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Sorption Kinetics and Intraparticle Diffusivities of Pb (II), Fe (III) and Cd (II) ions on Unmodified Raphia Palm Fruit (*Raphia hookeri*) Endocarp

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ABSTRACT

Sorption kinetics of Pb (II), Fe (III) and Cd (II) ions from aqueous solution by unmodified raphia palm (*Raphia hookeri*) fruit endocarp was carried out through time dependent studies. The kinetic behaviour of the metal ions towards the adsorbent was studied with the pseudo-second order rate model. The rate constants (g/mg-min) were determined to be 7.02×10^{-3}, 1.02×10^{-2} and 2.62×10^{-3} for Pb (II), Fe (III) and Cd (II) respectively. Sorption capacities based on the pseudo-second order model were found to be 196.08 mg/g, 169.5 mg/g and 188.68 mg/g for Pb (II), Fe (III) and Cd (II) respectively. Intraparticle diffusion models such as fractional attainment to equilibrium (FATE), McKay and Poots, Weber and Morris and Elovich equations were also used to investigate the predominant sorption mechanism. The poor fit of these intraparticle diffusion models as seen from their correlation coefficient values which ranged from 0.718 to 0.872 for Elovich equation, 0.730 to 0.837 for external film diffusion, 0.825 to 0.819 for particle diffusion, and 0.719 to 0.872 for percent adsorbed, showed that the sorption mechanism was not intraparticle diffusion controlled but film diffusion controlled.

Keywords: adsorption, agricultural by-products, diffusion transport, environment, heavy metals, kinetics

INTRODUCTION

One of the constant threats to environmental health is the lethal effects of heavy metals (HM) ions in the aqueous phase. Many industries such as mining, smelting, electroplating, dyes, textiles, tanneries, oil refineries, discharge HMs as wastewater into the environment. The amount of these HMs in the environment has been reported to increase as a result of industrialization (Igwe *et al*. 2011a). HMs are also found in storm water runoffs from urban and agricultural areas especially where atmospheric deposition, manure and fertilizer application have led to HM loads to soil (Kaczala *et al*. 2009). Studies have associated HMs such as lead, iron, cadmium, copper, zinc, mercury, vanadium and arsenate with toxic effects and the ability to produce reactive oxygen species (ROS), resulting in lipid peroxidation and antioxidant enzymes alterations, leading to oxidative stress (Hu 2000).

A lot of concern has been shown by many quarters of society and intellectual input has been made in the form of research into remediation or removal of hazardous HM ions from the aqueous environment. One of the methods in contemporary research work in this direction is the utilization of vegetable and agricultural waste materials to remove metal ions from the aqueous phase. Adsorption or biosorption by vegetable and agricultural by-products has been reported to be an effective method of removal of HMs. Such reported materials include cassava waste (Abia *et al*. 2003) maize cob and husk (Abia and Igwe 2003, 2005; Opeolu *et al*. 2009), fluted pumpkin waste (Horsfall and Spiff 2005), nipah palm shoot (Wankasi *et al*. 2006), maize tassel (Zvinowanda *et al*. 2009), orange peel, sugarcane bagasse, wheat husk, mango sawdust, neem sawdust (Vinodhini and Das 2009, 2010), sawdust of spruce (*Picea abies*) (Urik *et al*. 2009), *Pinus sylvestris* sawdust (Kaczala *et al*. 2009), luffa cylindrical fibre (Saueprasearsit *et al*. 2010), cocoa pod husk (Igwe *et al.* 2011a), coconut fibre (Igwe *et al.* 2011b), boiler fly ash (Okoronkwo *et al.* 2011), modified sugar beet pulp (Zolgharnein *et al*. 2011), to mention but a few. Such biosorbents have been reported to also be inexhaustible, low-cost, non-hazardous materials and easily disposed by incineration (Zolgharnein *et al.* 2010a, 2010b, 2011). Some of the adsorbents have been modified with chelating agents to increase the sorption capacity of the adsorbents, for example, Chen *et al.* (2011) reported on the use of Ferric-impregnated volcanic ash (FVA) for the adsorption of arsenic from contaminated water.

