Bioremediation of Al (III), Cr (VI) and Ni (II) Ions from Aqueous Solution using Cocoa Pod Husk: Kinetics and Intraparticle Diffusivities

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ABSTRACT

The occurrence of heavy metals (HMs) in aquatic ecosystems in excess of natural background loads has become a problem of increasing concern. As a result of the toxicity of these HMs on humans and other forms of life, their removal has become very important. Bioremediation *vis-à-vis* the kinetics of sorption, intraparticle diffusivities and mechanisms of Cr (VI), Ni (II), and Al (III) ions removal using two different particle sizes of cocoa pod husk (CPH) was studied. The amount of HM ions adsorbed increased with time. At initial HM ion concentration of 1000 mg/L, pH of 7.5 and temperature of 30°C, the highest sorption rates of the HM ions on size I and II of CPH were 97% for Al^{3+}, 88% for Cr^{6+} and 86% for Ni^{2+}; and 100% for Ni^{2+}, 99% for Cr^{6+} and 97% for Al^{3+}, respectively. The sorption process was modeled using the pseudo-first order, pseudo-second order and Ritchie's second order kinetic equations. The pseudo-second order gave a better fit to the kinetic sorption data especially for Al (III) ion with an R^2 value of 0.9999. The intraparticle diffusion equation was used to develop the mechanism of sorption, i.e., whether the sorption process was controlled by film diffusion or particle diffusion. The sorption of Cr^{6+}, Ni^{2+} and Al^{3+} ions on CPH was controlled by film diffusion since the R^2 values for the intraparticle diffusion equations were very low given as 0.6532 for Cr (VI), 0.4298 for Ni (II) and 0.0000 for Al (III). Therefore, this study shows that the contact time between the adsorbent and metal ions is a design parameter in the removal of Cr^{6+}, Ni^{2+} and Al^{3+} using CPH.

Keywords: agricultural by-products, adsorption, environment, heavy metals, kinetic models

INTRODUCTION

Heavy metals (HMs) have long been identified as major environmental pollutants. The problems associated with HM pollution are of great concern because of their toxicity to man and the environment. Most of these HMs belong to the fourth period of the periodic table and are carcinogenic; the carcinogenicity is related to the electronic structure of transition and inner transitional metals (Luckey and Venugopal 1977). Also, these HMs bioaccumulate in nature, hence are bound to accumulate in excess of the natural background load.

The chemistry and toxicology of these HMs are complex and interesting. For example, chromium (Cr) has both beneficial and detrimental properties. Two stable oxidation states of Cr persist in the environment, Cr (III) and Cr (VI) which have contrasting toxicities, mobility and bioavailability (Saifuddin and Kumaran 2005). While Cr (III) is relatively innocuous and immobile, Cr (VI) moves readily through soils and aquatic environments and is a strong oxidizing agent capable of being absorbed through the skin (Park and Jung 2001). Hexavalent chromium, Cr (VI), is the toxic form of Cr released during many industrial processes including electroplating, leather tanning and pigment manufacture (Faisal and Hasnain 2004). Trivalent chromium, Cr (III), is an essential element required for normal carbohydrate and lipid metabolism (Mertz 1993; Anderson 1998). Its deficiency leads to an increase in risk factors associated with diabetes and cardiovascular diseases including elevated circulating insulin, glucose, triglycerides, total cholesterol and impaired immune function leading to hemorrhage, respiratory impairment and liver lesions (Rhode and Hartmann 1980; Shah *et al.* 2009). Unlike deficiency symptoms, several factors make chromate contamination a matter of intense concern, particularly its toxic, mutagenic (Cheng and Dixon 1998), carcinogenic (Shumilla *et al.* 1999), and teratogenic (Asmatullah and Shakoori 1998) effects. Also, Cr (VI) forms stable anions such as $Cr_2O_7^{2-}$, $HCrO_4^-$, CrO_4^{2-} and $HCr_2O_7^-$, the fraction of any particular species is dependent upon the Cr concentration and pH (Udaybhaskar *et al.* 1990) which in turn affects the toxicity and bioavailability.

The conventional removal processes employed in HM pollution control includes precipitation, coagulation, filtration, reverse osmosis and oxidation-reduction. These methods have been found wanting as a result of cost of operation and production of sludge which is another problem of its own. Sorption has been an effective separation process for a wide variety of applications. The most widely used sorbent for industrial applications is activated carbon (Walker and Weatherly 1997; Khalil and Girgis 1998; Porter *et al.* 1999). There are still problems associated with its use; namely, activated carbon is expensive and the higher the quality the greater the cost (Ho and Chiang 2001).

The sorption of HM ions from aqueous solution plays an important role in water pollution control, and in recent years there has been considerable interest in the use of low-cost sorbents such as cocoa pod husk (CPH) for this purpose. Other low-cost agricultural by products that have been used include sphagnum moss peat (Ho and McKay 1999a, 1999b, 2000); maize cob and husk (Igwe and Abia 2003, 2005; Abia *et al.* 2005; Opeolu *et al.* 2009); coconut fiber (Igwe and Abia 2007a; Igwe *et al.* 2008); cassava waste (Egila and Okorie 2002; Abia *et al.* 2003); sunflower stalk (Sun and Shi 1998); shea butter seed husk (Eromosele and Abare 1998); groundnut husk (Okieimen *et al.* 1991); banana pith (Low *et al.* 1995); bamboo root (Babatunde *et al.*

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2009), *Caladium bicolor* (Horsfall and Spiff 2005); sawdust (Urik *et al*. 2009); boiler fly ash (Okoronkwo *et al*. 2008), and others. However, although the sorption kinetics of individual HM ions onto this type of material has been examined, the processes which occur are not completely understood, for instance, the rate limiting step and the binding mechanism (Ho and McKay 2000).

