Communication in Physical Sciences, 2020, 6(2): 852-861

Sorption Kinetics of Pb^{2+}, Cd^{2+} And Ni^{2+} Ions Sorption from Aqueous Medium Using Butterfly Pea (*Centrosema pubescens*) Seed Pod Powder

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Received 27 November 2020/Accepted 29 December 2020/Published online: 30 December 2020

Abstract: *Metal detoxification of waste water and industrial effluents is significant in preserving aquatic life especially in the current era of increasing environmental contamination from industrial and domestic wastes. In this study, the batch sorption process was employed to investigate the effect of pH and time on the adsorption mechanism of* Pb^{2+}*,* Cd^{2+} *and* Ni^{2+} *on the surface of Centrosema pubescens seed pod. The optimum time and pH for maximum adsorption of the three heavy metal ions were 120 min and 6.0 respectively. The adsorption process was best described by a pseudo second order kinetic models which provided data that were in best agreement with experimental data compared to a pseudo first order model. However, the mechanism occurred through both intra particle diffusion and liquid film diffusion. The transport mechanism for the process involved both intra-particle and liquid.*

Key Words: *Sorption kinetics, Heavy metal ion removal, Centrosema pubescens*

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1.0 Introduction

Heavy metal ions have been confirmed to be one of the major sources of environmental contamination especially in aquatic system (Jaishankar *et al*., 2014; Nagajyoti *et al*., 2010). Their pollution factor is founded on their potential to exert toxic impact on the environment, once the concentration is above permissible or tolerance limits (Järup, 2003). The present ecosystem is witnessing high concentration of heavy metal pollution arising mostly from industrial activities. The most commonly found heavy metals in waste water include arsenic, cadmium, chromium, copper, lead, nickel, and zinc, all of which cause risks for human health and the environment (Romdhane *et al*., 2020). Several industrial practices mostly release effluent in aqueous medium and discharge them to the surrounding water bodies, thereby altering the quality of the water and may interfere with the legitimate utilization of the water for domestic and other purposes (Ekop and Eddy, 2009' Odoemelam and Eddy, 2009). Studies conducted on the impart of heavy metal pollution on the ecosystem indicated that such contamination will ultimately extends their negative impart to man and even land and cultivated plants (if the water is used for irrigation of the plant during their nursery and other developmental stages (Eddy *et* al., 2004; Eddy, 2009). Heavy metal ions can bioaccumulate and become biomagnified through the food chain (Uchechukwu *et al*., 2015, 2018). Heavy metals can also enter the environment through natural processes such as soil erosion, natural weathering of the earth's crust, urban runoff, sewage discharge, insect or disease control agents applied to crops, and many others (Morais *et al*., 2012).
Realization of the toxic imparts of heavy metal ions to the aquatic environment and to man, had

long opens different research dimension toward the removal of heavy metal ions from industrial effluent before discharge. Consequently, methods such as ion exchange, reverse osmosis, membrane filtration, electrodialysis, electrochemical treatments, adsorption and chemical precipitation (Adedirin *et* al., 2011; Demirba *et al*., 2004). However, adsorption technique has been widely accredited as one of the best options because of the low cost of implementation, ease of regeneration and can be achieved through eco-friendly approaches (Dubey and Shiwani, 2012). In view of their significant role in environmental remediation, several adsorbents have been investigated for their heavy metal ions removal efficiency (Ekop and Eddy, 2010; Essien and Eddy, 2014; Uchechukwu and Eddy, 2013). However, the use of plant waste as adsorbent is receiving a great waste because it provides added advantages towards waste disposal management, resource recovery and can be implemented through green chemistry processes. Therefore, the present study seeks to investigate the adsorption removal capacity of Butterfly Pea waste for the removal of lead, cadmium and nickel ions from aqueous solution.

Biosorption involves the application of biowaste to remove contaminants from aqueous solution (Ekuma *et al.*, 2017). The success of biosorption process has been linked to the presence of suitable functional groups in the biomaterials used for the adsorption process. According to Gupta *et al.* (2000), biosorption offers the advantages of low cost, effectiveness for dilute effluents, minimum chemicals usage and reduced toxic sludge generation (Gupta *et al.*, 2000). The adsorption of toxic waste from industrial wastewater using agricultural waste and industrial by-products has been massively investigated (Srivastava *et al*., 2006). The maximum concentration limit standards for Pb^{2+}, Cd^{2+} and Ni^{2+} are 0.006 mg/L, 0.01 mg/L and 0.20 mg/L respectively as established by Babel and Kurniawan (Babel and Kurniawan, 2004).

The toxicity of lead, cadmium and nickel ions have been deeply investigated and reviewed. For example, lead is a highly toxic metal whose widespread use has caused extensive environmental contamination and health problems in many parts of the world. At very high concentrations, it may cause structural damage to cells, proteins, nucleic acid, membranes and lipids, resulting in a stressed situation at cellular level (Mathew *et al*., 2011). Children are more sensitive to lead exposure than adults. Young children are vulnerable to the effects of lead because they absorb a higher percentage of ingested lead and are more susceptible to the neurotoxicity, which may result in deficits in Intelligence Quotient (IQ) (ATSDR, 2007).

Cadmium is a highly toxic and nonessential heavy metal that is well documented recognized for its adverse influence on the enzymatic systems of cells, oxidative stress and for inducing nutritional deficiency in plants (Irfan *et al*., 2013). Cadmium and zinc have the same oxidation states and hence cadmium can replace zinc present in metallothionein, thereby inhibiting it from acting as a free radical scavenger within the cell. Cadmium causes tubular dysfunction possibly due to the formation of a cadmium metallothionine complex, although unbound cadmium may also play a part in the toxicity (Liu *et al.*, 1999).