The degree to which HM ions will adsorb per unit time on the surface of a biomass depends among other factors on the rate of transfer of the HM ions to the surface. The attainment of equilibrium is also a function of the rate of diffusion of the adsorbate. This is the reason why the kinetics of the process becomes important in the treatment of adsorption. Rate studies of adsorption are important in obtaining the optimal sorption conditions and the best adsorbate transfer dynamics for the process. Kinetic models have been developed over the years to explain the dynamics of adsorption. These include the first-order and second-order rate equations. The rate of transfer of adsorbates from the solution to the adsorbent is dependent on some other solution processes as bulk diffusion, film diffusion, chemical reaction and intraparticle diffusion (Ho *et al*. 2000). Therefore, the use of rate transfer models helps to highlight the prevailing transfer dynamics of a particular adsorption process.

Raphia palm fruit is abundant in the swamp forest of the Niger Delta. The fruits have no present economic value and available research work on this fruit does not point in this direction. This paper presents the kinetic properties of the adsorption of Pb (II), Fe (III) and Cd (II) on unmodified raphia palm fruit endocarp.

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Original Research Paper

MATERIALS AND METHODS

Adsorbent preparation

Raphia palm (*Raphia hookeri*) fruit bunches at maturity stage were collected from the swamp forest of Ogu village in Yenagoa Local Government Area of Bayelsa State, Nigeria. The fruits were separated from the bunch and left for about a week. The epicarp, mesocarp and endocarp were separated, washed and air dried. The endocarp (nut) was ground by ball mill abrasion after drying in the oven. Four sizes of ground endocarp were obtained by passing sample through the 75,150, 300, and 600 µm sieves. The sample sizes were soaked in 0.1M HCl for about two days and washed in distilled water until a constant pH (6.6 ± 0.2) was obtained. The washed samples were dried in the oven at 68°C for 2 days. The pretreated samples were stored in transparent and air-tight plastic bottles at ambient laboratory temperatures (about 28-30°C) for further analysis.

Adsorbate/ Instruments

Adsorbates for experiments were obtained from the following: Iron (III) ions from reagent grade iron (III) chloride Lab Chemicals Ltd, India; Lead (II) ions from analar grade lead (II) nitrate, BDH Poole, U.K. and cadmium (II) ions from reagent grade cadmium (II) acetate, Riedel-de-Hen,Germany. Agitation of solutions was carried out with Barnstead/Labline U.K. maxQ 2000 Orbital shaker (20-500 rpm). Centrifuging work was done with B. Bran Scientific & Instument Co., UK 80-1 Electric Centrifuge and temperature maintenance was with the aid of a Thermo Electron Corp., UK Precision water bath. Analysis of supernants was done with Unicam photon atomic absorption spectrophotometer.

Effect of contact time on adsorption

0.2 g sample of 600 µm of raphia palm fruit endocarp was put into five tubes and 10 mL of 40 mg/L of Fe (III), Pb (II) and Cd (II) solution was added to each tube respectively. The tubes were consecutively subjected to agitation by shaking on a Barnstead/Labline max Q 2000 shaker for intervals of 5, 10, 20, 40 and 60 min. The mixtures were centrifuged at 3500 rpm for 5 min and decanted. Supernatants were stored in plastic bottles for analysis in atomic absorption spectrophotometer.

RESULTS AND DISCUSSION

Sorption capacity

The effect of contact time required for maximum adsorption of HM ions by raphia palm nut is represented in **Fig. 1.** The percent adsorbed against time is shown in **Fig. 2**. Maximum adsorption for all the three HMs was attained under 10 min. The time curve flattens after 10 min and is continuous over the rest of the periods. This continuity indicates the formation of a monolayer on the outer interface of the adsorbent (Karhikeyan *et al.* 2005). It has been observed by previous workers (Ho *et al.* 1995; Gardea-Torresday *et al.* 1998) that a short contact time necessary to reach equilibrium in adsorption studies indicates that the predominant mechanism is chemisorption. From **Fig. 1** and **2**, the order of adsorption is Cd > Pb > Fe. The percent adsorption for all the contact times is highest for Cd which indicates that its rate of transfer and adsorption was highest among the three HM ions. The results also show a differentiated adsorption of the metal ions. Differentiated adsorption of metal ions from aqueous solutions has been ascribed to some factors (Ho *et al.* 1995): (i) sizes of metal ions (ii) affinity of the metal ions for some active groups on the biomass and (iii) nature of anions of the salt of the metals.

