Sorption Kinetics of Cr(lll), Cd(ll) and Pb(ll) ions from aqueous solution by Monkey bread (*Piliostigma thonningii*) seed pod

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Abstract Adsorbents of natural origin are widely used for industrial wastewater treatment in order to replace currently costly methods of heavy metals removal from solutions. For that purpose, the potential of an agricultural waste, *Piliostigma thonningii* pod as an adsorbent in the removal of Cr(III), Cd(II) and Pb(II) ions from aqueous solution was investigated. The removal of these metal ions by the biosorbent has been found to be dependent on contact time and adsorbent dose. Results showed that the adsorption process was fast and that equilibrium was achieved within 70 min. Results further showed that increase in adsorbent dose caused enhancement in the removal efficiencies for the metal ions by the adsorbent. The applicability of the pseudo first-order, pseudo second-order and intraparticle diffusivity models was also investigated. Results showed that the experimental data were better correlated by the pseudo second-order model. The transport mechanism of the process was found to follow intra-particle diffusion.

Keywords Adsorption kinetics, Heavy metals, Kinetic models, *Piliostigma thonningii*

Introduction

The world is faced with the problems of heavy metal contamination of the environment. Heavy metals are among the most common contaminants found in wastewater and have been observed to be significantly toxic to aquatic organisms and humans (and in some cases posing a great carcinogenic, mutagenic and terartogenic effects on humans who feed on the aquatic animals). Some of these heavy metals include: copper, cadmium, lead, mercury, arsenic, cobalt, zinc, chromium, nickel *etc*. Many of the elements considered as heavy metals have no known benefits for human physiology. Chromium, lead and cadmium are prime examples of such toxic metals and this forms the basis for their selection in the present study. Exposure to cadmium causes severe health effects to human ranging from renal dysfunction, liver damage, bone degradation and hypertension. It is also a potent neuro-toxic metal with a permissible limit of 0.003 mg/L in drinking water and has been identified as a potential carcinogen [1]. Exposure to lead had been known to cause encephalopathy, seizures and mental retardation particularly in young children [2]. Young children are more susceptible to the effect of lead exposure because they absorb several times the percent ingested compared with adults and because their brains are more fragile, even a brief exposure may influence development processes. Chromium occurs in the environment primarily in two valence states, trivalent chromium, Cr(III) and hexavalent chromium Cr(VI). Exposure may occur from natural or industrial sources of chromium. Chromium(III) is much less toxic than chromium(VI). The respiratory tract is the major target organ for chromium(III) toxicity.

Conventional methods of removing heavy metals such as chemical precipitation, ion-exchange, reverse osmosis, solvent extraction and adsorption onto activated carbon are expensive and some of these techniques most often generate post-sludge after treatment. Therefore, more effective, environmentally friendly and cheaper materials are therefore required for the removal of heavy metals from aqueous solution. In recent years, several studies have been carried out on the adsorption of toxic metal ions from aqueous effluents using agricultural by-products [3-5]. Agro-based materials have been reported as having the potential to adsorb and remove large amount of metal ions from aqueous solution [6, 7]. A few number of biosorbents that have been employed in heavy metals adsorption from aqueous solutions include: maize cob and husk [8], sunflower stalk [9], Chistosan and N-Carboxymethyl chitosan [10], African Breadfruit [11] *etc*.

In biosorption, removal of metal ions aids in effective usage of bio-wastes as the heavy metals stick on the surface of the biomass. The adsorption of heavy metals by these materials might be attributed to their proteins, carbohydrates, and phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate and amino groups that can bind metal ions [12]. Biosorption process generally requires biological materials which have high metal binding capability and specific heavy metal selectivity. It may involve one process or a blend of processes like adsorption, electronic interaction, chelation, micro-precipitation and ion-exchange [13] The present study therefore seeks to examine the potential of an agro-based material, the seed pod of *piliostigma thonningii* as an adsorbent in the removal of Cr(III), Cd(II) and Pb(II) ions from aqueous solution.