It Nickel predominantly affects the respiratory system, acute inflammatory on the nasal membrane, hypersensitive in nature, including bronchial asthma and contact dermatitis (Sivulka, 2005). Widely reported health consequences of nickel toxicity are decrease in body weight, stimulation of neoplastic transformation, kidney and liver damage, cardiovascular system poisoning and skin irritation and sensitisation (Denkhaus and Salnikow, 2002; Schollhammer *et al*., 1994).

2.0 Materials and Methods

2.1 Preparation of the adsorbent

The adsorbent, *centrosema Pubescens* seed pods were obtained from a plantation in Michael Okpara University of Agriculture, Umudike, Abia state Nigeria. The pods were carefully removed, washed with de-ionized water, dried and crushed to fine sizes using an electric blender. The crushed samples were sieved in order to obtain 180 μm mesh size and then soaked in 0.3 M HNO_3, stirred for 30 min and left for 24 hours. The resulting system was filtered through Whatman no. 41 hard ash less filter paper, rinsed with de-ionized water and sundried to constant weight after which it was activated for one hour in an oven at a temperature of 105 °C.

2.2 Adsorption Experiments

Batch adsorption studies for the removal of Ni^{2+}, Cd^{2+} and Pb^{2+} ions by *Centrosema pubescens* pod were investigated as a function of solution pH and contact time. The effect of solution pH on the adsorption of the metal ions was studied at a fixed temperature of 30 °C and at an initial metal ion concentration of 50 mg/L. The adsorption was carried out using varying pH of the solution ranging from 2 to 8 pH. This was done by respectively introducing 50 cm^3 of each metal ion solution into different 250 cm^3 Erlenmeyer flasks maintained at pH of 2, 4, 6, 7 and 8 and containing 0.05 g of the adsorbent respectively. The mixtures were agitated intermittently for 1 h in a rotary shaker and then filtered. The concentration of each filtrate was determined using Perkin Elmer Analyst 200 Atomic Absorption Spectrophotometer. The effect of contact time on adsorption of the metal ions was studied using the same method but at constant mass of adsorbent and constant pH. However, the time were varied. From the results of the analysis, percentage removal of heavy metal ions by the adsorbents as well as equilibrium amount absorbed at a given time interval and pH (respectively) were calculated using equations 1 and 2 (Onwu *et al.*, 2013),

$$\%R = \frac{C_o - C_t}{Co} \text{ x } \frac{100}{1} \qquad (1)$$

$$q_t = \frac{C_o - C_t}{1} \text{ x } \frac{v}{m} \qquad (2)$$

where % R is the percentage of concentration of 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.

3.0 Results and Discussion

3.1 Effect of pH on adsorption

Fig. 1 shows a plot for the variation of equilibrium amount of Cd^{2+}, Ni^{2+} and Pb^{2+} adsorbed with pH.

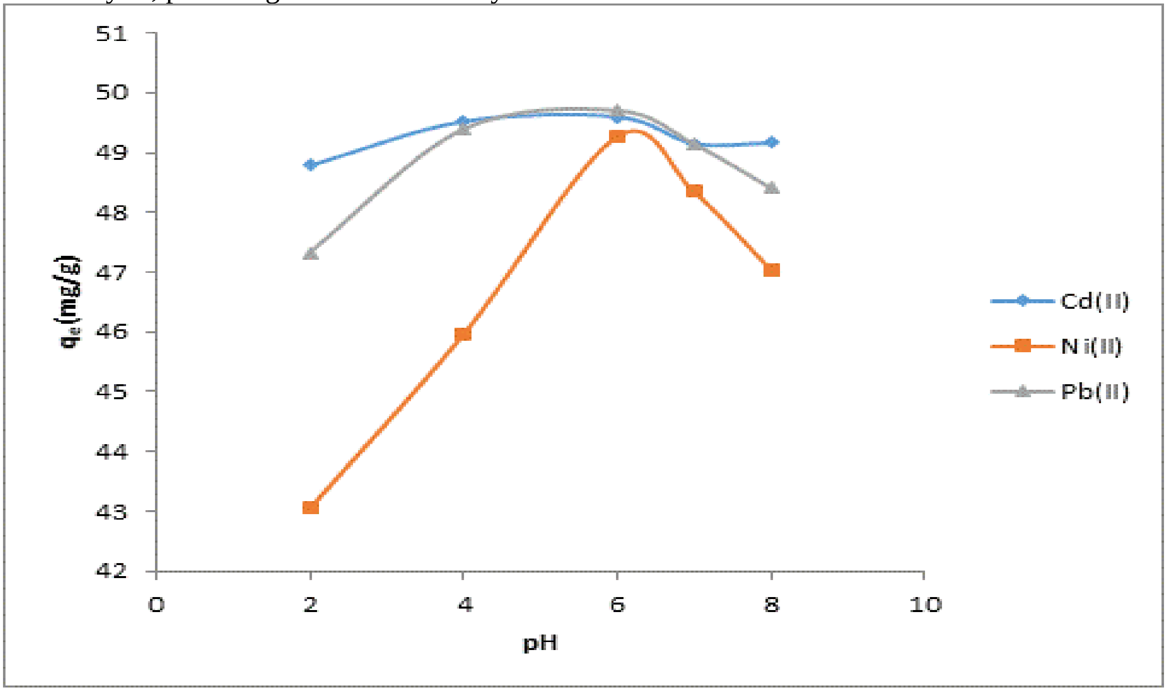

Fig. 1: Variation of equilibrium amount of heavy metal ions adsorbed with pH

The adsorption trend also indicated that Pb^{2+} was most adsorbed while Ni^{2+} was the least adsorbed heavy metal. Ionic radii of Pb^{2+}, Ni^{2+} and Cd^{2+} are 1.19, 0.69 and 0.97Å respectively which indicated that the adsorption increases with increase in ionic radius. Similar finding has been reported by Zhou *et al.* (2011). Generally, the extent of hydration tends to increase with decrease in ionic radius indicating that adsorption should favorably increase with decreasing ionic radius.