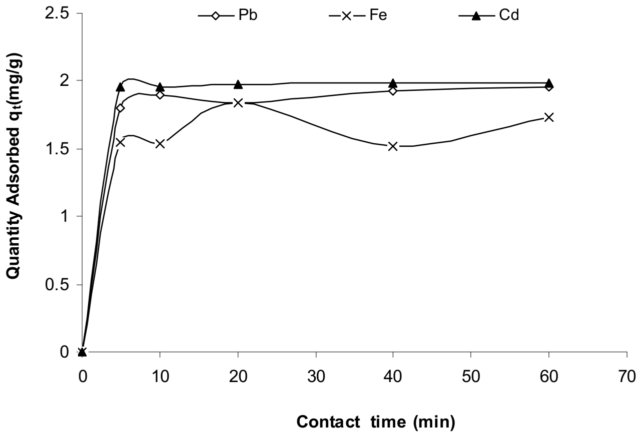

Fig. 1 Effect of contact time on adsorption of Fe^{3+}, Cd^{2+} and Pb^{2+} ions by unmodified raphia palm fruit endocarp (600 µm).

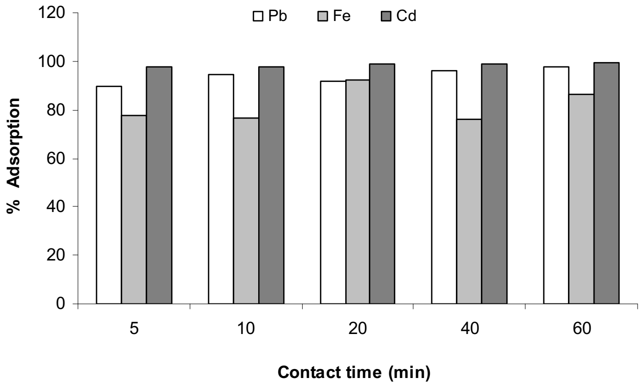

Fig. 2 Bar graph of percent adsorption of Fe^{3+}, Cd^{2+} and Pb^{2+} ions with contact time.

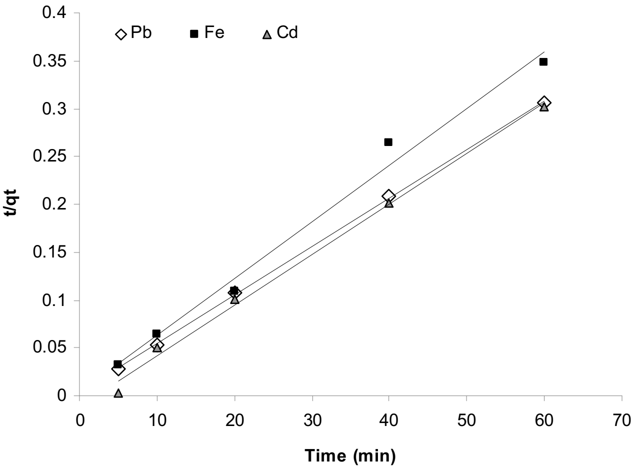

Fig. 3 Pseudo-second order rate plot for Pb (II), Fe (III) and Cd (II) ions adsorption on unmodified raphia palm fruit endocarp (600 µm).

Kinetics of metal ion adsorption

The kinetic behaviour of the HM ions towards the adsorbent was studied with the pseudo-second order rate model (Ho *et al.* 1995), which takes the form of equation 4:

$$t/q_t = 1/h_o + t/q_e \quad (4)$$

where q_t is the amount of HM ion adsorbed on the biomass surface (mg/g) at time, t, q_e is the amount of HM ion adsorbed at equilibrium (mg/g), h_o is the initial sorption rate given by:

$$h_o = k_2\, q_e^2 \quad (5)$$

k_2 is the pseudo-second order rate constant (g/mg-min). The kinetic parameters were obtained from a plot of t/q_t against t. A linear plot confirms the pseudo-second order kinetics as giving a good fit to the adsorption process. **Fig. 3** shows the pseudo-second order rate plot for all the three

Table 1 Kinetic parameters for adsorption of metal ions.