Therefore, it is understandable that the study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the reaction pathways and into the mechanism of sorption reactions (Ho and McKay 1999). In addition, the kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid solution interface. Therefore, it is important to be able to predict the rate at which pollutants are removed from aqueous solutions in order to design appropriate sorption treatment plants (Igwe and Abia 2005). To develop sorption kinetics, knowledge of the rate law describing the sorption system is required. The rate law is usually determined by experimentation and it cannot be inferred by mere examination of the overall chemical reaction stoichiometric equation. The rate law has three primary requirements (Ho and McKay 1999):

• Knowledge of all the molecular details of the reaction including the energetics and stereochemistry.
• Interatomic distances and angles throughout the course of the reaction.
• The individual molecular steps involved in the mechanism.

In this work, we investigated the kinetics of sorption of Aluminium (Al) (III), Cr (VI) and Nickel (Ni) (II) ions on CPH. Pseudo-first order, pseudo-second order and Ritchie's second order models were used to ascertain the rate kinetics for the sorption process. We also investigated the mode of diffusion by employing the various models for intraparticle diffusion. Our aim was to generate data that could be used to effectively design sorption treatment plants for HM bioremediation.

MATERIALS AND METHODS

Materials

The CPH used was obtained from a local farm in Umuahia, Abia State, Nigeria. It was thoroughly washed with deionized water, ground into a meal and then air-dried. The dried husk was sieved using a test sieve shaker to obtain particle sizes of < 125, 125, 250, 425, 500, 600 and > 850 μm. It was then soaked in 2% (v/v) dilute nitric acid for 24 hrs, filtered and washed copiously with deionized water, air dried and kept in an air-tight plastic container ready for use. All reagents used were of analytical grade and used as purchased without further purification. The stock solutions of Cr (VI), Al (III) and Ni (II) (2000 mg/L) were prepared in deionized water using chromium sulphate, aluminum sulphate and nickel sulphate respectively. All working solutions were prepared by diluting the stock solution with deionized water.

Methods

Adsorbent characterization

The unmodified CPH was characterized in terms of bulk density (BD), particle density, pore volume, porosity, cation exchange capacity (CEC), specific surface area (S_{AA}) and the surface charge density (SCD). BD was determined as the ratio of the bulk mass of the test sample to its bulk volume (BV). A clean dry density bottle was weighed and its weight was recorded (W_1). The density bottle was fully filled up to the stopper with the husk and measured (W_2). By difference ($W_2 - W_1$), the bulk weight of the husk was calculated. Then, the weighed sample in the sample bottle was carefully decanted into a clean dry measuring cylinder and the volume (V) was read from the calibration. BD was then calculated from the equation (Abia *et al*. 2003):

$$BD = (W_2 - W_1)/V \qquad (1)$$

Particle density was determined by the specific gravity bottle method and the pore volume was obtained as the inverse relation of particle density (Horsfall *et al*. 2004). The porosity was calculated as the percentage ratio of the difference between BV and the gram volume (GV) to the bulk density (BD). It is given by the equation (Abia *et al*. 2003):

$$Porosity = \frac{BV - GV}{BD} \times \frac{100}{1} \qquad (2)$$

CEC of the CPH was determined by the ammonium acetate saturation procedure (Santamarina *et al*. 2002). In this method, a 1.0-g sample of the husk was dispersed in 1.00 M sodium acetate solution. The resulting suspension was mixed with 1.00 M ammonium acetate and mechanically stirred at room temperature for 1 hr and centrifuged at 2800 rpm for 5 min to extract the Na^+ ions. The extracted Na^+ concentration of the solution was determined by Buck Scientific flame atomic absorption spectroscopy (FAAS) model 200A.

The Specific surface area (S_{AA}) of the adsorbent was determined using the methylene blue absorption test (MBT) method (Santamarina *et al*. 2002). 2.0 g of the adsorbent was dissolved in 200 mL of deionized water and 10 ppm of MB solution was added to the adsorbent suspension and agitated in a shaker for 2 hrs. Thereafter, it was kept for 24 hrs to reach equilibrium, after which a 10-ml aliquot was taken and centrifuged. The centrifuged aliquot was then analyzed using a UNICAM 8700 UV/Visible spectrophotometer to determine the amount of MB absorbed. Also, 20, 30, 40, 50, 60 and 70 ppm solutions of MB were then added sequentially and the previous steps repeated. A graph of concentration of MB added versus the amount of absorbed MB was used to identify the point. The specific surface area was calculated from the amount of absorbed MB at the optimum point of cation replacement as follows (Santamarina *et al*. 2002):

$$Specific\ surface\ area = ((mM_B \times Av \times AMB)/319.98) \times (1/Ms) \qquad (3)$$

where mM_B = the amount of MB absorbed at the point of complete cation replacement; Ms = mass of adsorbent; Av = Avogadro's number, 6.02×10^{23}; AMB = area covered by one MB (assumed to be 130$Å^2$). Then, SCD was calculated from the value of CEC and S_{AA} as the ratio of the two given by (Abia *et al*. 2003):

$$SCD\ meq/m^2 = CEC/S_{AA} \qquad (4).$$

Adsorption experiments

Two sizes of the CPH (850 and 425 μm) were used in this experiment. To determine the effect of contact time, 1 g of cocoa pod sample was placed in an Erlenmeyer flask with cork; 100 mL solution of the metal ion of initial concentration of 1000 mg/L was added to the flask and corked. Different samples were left in a constant speed rotary shaker at 30°C and pH of 7.5 for 10, 20, 30, 40, 50, 60, and 120 mins. The samples were then filtered rapidly and the HM content of the filtrates was determined using a UNICAM 919 solar atomic absorption spectrophotometer (AAS). The amount of HM ions adsorbed was obtained by difference. The intraparticulate diffusivity and the fractional attainment to equilibrium were then calculated.