3.2 Effect of period of contact on adsorption

Fig. 2 shows plots for the variation of the amount of Pb^{2+}, Cd^{2+} and Ni^{2+} adsorbed with time. The plots revealed that the percentage adsorption of the metal ions onto a biomass witnessed very sharp increases up to 40 min for Pb^{2+} ions but 60 min for both Cd^{2+} and Ni^{2+} ions and then gradually increases to reach an equilibrium value in approximately 60 min for Ni^{2+} and Cd^{2+} but 80 min for Pb^{2+} ion. After the equilibrium, further increase in time did not significantly affect adsorption. Therefore, 120 min becomes the saturation points for the three metal ions after which the rate of adsorption becomes equal to the rate of desorption. The observed trend can be link to overcoming influence of diffusion and consequence interaction between the adsorbent and the adsorbate as time increases.

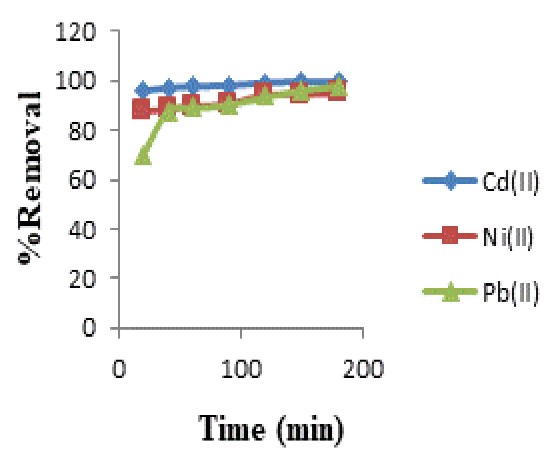

Fig. 2: Variation of percentage of heavy metal ion removal with time

3.2.1 Pseudo first order kinetic model

The Lagergren rate equation is a widely used rate equation for the description of adsorption kinetics and can be expressed according to equation 3, which is linearised to yield equation (4) (Lagergren and Svenska, 1898).

$$\frac{dq_t}{d_t} = k_1(q_e - q_t) \quad (3)$$

$$Ln(q_e - q_t) = \ln q_e - k_1 t \quad (4)$$

where q_e is the equilibrium biosorption capacity in mg/g, and q_t is the sorption capacity at any time, t in mg/g, k_1 is the pseudo-first order rate constant. A plot of ln (qe-qt) against t, was linear s shown in Fig. 3. Therefore, the adsorption of these heavy metals is consistent with a pseudo first order kinetic. Values of k_1 and q_e obtained from the slope and intercept as well as equilibrium sorption capacity, are presented in Table 1. However, calculated adsorption capacities are generally less than the experimental observed values of 49.08, 49.85 and 47.60 mg/g obtained for Pb^{2+}, Cd^{2+} and Ni^{2+} ions respectively. The disparity may be due to the influence of other factors that were not incorporated into the pseudo first order model.

3.2.2 Pseudo- second order model

Assumptions establishing the pseudo second order adsorption model can be summarised according to equation 5 (Ho and Mickay, 2000),

$$\frac{dq_t}{d_t} = k_2(q_e - q_t)^2 \quad (5)$$

where k2 is the rate constant of pseudo second-order adsorption (g/mg min), The integrated form of equation 5 within the boundary conditions is expressed in equation 6,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Consequently, equation 6 indicates that a plot of $\frac{t}{q_t}$ versus t should give a linear plot with slope and intercept equal to $1/q_e$ and $\frac{1}{k_2 q_e^2}$. The model also contains factors that enhance the estimation of the initial adsorption rate, ho (g/mg min) as it approaches zero, i.e., $h_o = k_2 q_e^2$ and by substitution into equation 6, equation 7 is obtained

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{t}{q_e} \quad (7)$$

The pseudo second order plots (Fig. 4) gave slopes and intercepts that lead to the estimation of the observed kinetic parameters, k_2 , q_e, h_o and R^2 which are recorded in Table 1. The estimated parameters are in strong agreement with experimental data x=compared to pseudo second order model. Therefore, the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} obeyed pseudo second order kinetic model more than pseudo first order. Generally, k_2 is a kinetic index which measures the speed of adsorption. The higher the value of k_2, the better is the adsorption rate. Therefore, the sorption of Cd^{2+} ion was faster than that of Ni^{2+} and Pb^{2+} other metal ions. The pseudo second-order model assumed that the assumption that the rate limiting step of an adsorption process may be chemical reaction involving valence forces resulting from sharing or exchange of electrons between adsorbent sites (Onwu *et al*., 2014).

The half-adsorption time $t_{1/2}$ is also a significant adsorption parameter which can be calculated from the equilibrium concentration and the diffusion coefficient rate values.

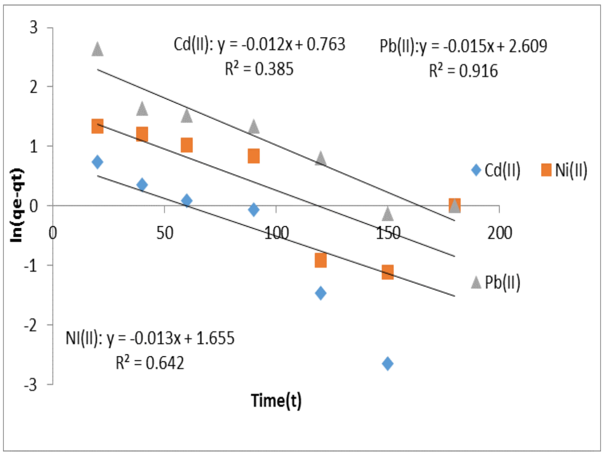

Fig. 3: Pseudo first order plot for the adsorption of the metal ions onto butterfly pea

This was calculated by using the following equation 8 (Shrihari *et al*., 2005)

$$t_{½} = \frac{1}{k_2 q_e} \qquad (8)$$

The experimental data for the adsorption of the Pb^{2+}, Cd^{2+} and Ni^{2+} ions onto *centrosema Pubescens* seed pod were also employed to evaluate the controlling mechanism of adsorption processes. The diffusion coefficients for the intra-particle transport of the Pb^{2+}, Cd^{2+} and Ni^{2+} ions were calculated using equation 9 (Ferreira, *et al*., 2019):

$$D = \frac{0.03r^2}{t_{1/2}} \qquad (9)$$

where *r* is the radius of the adsorbent particle in centimetres and D is the diffusion coefficient value in $cm^2.min^{-1}$. Estimated D values (Table 1) correlated with the equilibrium amount of heavy metal ion adsorbed. Consequently, lead which displayed best adsorption had the highest value of D.