Metal ion	K (g/mg min)	q	h (mg/g min)	R
Pb	7.03 × 10	196.08	270.0	0.9997
Fe	1.01 × 10	169.5	291.3	0.9879
Cd	-2.62 × 10	188.68	- 93.46	0.9948

metals. The plots are all linear with R^2 values above 0.9, which indicates that the sorption occurred at a pseudo-second order rate. The pseudo-second order kinetic parameters for the adsorption process are given in **Table 1**.

The pseudo-second order kinetic model for the adsorption process indicates a high capacity of the adsorbent for the HM ions. By this model, the sorption capacity (q_e) for Pb^{2+}, Fe^{3+} and Cd^{2+} are 196.08, 169.5 and 188.68 mg/g, respectively. The model gave the following sequence in the listed parameters:

R^2: $Pb^{2+} > Cd^{2+} > Fe^{3+}$
q_e: $Pb^{2+} > Cd^{2+} > Fe^{3+}$
k_2: $Fe^{3+} > Pb^{2+} > Cd^{2+}$
h_0: $Fe^{3+} > Pb^{2+} > Cd^{2+}$

The first two parameters (R^2 and q_e) nearly approximates the earlier adsorption order but for Pb^{2+} taking the place of Cd^{2+}. However, the sequence of the rate constants is the opposite of the earlier order based on the time of contact. Fe^{3+} has the highest values for k_2 and h_o and this implies that it will be adsorbed better than the other metals in a mixed metal ion solution (Horsfall *et al.* 2004). From **Table 1**, the values of k_2 obtained from this work, closely approximates to that reported in previous studies; 0.038 g μg^{-1} min^{-1} for adsorption of Pb^{2+} onto *Pinus sylvestris* sawdust (Kaczala *et al.* 2009), 0.0884 g mg^{-1} min^{-1} for adsorption of chromium (VI) onto neem sawdust (Vinodhini and Das 2010), 0.012 g mg^{-1} min^{-1} for adsorption of arsenic (V) onto sawdust of spruce (*Picea abies*) (Urik *et al.* 2009).

Also, intraparticle diffusion models for adsorption were applied to the data to determine the rate limiting mechanism. Three equations for intraparticle diffusivity in respect of external film diffusion, particle diffusion, and percent adsorbed (R) as well as the Elovich equation were applied to the data. The intraparticle diffusivity for particle diffusion mechanism was estimated using the linear driving force concept equation (Vinod and Anirudhan 2002) in which the fractional attainment to equilibrium (FATE) factor α is used. This is given by equation 3.

$$\ln(1-\alpha) = -k_p t \qquad (3)$$

$$\text{where, } \alpha = [M]_t^{n+} / [M]_\infty^{n+} \qquad (4)$$

k_p is the rate constant for intraparticle diffusivity and t is the time in minutes, $[M]_t^{n+}$ is the amount of HM ion of charge n+ adsorbed at time t and $[M]_\infty^{n+}$ is the amount of HM ions of charge n+ adsorbed at infinity or equilibrium. Intraparticle diffusivity for particle diffusion for all the metal ions from this equation is shown in **Fig. 4**. The intraparticle diffusion by external film diffusion mechanism was tested using equation 5 (McKay and Poots 1980). This equation is given as:

$$q_t = X_i + K_i t^{\frac{1}{2}} \qquad (5)$$

where q_t is the amount adsorbed at time t, X_i is the boundary layer thickness and K_i is the initial rate constant of adsorption. The plot of this equation is shown in **Fig. 5**.

Another model for intraparticle diffusivity applied to the data is that expressed as equation 6 (Weber and Morris 1963; Srivastava *et al.* 1989):

$$R = K_{id} (t)^a \qquad (6)$$

This is linearised to equation (7) as

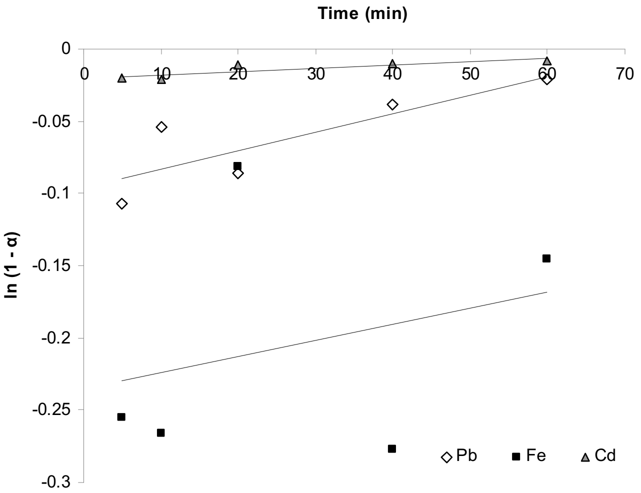

Fig. 4 Intraparticle diffusivity (particle diffusion) plot for Pb (II), Fe (III) and Cd (II) ions adsorption on unmodified raphia palm fruit endocarp (600 µm).