Materials and Methods
Preparation of the adsorbent
The adsorbent, *Piliostigma thonningii* seed was obtained at Michael Okpara University of Agriculture, Umudike, Abia state Nigeria. The pods were carefully removed, washed with de-ionized water, dried and crushed with a blender. The crushed samples were sieved through to obtain 60 μm mesh size. The sieved samples were soaked in 0.3 M HNO_3, stirred for 30 min and left undisturbed for 24 h. They were then filtered through Whatman no. 41 filter paper and rinsed thoroughly with de-ionized water and sundried for 2 h. The adsorbent was kept in an oven at 105 ºC for 2 h and finally stored in a tight plastic container. The treatment of the adsorbent with 0.3 M HNO_3 helps in the removal of debris or soluble biomolecules that might interact with the metal ions during sorption.

Adsorption Experiments
All the reagents used were of analytical grades and were used without further purification. De-ionized water was used in the preparation of all sample solutions. Batch adsorption studies of Cr(III), Cd(II) and Pb(II) ions onto *piliostigma thonningii* were investigated as a function of adsorbent dose and contact time. The effect of adsorbent dosage on the adsorption of the metal ions was studied at a fixed temperature of 30 ºC and at an initial metal ion concentration of 50 mg/L. The study was carried out at the optimum adsorption pH of the metal ions by the adsorbent which had been determined in our previous work [14]. The adsorption was carried out using varying masses of the adsorbent ranging from 0.05 g to 0.30 g. This was done by introducing 50 cm^3 of each metal ion solution into different 250 cm^3 Erlenmeyer flasks containing 0.05, 0.15, 0.20, 0.25 and 0.30 g of the adsorbent of particle size 60 μm. The mixtures were agitated intermittently for 2 h in a rotary shaker and then filtered. The metal ion content of each filtrate was finally determined using UNICAM Atomic Absorption Spectrophotometer (Solar AAS 500).

The effect of contact time on adsorption of the metal ions was studied by carrying out the adsorption process at different time intervals, at a temperature of 30 ºC and at an initial concentration of 50 mg/L of each of the metal ions Cr(lll), Pb(ll) and Cd(ll). Exactly 50 cm^3 portions of 50 mg/L of each of the metal ion solution was introduced into different 250 cm^3 Erlenmeyer flasks containing 0.5 g of the adsorbent. The mixtures were shaken intermittently in a rotary shaker at different contact times (20, 40, 60, 70 and 90 min). At the end of each time, the content of each flask was filtered with a filter paper, centrifuged and the residual concentration of metal ion analyzed using the UNICAM Atomic Absorption Spectrophotometer. The procedure was carried out in triplicates and mean residual concentration

of each metal ion taken. The amount adsorbed (mg/g) was calculated from the average residual metal ions in solution after adsorption.

The percentage adsorption of the metal ions by the adsorbent was evaluated using the relation.

$\% \ R = \frac{(C_o - C_e)}{C_o} \times 100$

While the adsorption capacity, q_t (mg/g) at different times was done using mass balance equation [15]:

$q_t = \frac{(C_o - C_t)v}{m}$

Where % R = percentage of the metal ion adsorbed, C_o = initial metal ion concentration in mg/L, C_t = residual metal ion concentration in solution (mg/L), V = volume of metal ion solution used in dm^3 and m = the dry mass of the adsorbent in g [16].