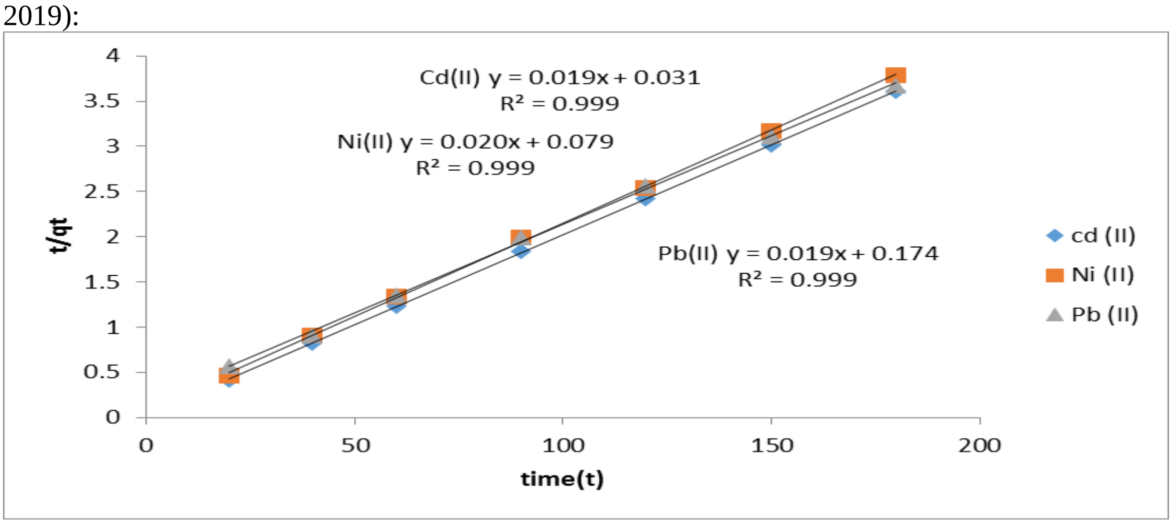

Fig.4: Pseudo second order plots for the adsorption of the metal ions onto butterfly pea.

3.2.3 Elovich kinetic model

The Elovich equation assumes that the actual solid surfaces are energetically heterogeneous and that neither desorption nor interactions between the adsorbed species could substantially affect the kinetics of adsorption at low surface coverage. The crucial effect of the surface energetic heterogeneity on adsorption equilibrium in the gas/solid systems has been demonstrated (Rudzinsk and Everett, 1992), but the extension of the same to a liquid/solid system is not known. The Elovich equation (Ho and Mckay, 2002) is given by equation 10

$$\frac{dq_t}{d_t} = \propto \exp(-\beta q t) \qquad (10)$$

Upon integration, the Elovich rate equation with boundary conditions q=qt at t=t and q=0 at t=0 becomes (11),

$$q_t = \frac{1}{\beta} \ln (1+\alpha\beta t) \qquad (11)$$

where q_t is the sorption capacity at time t ($mg\ g^{-1}$), α is the initial sorption rate ($mg\ g^{-1}min^{-1}$), and β is the desorption constant ($g.mg^{-1}$) during any one experiment. The initial sorption rate, α, and desorption constant, β, were calculated from the intercept and slope of the straight-line plots of qt against ln(t) (Fig. 5). The initial adsorption rate (Elovich α) had values of 226.577 mg $(g.min)^{-1}$, 7.1721 mg $(g.min)^{-1}$ and 691639484 mg $(g.min)^{-1}$ for Pb^{2+}, Cd^{2+} and Ni^{2+} ions respectively while the desorption coefficient (Elovich β) was 0.1797 mgL^{-1}, 1.0215 mgL^{-1} and 0.5254 mgL^{-1} for Pb^{2+}, Cd^{2+} and Ni^{2+} ions respectively.

Although the measured degree of linearity of the plots were relatively excellent (>80%), estimated values of the experimental data did not give a good correlation for these for Ni^{2+} and Pb^{2+} ion but Cd^{2+} ions.

3.3 Adsorption mechanisms

3.3.1 Intra particle diffusion model

In this model, it is assumed that the mechanism for metal ion removal by adsorption on a sorbent material is taking place through four steps (i) migration of metal ions through the surface of the adsorbent (i.e through bulk diffusion) (ii) diffusion of the metal ions through the surface of material by chemical reaction via ion exchange, complexation and/or chelation.