RESULTS AND DISCUSSION

Sorption capacity

The 2% (v/v) nitric acid used to soak the adsorbent for 24 hrs activated the adsorbent by opening up the pores making it ready for the sorption process. Also, it served to wash any soluble biomolecules that may interfere with the sorption process. The surface characteristics of the CPH are shown in **Table 1**. Surface characteristics are known to affect the adsorption properties of adsorbents (Santamarina *et al*. 2002). The amount of HM ions adsorbed was obtained from a simplified mass balance equation (Chu and Hashin 2001; Ho and Wang 2004):

Table 1 Surface characteristics of unmodified and activated cocoa pod husk.

Parameter	Value (unit)	Parameter	Value (unit)
Bulk density	0.398 (g/cm^3)	Specific surface area (S_{AA})	1.367×10^{25} (m^2/g)
Particle density	0.426 (g/cm^3)	Surface charge density (SCD)	6.43×10^{24} (Meq/m^2)
Pore volume	2.10 (cm^3/g)	Particle size	125-850 μm
Cation exchange capacity (CEC)	88.0 (mg/100 g)	pH	7.12 (*6.25)
Porosity	9.77 (%)	Colour	Dark brown

*Value of pH after 24 hours.
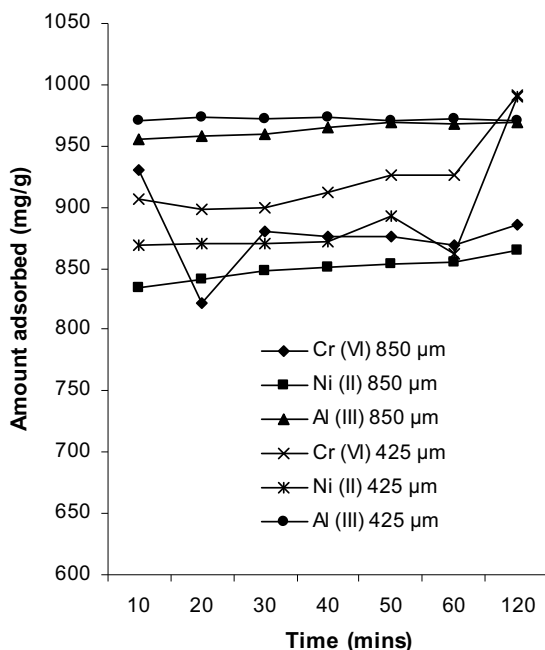
Fig. 1 Amount adsorbed (mg/g) against time (mins) for adsorption of Cr (VI), Ni (II) and Al (III) ions onto cocoa pod husk of two particle sizes.

Fig. 2 Distribution coefficient (R_d) against time for adsorption of Cr (VI), Ni (II) and Al (III) ions onto cocoa pod husk of two particle sizes.
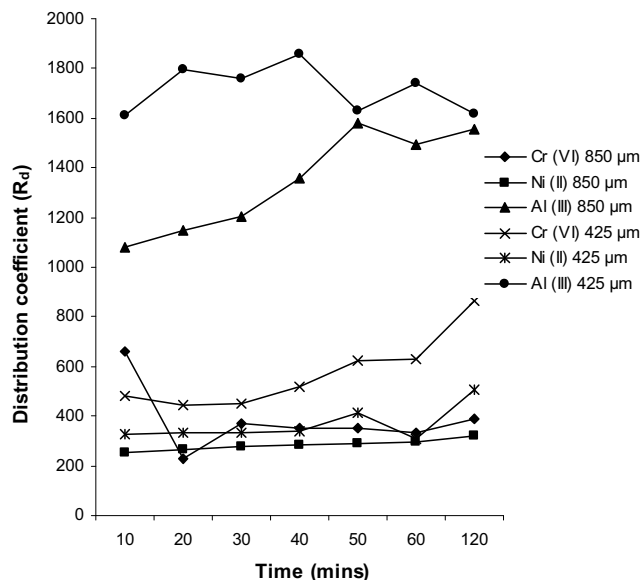
$$q_t = C_o - C_e \qquad (5)$$

where q_t is the amount absorbed (mg/g) at any time; C_o is the initial HM ion solution concentration and C_e is the equilibrium liquid phase HM ion concentration.

The amount of HM ions adsorbed as time increased is shown in **Fig. 1**. The sorption process was very rapid at the initial time from zero to 10 min before equilibrium was reached. Also, Al was absorbed more than Cr and then Ni ion. The differential sorption of these HM ions may be ascribed to the difference in the ionic radius of the HM ions. The smaller the ionic radius, the higher the amount absorbed. The ionic radii of the HM ions are (in pm) Al (67.0), Cr (75.0) and Ni (83.0), respectively. This trend in smaller ionic size have also been reported, for Cu (II) and Zn (II) adsorbed on cassava waste biomass (Horsfall *et al.* 2003); Ni (II) and Pb (II) on chemically modified and unmodified oil palm fruit fiber (Abia and Asuquo 2006) and Zn (II), Ni (II) and Cd (II) on chemically modified maize cobs (Akporhonor and Egwaikhide 2007).