Results and Discussion
Effect of adsorbent dose
The influence of adsorbent mass on the adsorption of the metal ions Pb(II), Cd(II) and Cr(III) by the adsorbent *P. thonningii* was measured at five different adsorbent concentrations (0.05, 0.15, 0.20, 0.25 and 0.30 g/L) for initial metal ion concentration of 50 mg/L. The equilibrium amount adsorbed and the removal efficiencies are presented in Figures 1 and 2. From Figure 1, it can be observed that the amount of the metal ions Pb(II), Cd(II) and Cr(III) adsorbed decreased as adsorbent concentration increases. This Result shows that more active sites are utilized at lower adsorbent concentration, producing a higher adsorption capacity, while only part of the active sites are occupied by these metal ions at higher adsorbent concentration, leading to a lower adsorption capacity and this is in accordance with previous study [17]. Also, from Figure 2, it is clear that percentage removal of Pb(II), Cd(II) and Cr(III) ions from their solution increased with increasing adsorbent concentration. This increase may be due to the presence of more active adsorption sites for these metal ions at higher adsorbent concentrations and a similar observation had been made [4]. The plots (Fig. 2) show in general that the percentage removal of these metal ions increased with increasing adsorbent dosage while the amount adsorbed per unit mass decreased and became almost constant at higher dosages (*i. e.,* $\geq 0.25 \ g/L.$). The increase in percent removal of these metals with increase in the dosage of the adsorbent is due to the greater availability of the exchangeable sites or surface area of the adsorbent while the decrease in sorption capacity with increasing adsorbent dosage is mainly due to unsaturation of adsorbent sites through the adsorption reaction. It was also observed that there was no significant observation in the amount adsorbed as the mass of adsorbent increased beyond 0.25 g/ L and this is reflected in the leveling effect observed with the curves. The increasing adsorption trend for the metal ions generally follows: Pb(II) > Cr(III) > Cd(II) for adsorption onto the adsorbent.
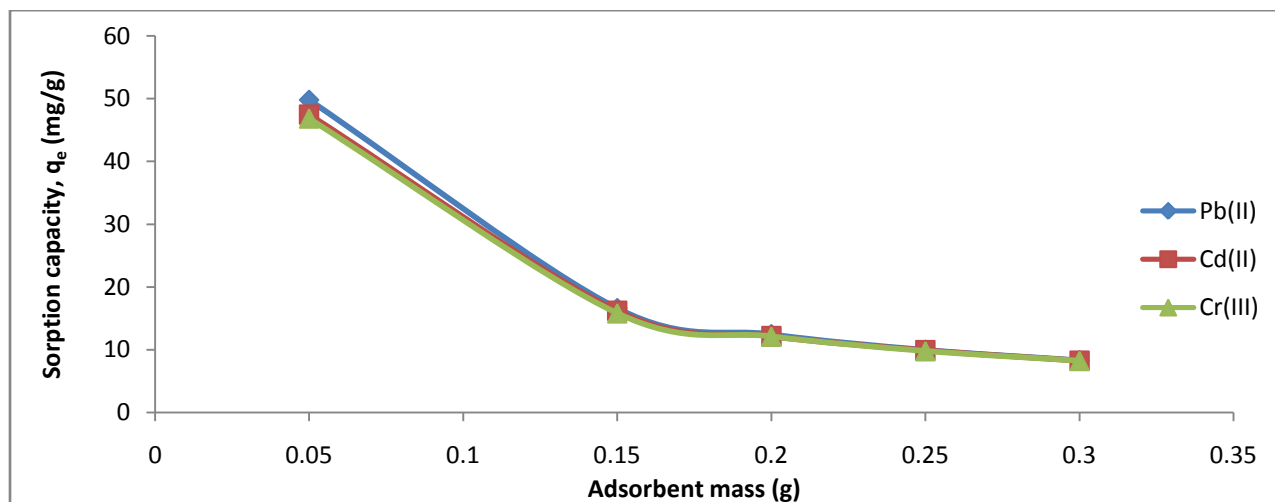