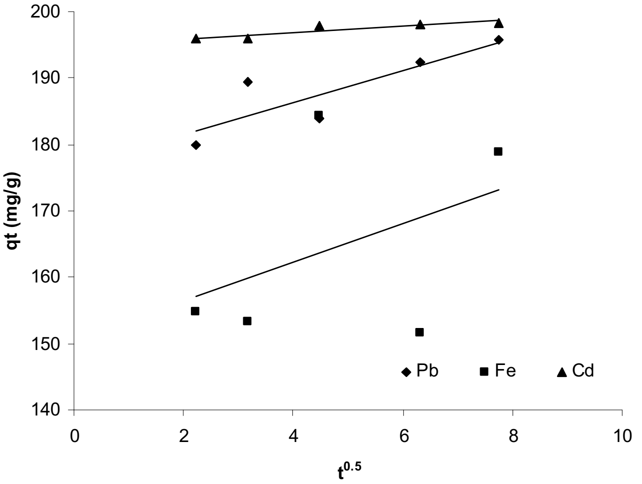

Fig. 5 Intraparticle diffusivity (external film diffusion) plot for Pb (II), Fe (III) and Cd (II) ions adsorption on unmodified raphia palm fruit endocarp (600 µm).

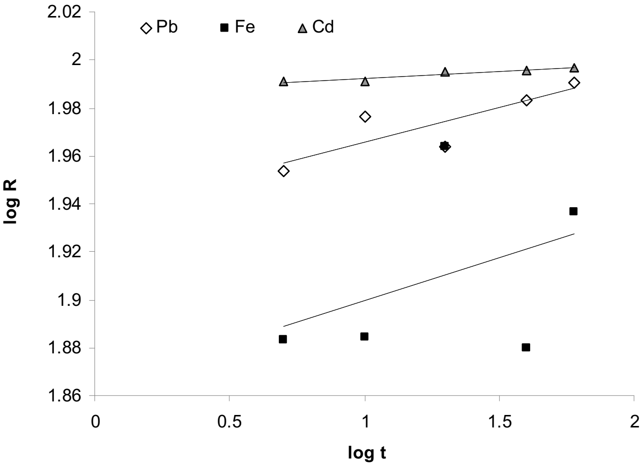

Fig. 6 Intraparticle diffusivity (percent adsorption) plot for Pb (II), Fe (III) and Cd (II) ions adsorption on unmodified raphia palm fruit endocarp (600 µm).

$$\log R = \log K_{id} + a \log(t) \qquad (7)$$

where R is the percent HM ion adsorbed, t is the contact time in minutes, a is constant that depicts the adsorption mechanism. The plot of this model is shown in **Fig. 6**.

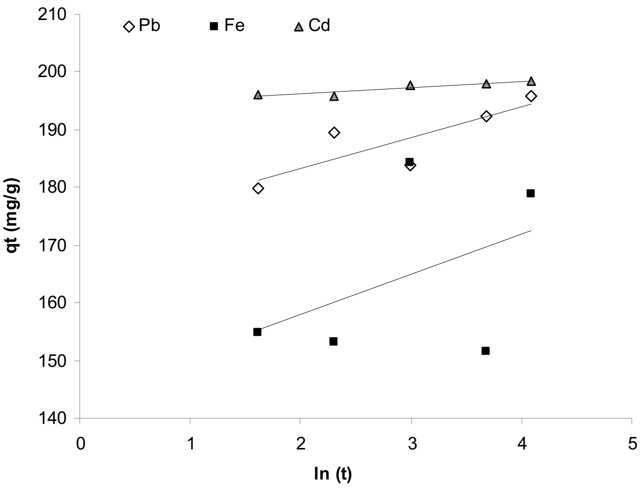

Fig. 7 Elovich plot for Pb (II), Fe (III) and Cd (II) ions adsorption on unmodified raphia palm fruit endocarp (600 µm).