In other to quantitatively estimate the amount of HM ions absorbed, the distribution coefficient of the HM ions between the solid and liquid phase as time increased was used. This is given by the equation below (Horsfall *et al.* 2003):

$$R_d = (V/m) \, (C_t/q_t) \qquad (6)$$

where R_d is the distribution coefficient, V is the volume of HM ion solution used (mL), m is the mass of adsorbent used (g) and C_t and q_t are the liquid phase and solid phase concentration of the HM ions at time t (mins) respectively. The distribution coefficient is shown in **Fig. 2**. Al ion on the absorbent of particle size 425 μm had the highest distribution in the solid phase.

Sorption kinetics and intraparticle diffusion

Adsorption kinetics deals with the rate at which sorption occurs; where the rate is defined as the change of a given quantity over a specified period of time (Ho 2004). Three kinetic equations for the pseudo-first order, the pseudo-second order and Ritchie's second order equations were used to model the sorption experimental results. The pseudo-first order equation is given as (Lagergren 1898):

$$\log (q_e - q_t) = \log q_e - K_1 t/2{,}303 \qquad (7)$$

where q_e is the equilibrium solid phase ion concentration (mg/g); K_1 is the pseudo-first order rate constant (min^{-1}). The pseudo-first order plot is shown in **Fig. 3**. Fairly straight lines were obtained with R^2 values of 0.3026, 0.9745 and 0.9522 for Cr (VI), Ni (II) and Al (III) ions, respectively on 850 μm adsorbent, and 0.6518, 0.0538 and 0.0233 for Cr (VI), Ni (II) and Al (III) ions, respectively on 425 μm adsorbent. The fitness of this equation to experimental data is very poor.

The pseudo-second order equation is given by Ho (2004):

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

where

$$h_o = K_2 q_e^2 \qquad (9)$$

The pseudo-second order plot is shown in **Fig. 4**. Good straight lines were obtained with R^2 values ranging from 0.8302 to 0.9999. This means that the pseudo-second order plot gave better fits to the sorption data more than the pseudo-first order. The constants for the pseudo-first and pseudo-second order equations are shown in **Table 2**.

Another kinetic equation employed for the analysis of experimental data is Ritchie's second order kinetic model. This equation is given by Ritchie (1977):
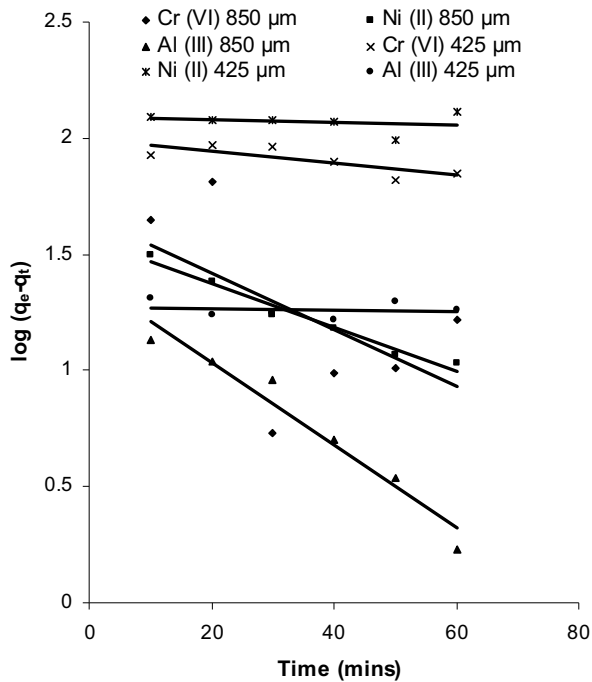
Fig. 3 Pseudo-first order plot for adsorption of Cr (VI), Ni (II) and Al (III) ions onto cocoa pod husk of two particle sizes.
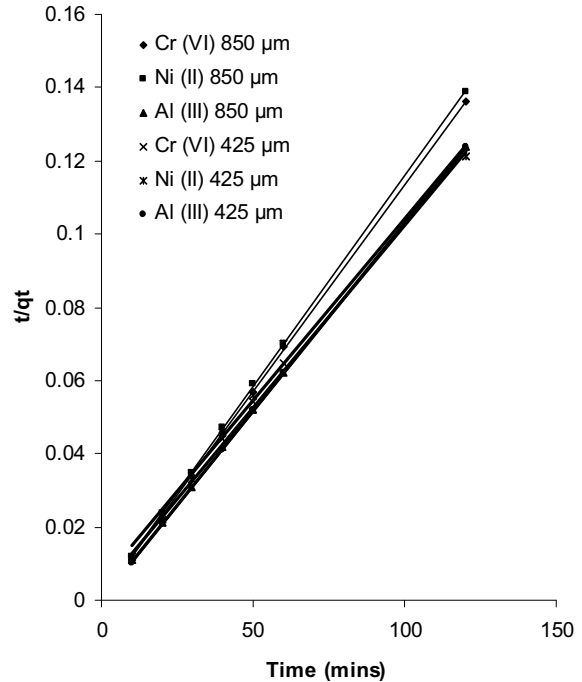

Fig. 4 Pseudo-second order plot for adsorption of Cr (VI), Ni (II) and Al (III) ions onto cocoa pod husk of two particle sizes.

$$1/q_t = 1/Kq_e t + 1/q_e \qquad (10)$$

where K is the rate constant (min^{-1}); q_e and q_t have the same meaning as in the pseudo-second order. The results of Ritchie's second order model are shown in **Fig. 5** and the constants and the coefficient of linear regression are also shown in **Table 2**.