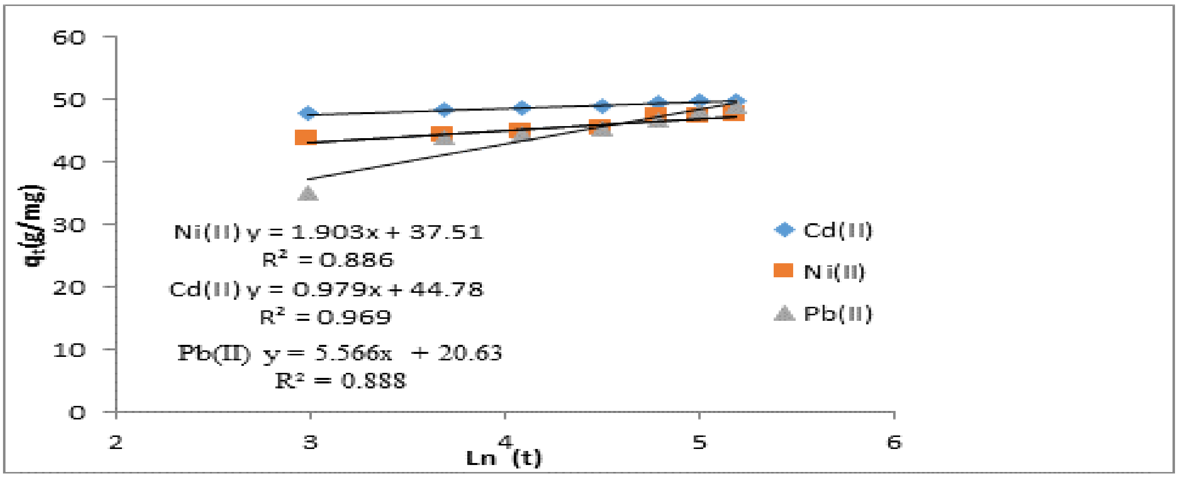

Fig. 5: Elovich plot for the adsorption of the metal ions onto butterfly pea

The adsorption process is a diffusive mass transfer process when the rate can be expressed in boundary layer to the surface of the adsorbent via film diffusion; (iii) the transport of the metal ions from the surface to the interior pores of the adsorbent occur through intra particle diffusion or pore diffusion mechanism and (iv) the adsorption of metal ions at an active site on the terms of the square root of time (t). Consequently, the intra particle diffusion model is expressed as follows (Weber and Morris, 1963).

$$q_t = k_d t^{1/2} + I \qquad (12)$$

where qt is the fraction uptake (mg/g) at time (t), K_d is the intra particle diffusion rate constant (mg/g min$^{1/2}$) and I is the intercept (mg/g). A plot of qt versus $t^{½}$ (Figure 5 below) will give k_d as slope and I as intercept and results are presented in Table 1. The factor, I represent the effect of boundary layer thickness. The smaller the intercept length, the lesser the adsorption is boundary layer controlled (Yang and Al-Duri, 2005). In the equation (12), k_d (mg.g^{-1}.min$^{-1/2}$) is defined

as the intraparticle diffusion rate constant and is related to the intraparticle diffusivity in the following way (13).

$$k_d = \frac{6q_e}{r}\sqrt{\frac{D}{\pi}} \qquad (13)$$

where r (cm) is the particle radius, D (cm^2.min^{-1}) is diffusion coefficient, and qe (mgg^{-1}) is the solid phase concentration at equilibrium (Yang and Al-Duri, 2005). From Fig. 6, it is evident that the plots are non linear but the double linear model was obtained which reveals that the adsorption is controlled by intra particle diffusion. In this first straight line, a sudden increase (within a short time period) in slope was observed which indicates that the metal ions are transported to the external of the adsorbent through film diffusion at a fast rate and was succeeded by penetration of the metal ion into the adsorbent. -However, both lines did not yield zero intercept which suggests that film diffusion and intra particle diffusion are occurring simultaneously during the adsorption. ki_1, I_1 and R^2_1 are the slope, intercept and correlation coefficient of the first steeper portion, ki_2, I_2 and R^2_2 are the slope, intercept and correlation coefficient of the second linear portion respectively. Since values of ki_1 are

almost equal to the observed values of ki_2, it can be stated that, both liquid film diffusion and intraparticle diffusion models simultaneously controlled the uptake of the metal ions onto the adsorbent (Inyinbor *et al.*, 2016; Norroozi *et al.*, 2007).

4.3.2 Liquid film diffusion model

The fractional attainment of equilibrium is the ratio of the amounts of sorbate removed from solution after a certain time to that removed when sorption equilibrium is attained.

The rate of attainment of equilibrium may be either film diffusion controlled or particle diffusion controlled, even though the two-mechanisms cannot be sharply demarcated (Itodo *et al.*, 2010).

The film diffusion model, proposed by McKay (where kp is the rate constant for film diffusion, min^{-1}; F is the fractional attainment):

$$\text{In}\,(1-F) = -k_p t + D_F. \qquad (14)$$

$$F = qt/qe. \qquad (15)$$

A plot of In(1-α_e) versus time (t) was linear as shown in Fig. 7.

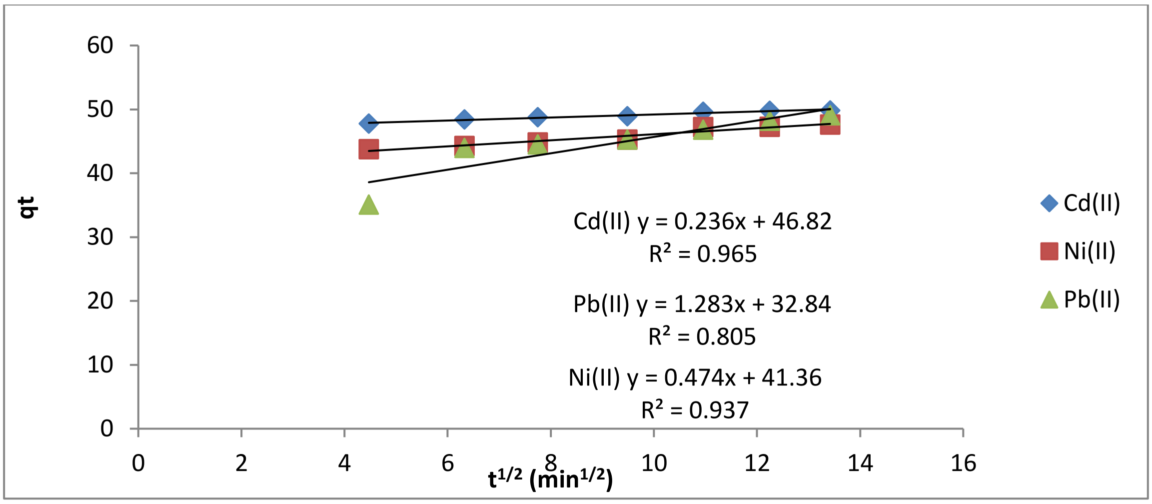

Fig. 6: Weber -Morris Intra particle diffusion plots for the heavy metal ions adsorption onto butterfly pea.