Figure 1: Effect of adsorbent mass on the amount of metal ion adsorbed onto P. thonningii
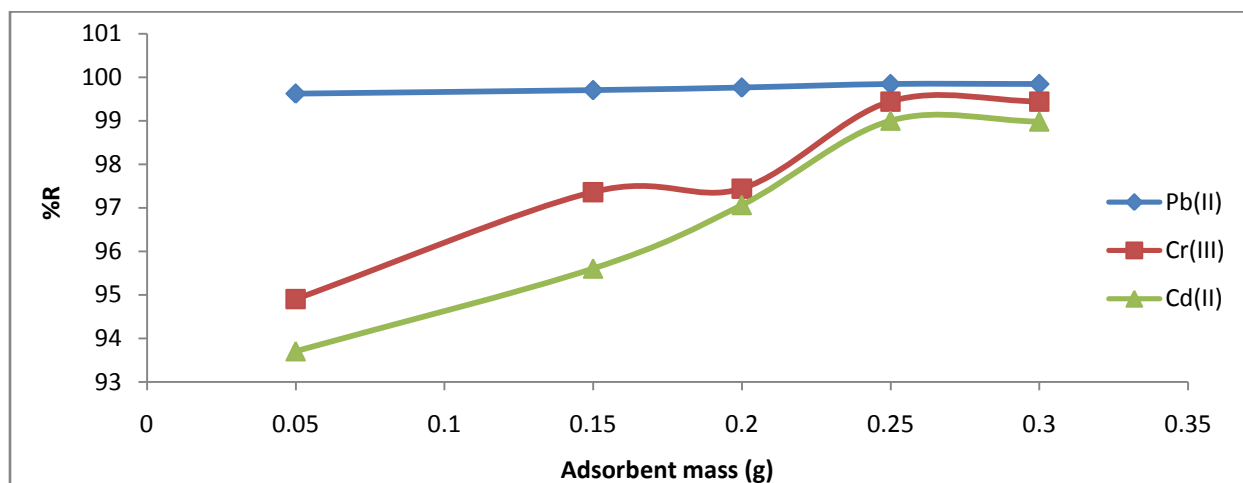
Figure 2: Effect of adsorbent mass on the metal-removal efficiencies of P. thoningii as an adsorbent

Effect of Contact Time

The effect of contact time on the adsorption of the metal ions is presented in Figure 3 and the results indicate that adsorption efficiencies increased with increase in contact time before equilibrium was attained. Optimum contact time for adsorption of the metal ions Cd(II), Cr(III) and Pb(II) by 0.5 g of the adsorbent was 70 min. This result is vital since equilibration time is one of the important parameters to be considered for an economical wastewater treatment system. The plots indicate that greater amount of the heavy metal ions were taken up by the adsorbent within 70 min and that equilibrium was attained in less than 90 min.
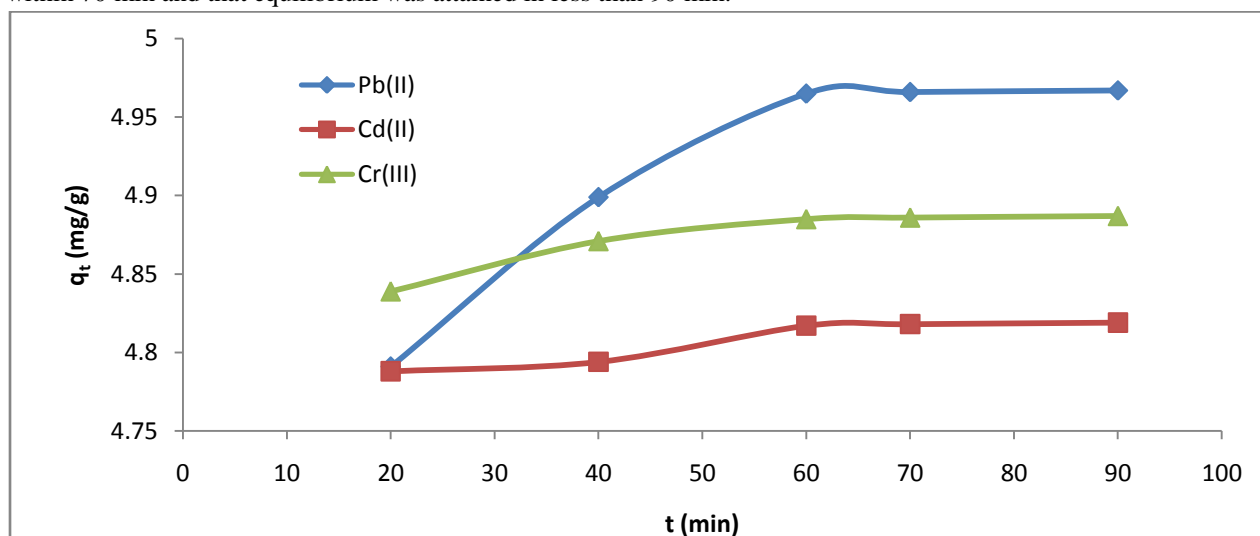

Figure 3: Effect of contact time for adsorption of metal ion onto Piliostigma thoningii

Adsorption Kinetics

In order to establish the adsorption rate and the mechanisms of the adsorption of the metal ions Cr(III), Cd(II) and Pb(II) onto the *P. thonningii*, the following kinetic models were applied to the experimental adsorption data viz., pseudo first-order, pseudo second-order and intra-particle diffusion models.