Among the three kinetic models, the pseudo second order model gave a better fit to the sorption experimental data. The pseudo second order model was based on chemi-

sorption assumptions (Ho and McKay 1999). This means that the rate limiting step may be chemical sorption or chemisorption. Similar results have been observed in the adsorption of Cr (VI) onto used tyres and sawdust (Hamadi *et al*. 2001); activated carbons derived from agricultural waste materials (Mohan *et al*. 2005) and neem and mango sawdust (Vinodhini and Das 2010).

Diffusion mass transport models have been applied to sorption systems and their role in pollutant sorption is extremely important, particularly in processes where ion ex-

Table 2 Adsorption kinetics and intraparticle diffusion model rate constants for Cr (VI), Ni (II) and Al (III) ions on cocoa pod husk.

| Metal ions	850 µm			425 µm			
Pseudo-first order							
	K_1	q_e (mg/g)	R^2	K_1	q_e (mg/g)	R^2	
Cr	0.028	46.13	0.3026	0.0060	99.08	0.6518	
Ni	0.022	36.92	0.9745	0.0010	122.46	0.0538	
Al	0.041	24.70	0.9522	0.0007	18.76	0.0233	
Pseudo-second order							
	K_2	h	q_e (mg/g)	R^2	K_2	h	q_2 (mg/g)	R^2
Cr	2.4×10^{-3}	2000.0	909.09	0.9998	0.020	80.65	64.10	0.8620
Ni	1.8×10^{-3}	1250.0	833.33	0.9999	0.022	88.50	63.29	0.8869
Al	0.018	70.92	63.29	0.8302	0.025	25000	1000.0	0.9999
Ritchie's Pseudo-second order							
	K	q_e (mg/g)	R^2	K	q_e (mg/g)	R^2	
Cr	2.40	833.33	0.1449	1.83	909.09	0.3061	
Ni	3.00	833.33	0.8619	1.57	909.09	0.1931	
Al	5.00	1000.0	0.7509	111.11	1000.0	0.0253	
Intraparticle diffusion model							
	K_{id}	a	R^2	K_{id}	a	R^2	
Cr	63.93	0.07	0.1631	87.10	0.006	0.6532	
Ni	80.69	0.02	0.8016	83.73	0.007	0.4298	
Al	48.98	0.11	0.3849	10.00	1.99	0.0000	
Elovich equation							
	α	β	R^2	α	β	R^2	
Cr	7.19×10^3	0.126	0.0403	2.60×10^4	0.031	0.6444	
Ni	1.02×10^4	0.079	0.9936	2.89×10^4	0.026	0.4628	
Al	5.88×10^3	0.160	0.8466	1.56×10^2	6.165	0.0068	
McKay and Poots							
	K'	X_i	R^2	K'	X_i	R^2	
Cr	1.05	883.60	0.0070	11.67	847.71	0.8250	
Ni	3.95	824.11	0.9624	14.43	795.97	0.6373	
Al	1.88	951.32	0.7594	0.143	972.54	0.0527	
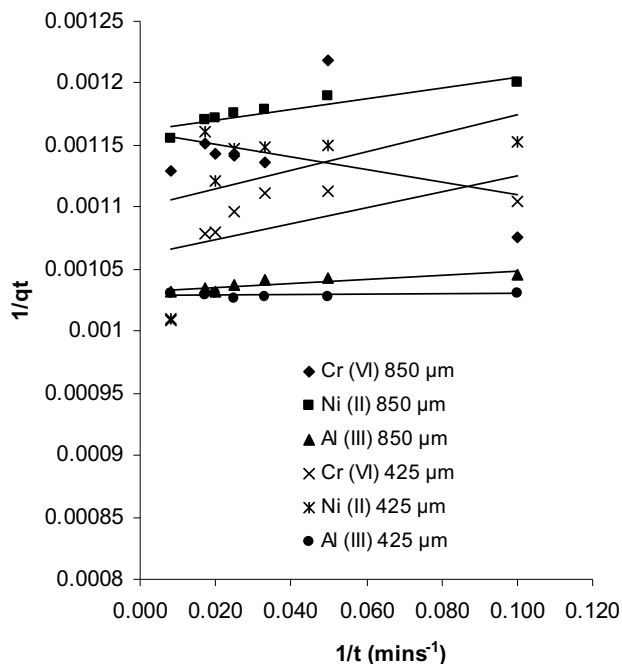
Fig. 5 Ritchie's second order plot for adsorption of Cr (VI), Ni (II) and Al (III) ions onto cocoa pod husk of two particle sizes.

Fig. 7 Elovich equation plot for adsorption of Cr (VI), Ni (II) and Al (III) ions onto cocoa pod husk of two particle sizes.
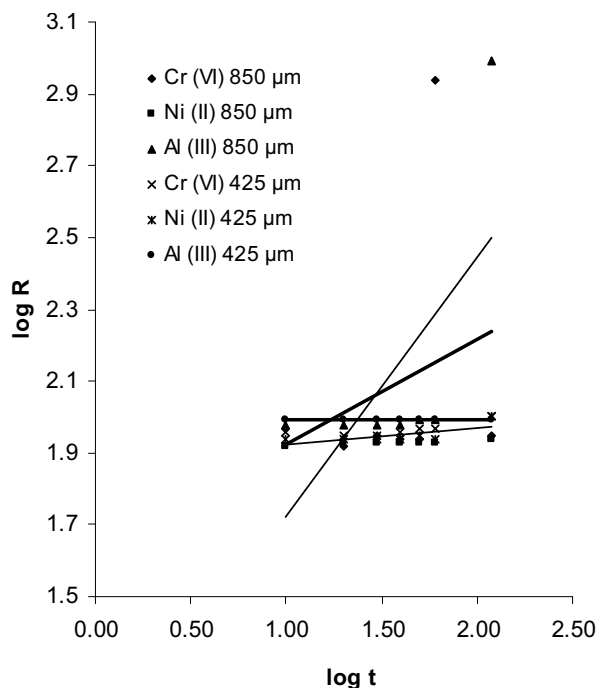