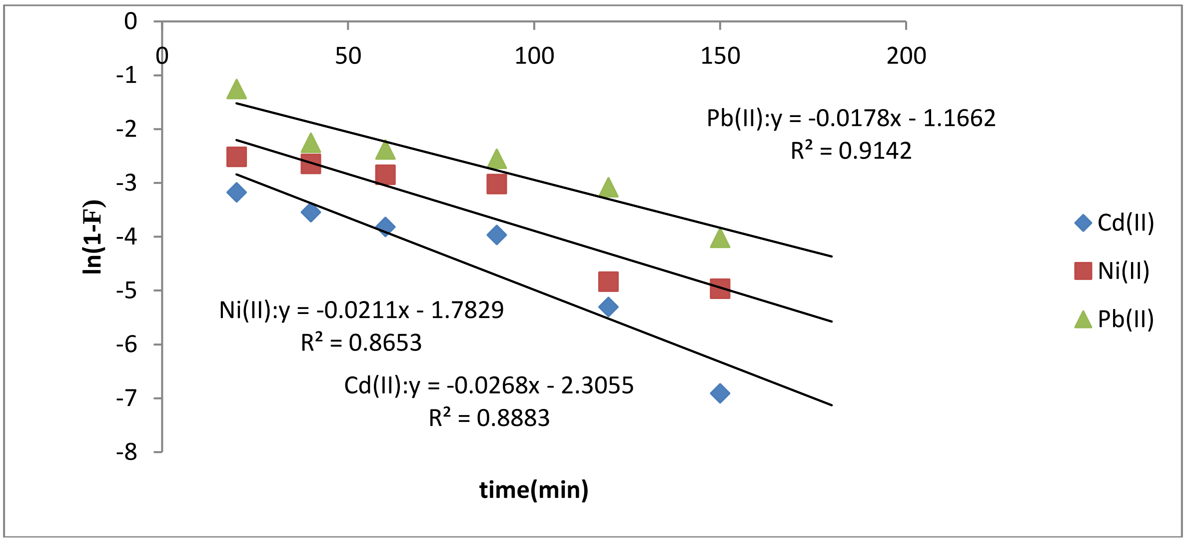

Fig. 7: Liquid film diffusivity plots for adsorption of Pb(II), Cd(II) and Ni(II) ions adsorption onto butterfly pea.

The rate constant, K_p was obtained from the slope while the dimensionless constant D_F was obtained from the intercept. The linearity of the plots confirms that film diffusion is involved in the adsorption of the three heavy metal ions. Also, since the linear plots did not display zero intercept, film diffusion and intra particle diffusion mechanism are the limiting steps in the adsorption processes. The thin liquid film surrounding the adsorbent may produce a diffusion barrier for the metal ions to penetrate before they arrive at the binding site on the adsorbent. This also indicates that the metal ion must overcome this film barrier before adsorption (Abia and Asuquo, 2007; Amadi *et al*., 2019). In a particle diffusion-controlled sorption process, the intra particle mass transfer resistance is the rate limiting step. This means that in the presence of a mixture of metal ions, competition for available adsorption sites will set in and the diffusion properties of the respective ions would be affected, hence the adsorption capacity of the individual metal ion will likely decrease. Consequently, the metal ion that successfully reaches the adsorption site faster depends must have satisfied several conditions more than others (Igwe *et al*., 2005).

Table 1: Kinetic parameter for the adsorption of Pb(II), Cd(II) and Ni(II) ions onto *centrosema pubescens* seed pod

Adsorption Kinetic models	Parameter	Pb(II)	Cd(II)	Ni(II)
Pseudo First-Order	q_{cal} (mg/g)	13.589	2.1447	5.2331
	q_{exp} (mg/g)	49.08	49.85	47.60
	k_1 (min^{-1})	0.015	0.012	0.013
	R^2	0.916	0.385	0.642
Pseudo Second-Order	q_{cal} (mg/g)	52.631	52.631	50.000
	q_{exp} (mg/g)	49.08	49.85	47.60
	k_2(dm^3mol^{-1} min^{-1})	0.00207	0.0116	0.00506
	h_o(g/mgmin)	5.734	32.132	12.650
	t½ (min)	9.17884	1.63794	$3.952x10^{-3}$
	D ($cm^2.min^{-1}$)	2.647×10^{-7}	$14.84x10^{-7}$	$6147.9x10^{-7}$
	R^2	0.999	0.999	0.999
Elovich	α (mg/g)	226.577	7.1721	691639484
	β(g mgmin)	0.17966	1.02145	0.5254
	R^2	0.888	0.969	0.886
Weber and Morris intraparticle diffusion	C_{i1} ($mg.g^{-1}$)	28.762	46.843	42.388
	k_{i1} ($mg.g^{-1}$ min-$^{1/2}$)	1.9184	0.2311	0.3053
	R_i^2	0.7355	0.9251	0.9909
	C_{i2} ($mg.g^{-1}$)	35.999	46.855	40.463
	k_{i2} ($mg.g^{-1}$ min-$^{1/2}$)	0.9841	0.2329	0.5528
	R_2^2	0.9946	0.8355	0.7810
Liuid Film Diffusion Model	K_p	0.0178	0.0268	0.021
	D_F	-1.1662	-2.3055	-1.7829
	R^2	0.9142	0.8883	0.8653