The pseudo first-order model

The pseudo first-order equation is generally given as:

$$\log (q_e - q_t) = \log q_e - \frac{k \cdot t}{20303}$$

Where q_e and q_t are the adsorption capacities (mg/g) at equilibrium and time t, respectively, k_1 is the rate constant of pseudo first-order model (min^{-1}). The plots of ln ($q_e - q_t$) vs t yielded straight lines from which k_1 and q_e were determined from the slope and intercept of the linear plots. The pseudo first-order plots for the adsorption process are shown in Figure 4, while the calculated kinetic parameters are presented in Table 1. The linear plots show that the biosorption of the metal ions onto *P. thonningii* did not follow pseudo first-order kinetics as observed from the low R^2 values obtained from the plots.
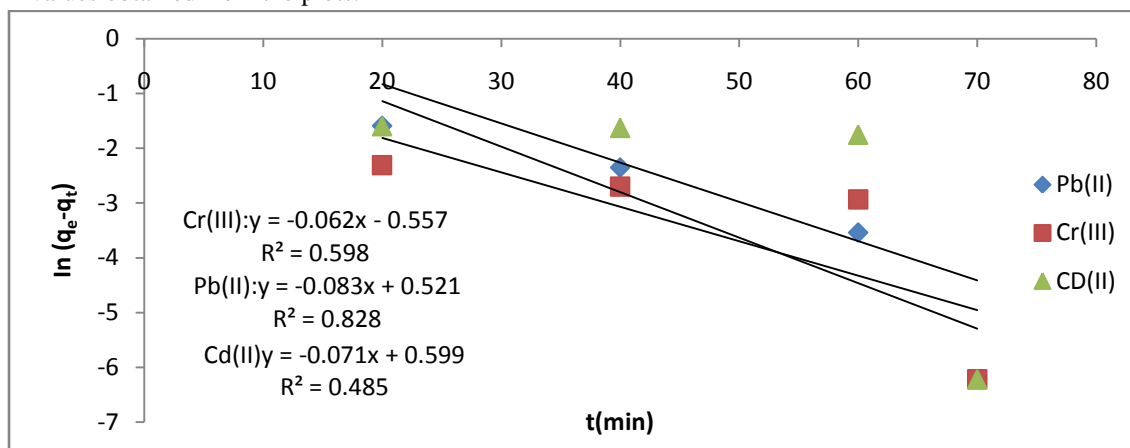

Cr(III):y = -0.062x - 0.557
R² = 0.598
Pb(II):y = -0.083x + 0.521
R² = 0.828
Cd(II)y = -0.071x + 0.599
R² = 0.485

Figure 4: Pseudo first-order plot for adsorption of meal ions onto P. thonningii

Table 1: Pseudo first-order kinetic parameters for adsorption of the metal ions onto *P. thonningii*

Parameters	Pb (II)	Cr (III)	Cd (III)
k_1	0.083	0.062	0.071
q_e (mg/g)	1.684	0.573	1.8203
R^2	0.828	0.598	0.485

The pseudo second – order kinetic model

The pseudo second-order kinetic model relies on the assumption that the rate-limiting step of an adsorption process may be chemical reaction involving valence forces resulting from sharing or exchanging of electrons between adsorbates and the adsorbent sites [18]. The pseudo second – order model is expressed as [19]:

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \tag{3}$$

Where k_2 is the rate constant for pseudo second-order kinetic process. After integration and applying boundary conditions at t = 0 to t = t and q_t = 0 to q_t = q_t, the integrated form of equation (3) becomes;