Table 2 Correlation values for some kinetic models for adsorption.

Metal ion	Elovich equation	Intraparticle diffusivity (External film)	Intraparticle diffusivity (Particle diffusion)	Intraparticle diffusivity (% adsorbed)
	R^2	R^2	R^2	R^2
Pb^{2+}	0.718	0.730	0.825	0.719
Fe^{3+}	0.196	0.101	0.0047	0.166
Cd^{2+}	0.872	0.837	0.819	0.872

The fifth kinetic model employed in data analysis is the Elovich equation, which is simplified (Chien and Clayton 1980) as equation 8:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \qquad (8)$$

where α is the initial adsorption rate (mg/g-min), β is the desorption rate constant (g/mg) during one experiment. The plot for Elovich equation is shown in **Fig. 7**.

The linear regression coefficient (R^2) was used as the fitting parameter for all the equations used for the kinetic models. The R^2 values of all the models used are given in **Table 2**. The R^2 values for the models used for the data show that they could not perfectly describe the sorption of all the three metal ions. Though Pb^{2+} and Cd^{2+} were better and more highly correlated than Fe^{3+} in all, none of the models could be said to be the rate limiting mechanism for the adsorption. The application of intraparticle diffusion models to sorption processes has been reported. Film diffusion mechanism as against particle diffusion mechanism have been reported as the rate limiting mechanism for sorption processes (Horsfall *et al.* 2003; Kaczala *et al.* 2009; Urik *et al.* 2009; Igwe *et al.* 2011a). Also, some researchers have reported intraparticle diffusion as the rate limiting mechanism for sorption processes (Juang and Lin 1994; Abia and Igwe 2005; Abia and Asuquo 2006).

Going by the observed order of adsorption of the metal ions in **Figs. 1** and **2** (Cd > Pb > Fe), it may be deduced that the anions of the metal salts played significant contributory roles in the extent of adsorption. If ionic size is to rank first in the above mentioned determinants, then the capacity of Fe^{3+} ion should be greater than the other metals by reason of its smaller ionic size (0.64 Å). However, it (Fe^{3+}) comes last in the order. The order of increasing basic strength of the anions in this work is: $Cl^- < NO_3^- < C_2H_3O_2^-$. The anion of Fe^{3+}, Cl^- is the weakest Lewis base among the three anions, therefore a chemisorption process will proceed slower in $FeCl_3$ than for $Pb(NO_3)_2$ and $(CH_3COO)_2Cd$. The chloride ion has a higher tendency to remain in solution with its cation than the other two anions. Likewise, the NO_3^- ion in Pb is less basic than $C_2H_3O_2^-$ in Cd, thus the rate of Pb adsorption will be less than Cd. Besides the anionic nature, Cd^{2+} has a smaller ionic size (0.97 Å) than Pb^{2+} (1.20 Å), so adsorption rate will be higher for Cd because the smaller the ionic radius the faster the rate of adsorption (Ho *et al.* 1995). The position of Fe^{3+} in the order of the two rate constants (k_2 and h_o) from the pseudo-second model, suggests that its smallest ionic size may be the major enhancement factor, while the precedence of Pb^{2+} over the much smaller sized Cd^{2+} may be due to greater affinity for active functional groups in the adsorbent. The highest rate constants of Fe^{3+} may be attributed to its smallest ionic size and the highest ease of "physisorptive" transfer of substrate to the adsorbent. Physisorption is usually faster than chemisorption.

CONCLUSION

The pseudo-second order model was the controlling transfer kinetics for the adsorption. The high pseudo-second order kinetic parameters show that raphia palm fruit endocarp is an excellent adsorbent for Fe (III), Pb (II) and Cd (II) ions. The short contact time was indicative of chemisorption as the predominant process. Though significantly correlated in Cd (II) and Pb (II), intraparticle diffusivity was not the rate limiting mechanism for the adsorption. The sequence of adsorption parameters of the metal ions indicates that ionic size and anion of the salts played significant roles in the dynamics of the adsorption. Adsorption of Cd (II) onto unmodified raphia palm nut attained 99% capacity. This observation signifies that modification and proper choice of experimental conditions could attain a complete removal capacity of the biomass.

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