4.0 Conclusion

In this study, butterfly pea (*centrosema pubescens)* biomass was used for the biosorption of the aqueous solution containing Cd^{2+}, Ni^{2+} and Pb^{2+} ions. Batch experiment showed that the solutions pH strongly influenced the biosorptive capacity of the biomass. As the solution pH increased, the equilibrium sorption capacity of Ni^{2+}, Cd^{2+} and Pb^{2+} ions increased. However, optimum pH for maximum adsorption was 6 and occurred within the first 120 minutes for Cd^{2+}, Ni^{2+} and Pb^{2+} ions. A pseudo second order kinetic model provided better data than pseudo first order model. The biomass of the metal tolerant butterfly pea successfully removed the metal ions such as Cd^{2+}, Ni^{2+} and Pb^{2+} from aqueous solution. This study validates that the biomass of butterfly pea could be used as inexpensive and highly efficient reliable biosorbing bio-agent for effectively removing heavy metal ions from aqueous environment.

5.0 References

Abia, A.A. & Asuquo, E.D. (2007). Kinetics of Cd^{2+} and Cr^{3+} sorption from aqueous solutions using Mercaptoacetic acid modified and unmodified oil palm fruit fibre (Elaeis guineensis) Adsorbents. *Tsinghua Science and technology,* 12, 4, pp. 485-492.

Adedirin, O., Adamu, U. & Eddy, N. O. (2011). Biosoprption of Cr(IV) and Ni(II) from aqueous solution onto *Bacillus subtillis* immobilized in agarose gel. *Der Chemica* Amadi *Sinica* 2, 5, pp. 173-188.

, O. K., Ekuma, F. K., Okoro I. A. and Aleruchi C. C. (2019). Kinetics studies of sorption of Pb(II), Cd(II) and Ni(II) ions from aqueous solution using functionalized calopo (*Calopogonus mucunoides*) seed pod. *Journal of Chemical Society of Nigeria*, 44, 6, pp. 1183 -1190

ATSDR (2007). *Toxicological Profile for Lead.* Agency for Toxic Substances and Disease Registry. Atlanta, GA: Department of Health and Human Services.

Babel, S. & Kurniawan, T. A. (2004). Cr (VI) removal from synthetic wastewater using coconut shell charcoal and commercial activated carbon modified with oxidizing agents and/or chitosan. *Chemosphere,* 54, 7, pp. 951-967.

Demirbas, E., Kobya, M., Senturk, E., Ozkan, T (2004). Adsorption kinetic for the removal of chronium(III) from aqueous solution by activated carbon prepared from agricultural waste, *Water S. A*, 30, 4, pp. 533 – 539.

Denkhaus, E., Salnikow, K. (2002). Nickel essentiality, toxicity, and carcinogenicity. *Critical Review in Oncology/Hematology*, 42, pp. 35-56.

Dubey, A. and Shiwani, S. (2012) Adsorption of lead using a new green material obtained from Portulaca plant. *Int J Environ Sci Tech* 9(1):15–20. doi:10.1007/s13762-011-0012-8

Eddy, N. O. (2009). Modeling of the adsorption of Zn2+ from aqueous solution by modified and unmodified Cyperus esculentus shell. *Electronic Journal of Environmental, Agriculture. & Food Chemistry*, 8, 11, pp. 1177-1185.

Eddy, N. O. (2009). Modeling of the adsorption of Zn^{2+} from aqueous solution by modified and unmodified *Cyperus esculentus* shell. *Electronic Journal of Environmental, Agriculture. & Food Chemistry* 8, 11, pp. 1177-1185.

Eddy, N. O., Udoh, C. L. & Ukpong, I. J. (2004). Heavy metals in the sediment of the Cross River Estuary at Oron, South Eastern Nigeria. *African Journal of Environmental Pollution and Health*, 3, 1, pp. 6-10.

Ekop, A. S. & Eddy, N. O. (2010). Thermodynamic study on the adsorption of Pb^{2+} and Cd^{2+} from aqueous solution by human hair. *E. Journal of Chemistry*, 7, 4, pp. 1296-1303.

Ekop, A. S. and Eddy, N. O. (2009). Adsorption of Pb^{2+}, Zn^{2+} and Ni^{2+} from aqueous Solution by Helix aspera shell. *E. Journal of Chemistry*, 6, 4, pp. 1-6.

Ekuma, F. K. Amadi, O.K., Ngwu, C.M. and Ogu, H. (2017). Sorption Kinetics of Cr(lll), Pb(ll) and Cd(ll) ions from aqueous solution by Monkey bread (*Piliostigma thonningii)* seed pod. *Chemistry Research Journal*, 2(5):163-171.

Essien, N. B. & Eddy, N. O. (2014). Adsorption of lead and chromium ions from aqueous solution using Sorghum waste. *International Journal of Engineering and Research*, 3, 6, pp. 662-672.

Feng, N. C., Guo, X. Y., Liang, S., Zhu, Y. S. & Liu, J.P (2011). Biosorption of Heavy Metals from Aqueous Solutions by Chemically Modified Orange Peel. *Journal of Hazardous Materials*, 185, pp. 49-54.

Ferreira, A.S., Mota, A.A., Oliveira, A.M., Rodrigues, F.I.L., Pacífico, S.N., da Silva, J.E., Abagaro, B.T.O., Saraiva, G.D., de Castro, A.J.R., Teixeira, R.N.P. & Neto, V.O.S. (2019). Equilibrium and Kinetic Modelling of Adsorption: Evaluating the Performance of Adsorbent in Softening Water for Irrigation and Animal Consumption, *Rev. Virtual Quim.* 11, 6, pp. 1752-1766

Gupta, V. K., Gupta, M., and Sharma, S. (2000). Process development for the removal of lead and chromium from aqueous solutions using red mud—an aluminum industry waste. *Water Res.* 35, pp. 1125–1134.

