927 mg g⁻¹. This shows high tendency for adsorption capacity adsorbents. Furthermore, high value of the regression (correlation) coefficients (R^2) close to 1 indicates that the model fits the experimental data very well and confirms the sorption process is intraparticle diffusion controlled. However, R^2 values from Table 3 show fairly high values by the MCPH adsorbent while UCPH displayed very low R^2 values. In general terms, the sorption process (or the experimental data) did not give a better fit with McKay and Poots model.

Weber and Morris intraparticle diffusion Model: The intraparticle diffusion model can also be expressed as (Weber and Morris, 1963; Srivastava *et al.*, 1989):

$$R = K_{id}(t)^n \qquad (10)$$

A linearised form of the equation is followed by:

$$R = \log K_{id} + n \log(t) \qquad (11)$$

Where:
R = The percent heavy metal adsorbed
t = The contact time (min)
n = The gradient of linear plots
K_{id} = The intraparticle diffusion rate constant (min⁻¹)
n = Depicts the adsorption mechanism
K_{id} = May be taken as a rate factor, i.e., percent heavy metal adsorbed per unit time

Higher values of the intraparticle rate constants (K_{id}) illustrate an enhancement in the rate of adsorption whereas larger values illustrate a better adsorption
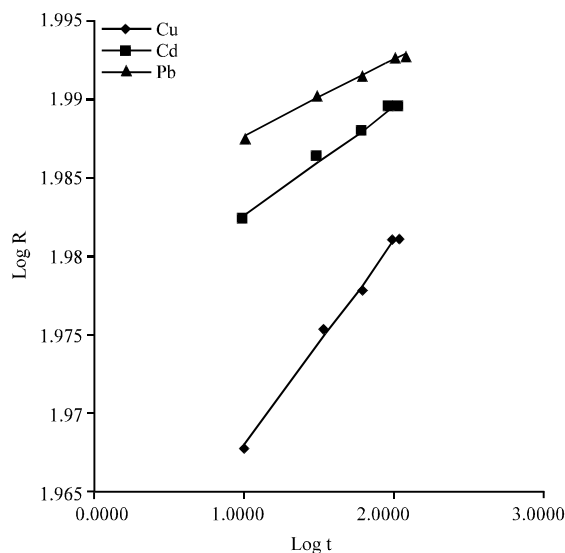

Fig. 9: Weber and Morris plot for the adsorption of Cu (II), Cd (II) and Pb (II) ions on Modified Cocoa Pod Husk (MCPH)

mechanism. Several workers have employed one or combinations of this model in the analysis of the intraparticle diffusion processes for heavy metal adsorption on adsorbents/biosorbents (Igwe and Abia, 2006; Demirbas *et al.*, 2004; Guibal *et al.*, 1998).

This model was used to analyze the experimental data in order to estimate its fitness with the experimental data. The plots of log R versus log t from Eq. 11 were plotted in Fig. 8 and 9. The unmodified adsorbent (UCPH) is shown in Fig. 8 and modified adsorbent (MCPH) in Fig. 9. From the plots, n (the gradient of linear plots) and K_{id} (the intraparticle diffusion rate constant in min⁻¹) formed the slope and intercept of the linear plots, respectively. R which is the fraction of the amount adsorbed and t the contact time (min) were calculated from the experimental data for the effect of time. The values for the constants K_{id} and n of the model are shown in Table 4. R^2 values are also shown in Table 4.

The values of n depict the adsorption mechanism and K_{id} may be taken as a rate factor (Demirbas *et al.*, 2004). The values of K_{id} increases in the order: $Pb^{2+} > Cd^{2+} > Cu^{2+}$ for both unmodified and modified adsorbent (UCPH and MCPH) as also shown in Table 4. However, higher value of K_{id} illustrates an enhancement in the rate of adsorption whereas larger n values illustrate a better adsorption mechanism which is related to an improved bonding between the metal ions and the adsorbent particles. From Table 4, Cu^{2+} ions adsorbed onto MCPH had the highest n-value of 0.0125 and Pb^{2+} ions adsorbed onto UCPH had the lowest n-value of 0.00002 and the order of increase is

Table 4: Kinetic parameters (constants) and correlation coefficients (R^2 values) for Weber and Morris intraparticle diffusion models for sorption of Cu^{2+}, Cd^{2+} and Pb^{2+} onto unmodified and modified cocoa pod husk (UCPH and MCPH)

Constants (units)	Unmodified and modified cocoa pod husk					
	UCPH			MCPH		
	Cu^{2+}	Cd^{2+}	Pb^{2+}	Cu^{2+}	Cd^{2+}	Pb^{2+}
N	0.0009	0.0004	0.00002	0.0125	0.0068	0.0048
K_{id} (min^{-1})	97.0060	98.5830	99.93100	90.3030	94.5800	96.1390
Correlation coefficients (R^2)						
R^2	0.0805	0.1043	0.02430	0.9702	0.9724	0.9691

$Cu^{2+}>Cd^{2+}>Pb^{2+}$. With relatively large n-values got it means that the sorption process is particle diffusion controlled and that the intraparticle mass transfer resistance is the rate limiting step. This is also similar to results of previous reports (Abia and Igwe, 2005; Demirbas *et al.*, 2004; Horsfall *et al.*, 2004). Looking at the values of the R^2 (correlation coefficients) from Table 4, relatively high values approaching 1 were got with the highest value of 0.9724 by Cd^{2+} ions onto the MCPH and the lowest value was 0.0243 by Pb^{2+} ions onto UCPH. In general terms, the sorption process was better described by intraparticle diffusion model by Weber and Morris than the McKay and Poots mode.

CONCLUSION

From the studies, it has been found that low cost agricultural wastes are excellent adsorbents for the removal of Cu^{2+}, Cd^{2+} and Pb^{2+} from aqueous solutions. From the result of the experiment the following were deduced: adsorption capacity and capability was rapid at a lower time-lag. At least 90% adsorption was achieved at 10 min contact time adsorption capacity increased as contact time increased between 10 and 60 min, slight drop in adsorption capacity was noticed between 90 and 120 min. Increase in adsorption capacity seemed not favourable at 120 min, modification by thiolation slightly dropped the adsorption capacity of the adsorbent for metal ions and Pseudo second-order kinetic model best described the sorption process with high R^2 values.

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