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{4}$$

The initial adsorption rate, h_o (mg/g min) as t approaches zero is expressed as:

$$h_o = k_2 q_e^2 \tag{5}$$

Equation (4) then becomes:

$$t/q_t = 1/h_o + t/q_e \tag{6}$$

The plot of t/q_t versus t using equation (6) should yield linear relationship if the adsorption data fit into the equation. The pseudo second – order was applied in this analysis and plots of $\frac{t}{qt}$ vs t gave linear relationships from where the pseudo second–order parameters q_e and k_2 were evaluated as shown in Table 2. The linear plots obtained in Figure 5 shows that the adsorption process follows pseudo second-order kinetics perfectly as observed by the high R^2 values which fall within 0.999 – 1.0000. This suggests that the rate limiting step of the adsorption of Cr(III), Pb(II) and Cd(II) ions by the adsorbent in this study is by chemical reaction.

The rate constant k_2, the equilibrium adsorption capacity, q_e, and the initial sorption rate, h_o and R^2 values are presented in Table 2. The equilibrium adsorption capacities, q_e calculated from the pseudo second-order kinetic model were very close to the experimental values. Therefore, the fitting of the adsorption data into pseudo second-order model explains that the rate of occupation of active sites is proportional to the square of the number of the unadsorbed sites [4].
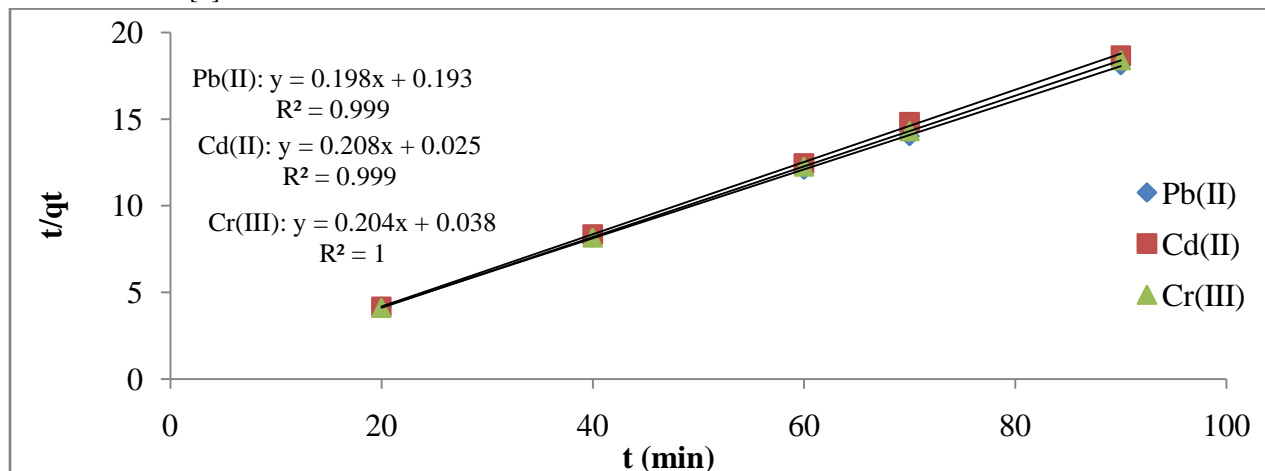

Pb(II): y = 0.198x + 0.193
R^2 = 0.999
Cd(II): y = 0.208x + 0.025
R^2 = 0.999
Cr(III): y = 0.204x + 0.038
R^2 = 1

Figure 5: Pseudo second order for adsorption at metal ions onto P. thonningii

Table 2: Kinetic parameter of Pseudo Second-order model for adsorption onto *Piliostigma thonningii*

Parameters	Pb (II)	Cr (III)	Cd (III)
h_o	5.179	26.312	39.992
k_2	0.203	1.095	1.730
q_e	5.051	4.902	4.808
R^2	0.999	1.000	0.999