Fig. 6 Intraparticle diffusion plot for adsorption of Cr (VI), Ni (II) and Al (III) ions onto cocoa pod husk of two particle sizes.

change and ionic bonding are not as prevalent as in chemisorptions processes (Ho and McKay 1998). The mechanism of sorption has been reported to be controlled either by film diffusion or particle diffusion (Okeimen *et al.* 1991). Diffusion precedes adsorption and the factors which affect diffusion processes will definitely affect the mechanism of sorption. Generally, these diffusion models are usually based on one or more of the following mechanistic steps, which include bulk diffusion, external diffusion, surface or pore diffusion and then the proper mechanism of HM uptake such as physicochemical sorption, ion-exchange, precipitation or complexation (Findon *et al.* 1993; Weber and Digiano 1996). Bulk diffusion is counteracted when there is better and more uniform mixing which is achieved by increased agitation. Also, there may possibly be some boundary layer resistance to reaction which is decreased by in-
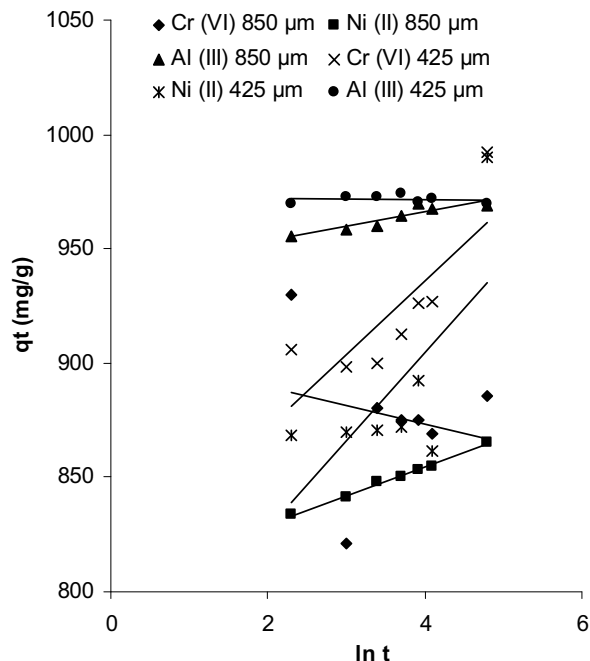
creasing the agitation. The more the agitation, the greater is the shear on the boundary layer surrounding the particles (Ho and McKay 1999). This means that there are no concentration gradients in solution making bulk diffusion nonlimiting. Guibal *et al.* (1998) reported that when this happens, then a quasi-instantaneous mechanism results. Therefore, intraparticle mass-transfer resistance is likely to be rate controlling.

Therefore, diffusion studies help to ascertain the mechanism of sorption for the sorption process. The mechanism of sorption can be broadly classified as controlled by film diffusion or particle diffusion (Okeimen *et al.* 1991) depending on whether external mass transfer resistance or intraparticle mass transfer resistance is rate limiting, respectively. For intraparticle diffusion and the establishment of a mechanism of sorption, three equations were used. The first one is termed the penetrant transport equation and is given as (Abia and Didi 2007):

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

where R is the percentage of HM ions adsorbed and K_{id} is the intraparticle rate constant. The penetrant transport plot is shown in **Fig. 6**.

Another equation that was used is called the Elovich equation, given by (Dermibas *et al.* 2004):

$$q_t = 1/\beta \ln (\alpha\beta) + 1/\beta \ln t \qquad (12)$$

where α is the initial adsorption rate (mg g^{-1} min^{-1}) and β is the desorption constant (g mg^{-1}) during any one experiment. The third intraparticle equation used for the analysis of the experimental result is that by McKay and Poots (1980):

$$q_t = X_i + K' t^{0.5} \qquad (13)$$

where X_i is called the boundary layer diffusion effect while K' is the McKay and Poots rate constant (min$^{-0.5}$). The Elovich and the McKay and Poots plot are shown in **Figs. 7** and **8**, respectively.

The R in the penetrate transport represents the percent of HM ion removed while K_{id} and a are constants. K_{id} is the rate constant while value of "a" determines the type of transport mechanism. The penetrant a-values represent the likelihood and degree of strive, that is, the HM ion's ability
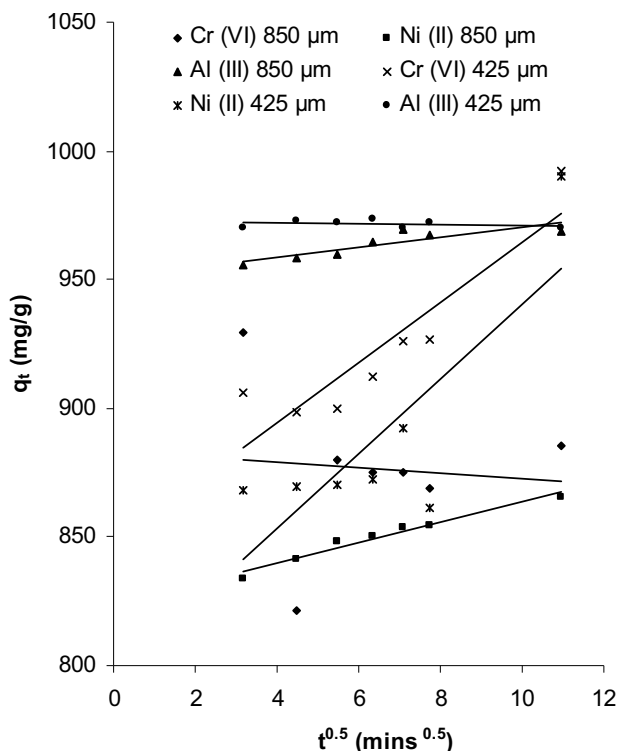
Fig. 8 McKay and Poots intraparticle diffusion plot for adsorption of Cr (VI), Ni (II) and Al (III) ions onto cocoa pod husk of two particle sizes.

ions had "a" < 1, which means that the adsorption process may not be due to HM ion core strive. For 425 µm size, Al (III) had "a" > 1 while Cr(VI) and Ni(II) ions had "a" < 1. All K_{id} values were high, far greater than one, which means that dipole induced dipole interaction are dominant in the adsorption process.

The constants for the Elovich and McKay and Poots equations are also shown in **Table 2**. The X_i in the McKay and Poots equation is very important as it represents the boundary layer diffusion effects on the adsorption process. The boundary layer acts as a shear interface between the adsorbent surface and the liquid phase film at the immediate vicinity of the adsorbent. Generally, a good fit by any of these equations indicates the types of mechanisms, and whether this is intraparticulate diffusion or film diffusion mechanism.

Again, to further analyze the results and investigate the differences in the fitness of the different kinetic and intraparticle models to the experimental data, a two-way analysis of variance (ANOVA) without replication at $P < 0.05$ was used to describe the relationships (1) between the six kinetic and intraparticle models in describing the adsorption of the three HM ions on the adsorbent and (2) between the three HM ions for binding sites on the adsorbent. The results are presented in **Table 3**. From this table, it can be seen that the differences in the fitness of the different kinetic models to the sorption data was not significant for the 425-µm size-HM ions and for the 850-µm size-HM ions but was significant for the 850-µm particle size models.

Application of models to other low-cost agricultural by-products

Generally, diffusivity, permeability and sorptivity are often coupled processes in the adsorption system. In most cases, time dependency of the sorption process is based on the outline that the curves derived exhibit a linear relationship initially followed by a plateau region which goes flat at extended times (Abia and Didi 2007). Abia and Didi (2007) reported that the adsorbent surface and the overlying interface could be considered as a mass transfer zone. Therefore, this presents a picture of a partial electrical double layer of the adsorbent stationary phase and the liquid mobile phase. The adsorbent active sites are considered negatively charged and the HM ions in solution notwithstanding the covalent orientations of some of their moieties have a positively charged core (Abia and Didi 2007). Therefore, adsorption onto the adsorbent surface translates into a decrease in the concentration of the adsorbate in solution, and considering a situation where applied pressure is zero and temperature is kept constant, for adsorption to take place diffusion becomes the operating transport phenomena (Aithal and Aminabhavi 1990).

Also, studies of membrane processes and diffusion have shown that diffusivities in membranes and solids are controlled by the ratio of the size of the solute to the size of the

Table 3 A two-way analysis of variance (ANOVA) for Cr (VI), Ni (II) and Al (III) ions on cocoa pod husk.

Source of variation	df	ss	ms	F_{cal}	F_{tab}
850 µm					
Model	5	0.43634116	0.08726823	1.78	3.33
Metal ions	2	1.38302599	0.69151300	14.08	4.10
Error	10	0.49117617	0.04911762		
Total	17	2.31054332			
425 µm					
Model	5	1.059438153	0.21188630	5.64	3.33
Metal ions	2	0.663621260	0.33181063	8.83	4.10
Error	10	0.375934630	0.03759346		
Total	17	2.098994040			

to penetrate the partial electrical double layer preceding adsorption (Abia and Didi 2007). "a" >1 indicates the presence of high strive. "a" ≈ 1 depicts moderate strive while for "a" <1, the adsorption process may not be due to HM ion core strive. Values of K_{id} and "a" for our study are shown in **Table 2**. For an 850-µm size adsorbent, all metal

Table 4 Kinetics rate constants reported in literature.

Adsorbents	Constants (Units)	Values	HMs and conditions	References
Pseudo-first order				
a. Waste acorn (*Quercus ithaburensis*)	K_1 (min^{-1})	0.0267	Cr (VI) at 100 mg/L and 25°C	Malkoc and Nuhoglu 2007
b. Almond shells (*Prunus dulcis*)		0.0510	Cr (VI) at pH of 4.0	Demirbas *et al.* 2004
c. Lichen biomass (*Cladonia furcata*)		0.060	Pb (II) at 20°C	Sari *et al.* 2007
d. Sawdust of neem (*Azadirachta indica*)		0.023	Cr (VI) at adsorbent dose of 1 mg/L	Vinodhini and Das 2010
e. Maize cob (*Zea mays*)		0.0751	Co (II) unmodified adsorbent	Igwe and Abia 2007b
f. Cocoa pod husk (*Theobroma cacao*)		0.028	Cr (VI) at 1000 mg/L initial conc. and 30°C	This study
Pseudo-second order				
a. Bamboo root (*Poaceae bambusoideae*)	K_2 (g mg^{-1} min^{-1})	0.0913	Cu (II) at 100 mg/L initial conc.	Babatunde *et al.* 2009
b. Sawdust of spruce (*Picea abies*)		(i) 0.012	As (V) at 230 µg/L and mod. adsorbent	Urik *et al.* 2009
		(ii) 0.0884	Cr (VI) at adsorbent dose of 1 mg/L	Vinodhini and Das 2010
c. Lichen biomass (*Cladonia furcata*)		0.060	Pb (II) 20°C	Sari *et al.* 2007
d. Palm kernel fibre (*Elaeis guineensis*)		0.018	Pb (II) at initial conc. of 30 mg/L	Ofomaja *et al.* 2005
e. Cocoa pod husk (*Theobroma cacao*)		0.0024	Cr (VI) at 1000 mg/L initial conc. and 30°C	This study

Table 5 Intraparticle diffusion rate constants reported in the literature.