Intraparticle diffusion models

Intra particle diffusion is a transport process that involves the movement of species from the bulk of the solution to the solid phase in a well stirred batch adsorption system. The intra-particle diffusion model is usually applied to describe an adsorption process occurring on a porous adsorbent. The kinetic adsorption data were analyzed by the intraparticle diffusion model to provide useful information on the proper transport mechanism involved in the adsorption study. Two models have been employed for studying the mechanism of the adsorption process by intraparticle diffusion and they are:

McKay & Poots model: In this model, McKay and Poots, 1980 [20] states that the amount of solutes adsorbed can be expressed in terms of the square root of time and is expressed as:

$$q_t = X_i + k^i \, t^{1/2} \qquad\qquad (7)$$

Where X_i is the boundary layer diffusion effects (mg/g), k^i is the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$). The plots of amount of metal ions adsorbed, q_t, versus square root of time, $t^{1/2}$ for adsorption of the metal ions in the current study are shown in Figure 6. From the linear plots, the initial sorption rate controlled by intraparticle diffusion, k^i can be determined from the slope while extrapolation of the linear plots to the time axis gives the intercepts of the plots, X_i and is proportional to the boundary layer thickness. The intra-particle diffusion constants and the correlation coefficients (R^2 values) are presented in Table 3. It could be observed from the table that the values of X_i (*i.e.*, boundary layer thickness) are high and this represents high adsorption capacities. The boundary layer provides information on the ability of the metal ions to either adsorb onto the adsorbent phase or remain in solution. Since diffusion occurs during an adsorption process, the boundary layer is estimated as a viscous drag that

exists between the adsorbent surface and the metal ion solutions as they are diffusing across the adsorbent surface. From the results, it could be seen that the model provides a good interpretation to the experimental adsorption data judging from the high R^2 values and this confirms that the adsorption process may be intra-particle diffusion controlled.
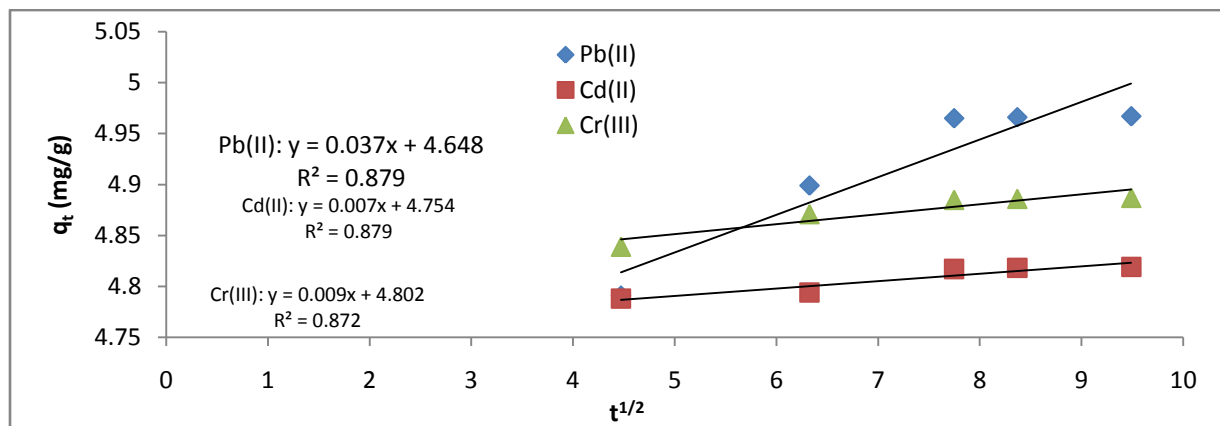

Figure 6: Mckay & Poots Intraparticle diffusion plot for adsorption of the metal ions onto P. thonningii

Table 3: Mckay& Poots intra particle diffusion parameters

Parameters	Pb (II)	Cr (III)	Cd (III)
k^i	0.037	0.009	0.007
Xi	4.648	4.802	4.754
R^2	0.879	0.872	0.879

Weber & Morris Model: To further confirm whether the transport process for the heavy metals adsorption follows intra-particle diffusion, the Werber and Morris intra-particle diffusion model was applied and is expressed as [21, 22]:

$$R = k_{id} t^n \tag{8}$$

Taking logarithm of equation (8) gives:

$$\ln R = \ln k_{id} + n \ln t \tag{9}$$

Where R is the per cent of the metal ions adsorbed, t is the contact time (min), n is the slope of linear plots, which depicts the adsorption mechanism; k_{id} is the intra-particle diffusion rate constants (min^{-1}) which may be taken as a rate factor, i.e. per cent metal ion adsorbed per unit time. The plots of log R versus log t for adsorption of the metal ions by the adsorbent, *P. thonningii* are shown in Figure 7. From the plots, the values of n were evaluated from the slope of the linear plots while the intra-particle diffusion rate constants, k_{id} were determined from the intercept of the linear plots and are presented in Table 4. The high R^2 values obtained (Table 4) show good fitting of the adsorption kinetic data to the Werber-Morris intra-particle diffusion model and ultimately confirm that the adsorption transport mechanism is particle diffusion controlled.

Table 4: Werber-Morris intra particle diffusion parameters

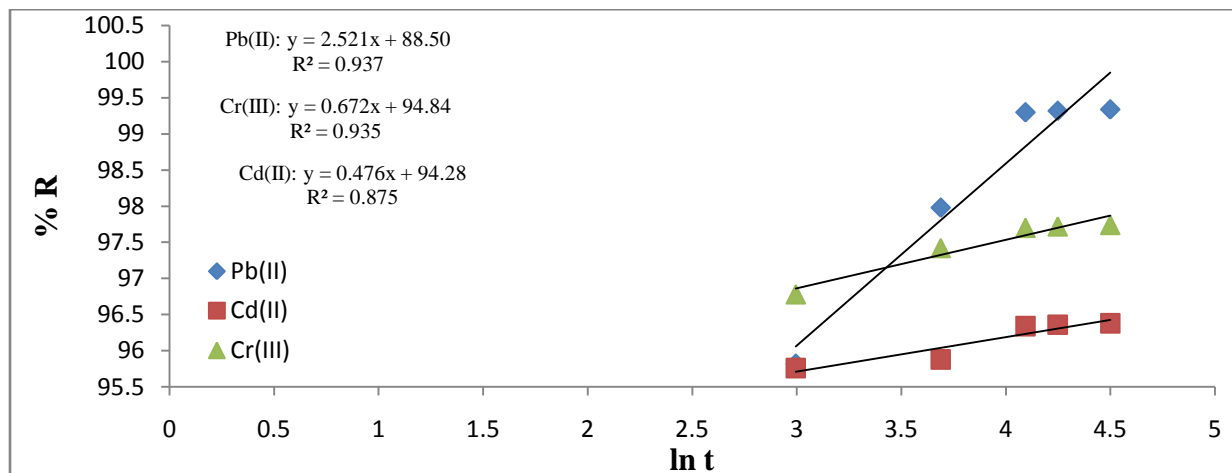| Parameters	Pb (II)	Cr (III)	Cd (II)
k_{id}	2.72 x 10^{38}	1.54 x 10^{41}	8.82 x 10^{40}
n	2.521	0.672	0.476
R^2	0.937	0.0.935	0.875

Figure 7: Weber-Morris intra-particle diffusion plot for the adsorption of the metal ions by P. thonningii

Conclusion

Cheap biosorbent materials based on natural and waste biomass constitute the basis for a new cost effective technology that has found its largest application in the removal of metal contaminated industrial effluents. The current research has provided a good understanding of biosorption of three heavy metals, Cr(III), Cd(II) and Pb(II) by a novel biosorbent, *P. thonningii*. The adsorption studies were dependent on contact time and adsorbent mass. Adsorbent dosage range of 0.05 g/L to 0.30 g/L was observed to be highly efficient in the metal ions removal. The effect of contact time shows that the adsorption efficiency increased with an increase in contact time and that the adsorption process followed a pseudo second-order kinetics. This study has therefore contributed in the establishment of the fact that *Piliostigma thonningii* seed pod could be employed in the removal of Cr(III), Cd(II) and Pb(II) ions from aqueous solution.

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