Adsorbents	Constants (Units)	Values	HMs and conditions	References
Intraparticle diffusion equation				
a. Oil palm fibre (*Elaeis guineensis*)	K_{id} (min^{-1})	65.539	Pb (II) unmodified adsorbent	Demirbas *et al.* 2004
b. Apricot stone (*Prunus armeniaca*)		13.662	Cr (VI) at pH of 4.0	Demirbas *et al.* 2004
c. Almond shells (*Prunus dulcis*)		11.847	Ni (II) at pH of 4.0	Demirbas *et al.* 2004
d. Maize cob (*Zea mays*)		49.42	Co (II) unmodified adsorbent	Igwe and Abia 2007
e. Cassava fibre (*Manihot esculenta*)		4.234	Mn (II) unmodified adsorbent	Abia and Didi 2007b
f. Cocoa pod husk (*Theobroma cacao*)		63.93	Cr (VI) at 1000 mg/L initial conc. and 30°C	This study
Elovich equation				
a. Cornelian cherry (*Cornus mas*)	α (mg g^{-1} min^{-1})	0.641	Cr (VI) at pH of 4.0	Demirbas *et al.* 2004
b. Waste acorn of *Quercus ithaburensis*		536.86	Cr (VI) at 100 mg/L initial conc. and 25°C	Malkoc and Nuhoglu 2007
c. Cocoa pod husk (*Theobroma cacao*)		7190	Cr (VI) at 1000 mg/L initial conc. and 30°C	This study
a. Cornelian cherry (*Cornus mas*)	β (g mg^{-1})	3.794	Cr (VI) at pH of 4.0	Demirbas *et al.* 2004
b. Waste acorn of *Q. ithaburensis*		1.578	Cr (VI) at 100 mg/L initial conc. and 25°C	Malkoc and Nuhoglu 2007
c. Cocoa pod husk (*Theobroma cacao*)		0.126	Cr (VI) at 1000 mg/L initial conc. and 30°C	This study
McKay and Poots Equation				
a. Chitosan beads	K (mg g^{-1} min$^{-0.5}$)	(i) 8.2	Molybdate at initial conc. of 12 mg/L	Guibal *et al.* 1998
		(ii) 3.0	Vanadate at initial conc. of 10 mg/L	Guibal *et al.* 1998
b. Coconut fibre (*Cocos nucifera*)		(i) 127.54	Pb (II) unmodified adsorbent	Igwe *et al.* 2008
		(ii)125.70	Hg (II) unmodified adsorbent	Igwe *et al.* 2008
c. Cocoa pod husk (*Theobroma cacao*)		1.05	Cr (VI) at 1000 mg/L initial conc and 30°C	This study

pore (Michard *et al.* 1996). Renkin (1954) established empirical relationships between the solid diffusivity/molecular diffusivity ratio and the moleculer size/pore size ratio. This has been described by Papelis *et al.* (1995), for the adsorption of cadmium and selenite on micro- and mesoporous transition alumina, by relating the ion diffusivities to their hydrated radii and to the pore size distribution of the materials. Tanaka *et al.* (1984) observed that diffusion in alginate beads was controlled by the molecular size of the substrate: for the smallest substrates the diffusivity was equivalent to those obtained in water while for the largest substrates, no transfer was observed from the solution to the particle. Guibal *et al.* (1998) reported that the difference in the sorption behaviour may be related to the size of hydrated ions: single cadmium ions in contrast to polynuclear molybdate or vanadate forms.

A comparison of the kinetic rate constants and intraparticle diffusion rate constants reported in literature with this study is shown in **Table 4** for the kinetics and **Table 5** for the intraparticle diffusion equations. It could be seen that on the average, the result of the present study agrees well with that reported in literature for different metal ions and different adsorbents. It could be observed that the values obtained for the constants in this study agree well with those reported in literature. Although the values lie within the same range, it could be seen from **Tables 4** and **5** that there were little variations which depended on the metal ion; adsorbent type and adsorption conditions. For instance, Guibal *et al.* (1998), reported that the McKay and Poots constant depended on the particle size of adsorbent, initial concentration of metal ion, and adsorbent type, whether the chitosan used was in beads or in flakes (i.e. adsorbent condition or state).

CONCLUDING REMARKS

CPH has been primarily applied in very small quantity as additive to animal feed. Hence, greater quantity of this husk is still available as waste in the environment. HMs have been established to be detrimental to both man and biodiversities. Therefore, the adsorption of these HMs; Al (III), Ni (II) and Cr (VI) ions from aqueous solution using CPH was feasible, hence depicting a promising technology in water and wastewater treatment and re-use. Also CPH has shown to be a good adsorbent for HM removal. The validity of the kinetic models was tested by the magnitude of the regression coefficients R^2 and the differences in their fitness was tested using a two-way ANOVA without replication at $P < 0.05$. The sorption process was well correlated by the pseudo-second order kinetic equation and was also found to follow film diffusion mechanism.

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