Ho, Y. S. & Mckay, G. (2002). Application of Kinetic Models to the Sorption of Copper(II) on to Peat. *Adsorption Science and Technology*, 20, 8, pp. 797-815, DOI:

Ho, Y.S. & Mickay, G. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *water research*, 34, 3, pp. 735-742

Igwe, J. C., Nwokennaya, E. C. & Abia, A. A., (2005). The role of pH in heavy metal detoxification by biosorption from aqueous solution containing chelating agents. *African Journal of Biotechnology*. 4, 10, pp. 1109-1112.

Inyinbor, A. A., Adekola, F.A. & Olatunji, G.A. (2016). Kinetics, isotherms and thermodynamic modeling of liquid phase adsorption of Rhodamine B dye onto *Raphia hookerie* fruit epicarp, *Water Resources and Industry*, 15, pp. 14–27

Irfan, M., Hayat, S., Ahmad, A. &. Alyemeni, M. N. (2013). Soil cadmium enrichment: Allocation and plant physiological manifestations. *Saudi Journal of Biological Science*, 20, 1, pp.1–10.

Itodo, A.U., Abdulrahman, F.W., Hassan, L.G., Maigandi, S.A. and Itodo, H.U., (2010). "Intraparticle diffusion and intra particulate diffusivities of herbicide on derived activated carbon".*http//www.sciencepub.net/researcher*, pp. 74-86.

Jaishankar, M., Mathew, B. B., Shah, M. S. & Gowda, K. R. S. (2014) Biosorption of Few Heavy Metal Ions Using Agricultural Wastes. *Journal of Environment Pollution and Human Health*, 2, 1, pp. 1–6.

Järup, L. (2003). Hazards of heavy metal contamination. *British medical Bulletin* 68, 1, pp. 167-182

Lagergren,,S. & Svenska, B. K. (1898). On the theory of so-called adsorption of materials, *R. Swed. Acad. Sci. Doc Band* 24, pp. 1–13.

Mathew, E., Bajaj, A., Connelly, S. M., Sargsyan, H., Ding, F. X., Hajduczok, A. G., Naider, F. & Dumont, M. E .(2011). Differential interactions of fluorescent agonists and antagonists with the yeast G protein coupled receptor Ste2p. *Journal of Molecular Biology,* 409, 4, pp. 513-28

Morais S, Correia M, Domingues V & Delerue-Matos C (2012). Urea pesticides", in pesticides - strategies for pesticides analysis" (Ed. Margarita Stoytcheva; ISBN: 978-953-307-460-3), *In Tech, Rijeka,* pp. 241-262.

Nagajyoti, P. C., Lee, K. D. & Sreekanth, T. V. M. (2010) Heavy metals, occurrence and toxicity for plants: a review.*Environmental Chemistry Letters,* 8, pp.199–216

Norroozi, B., Sorial, G.A., Bahrami, H. and Arami, M.J., Hazard Mater (2007). B139, pp. 167-174.

Odoemelam, S. A. & Eddy, N. O. 2009). Studies on the use of oyster, snail and periwinkle shells as adsorbents for the removal of Pb^{2+} from aqueous solution. *E. Journal of Chemistry* 6, 1, pp. 213-222.

Odoemelam, S. A., Emeh, N. U. & Eddy, N. O. (2018). Experimental and computational Chemistry studies on the removal of methylene blue and malachite green dyes from aqueous solution by neem (*Azadiractha indica*) leaves. *Journal of Taibah University of Science* 12, pp. 255–265.

Okwunodulu, F. U. & Eddy, N. O. (2013). Equilibrium and thermodynamic consideration of Cd^{2+}, Ni^{2+} and Pb^{2+} removal from aqueous solution onto treated and untreated *Cola nitida* waste biomass. *International Journal of Science and Research* (IJSR). 2, 3, pp. 567-569.

Onwu, F. K., Abia, T.A. & Ogbonna, A.C. (2014). Kinetics studies on the use of agricultural wastes for the removal of lead, cadmium and nickel from aqueous solution. *Journal of Chemical and Pharmaceutical Research* 6, 12, pp. 471-480.

Onwu, F.K. Ogah, S.P.I. & Ngele, S.O. (2013). Biosorption of Cadmium(ll) ions from aqueous solutions by *Afzelia Africana*. *African Journal of Biotechnology,* 12(32):5060-5068

Romdhane, D. F., Satlaoui, Y., Nasraoui, R., Charef, A. & Azouzi, R. (2020). Adsorption, modeling, thermodynamic, and kinetic studies of methyl red removal from textile-polluted water using natural and purified organic matter rich clays as low-cost adsorbent, *Journal of Chemistry,* doi.org/10.1155/2020/4376173

Rudzinsk, W. & Everett, D. D. (1992) *Adsorption of gases on heterogeneous surfaces*. Academic Press: London.

Schollhammer M, Guillet MH, Guillet G. (1994) Nickel and skin. *Ann Dermatol Venereol*, 121: 338-345.

Shrihari, V., Madhan, S. & Das, A. (2005). kinetics of phenol sorption by Raw Agrowastes. *Applied Sciences*.6, 1, pp. 47-50.

Sivulka, D. J. (2005). Assessment of respiratory carcinogenicity associated with exposure to metallic nickel: A review. *Regul. Toxicol. Pharmacol.,* 43, pp. 117-133.

Srivastava, V. C., Mall, I. D. & Mishra, I. M. (2006). Characterization of mesoporous rice husk ash (RHA) and adsorption, *Journal Chemical Society of Nigeria*, 45, 4, pp. 580 - 586

Uchechukwu, O. F., Azubuike, O. S., Odoemelam, S. A. & Eddy, N. O. (2018). Kolanut pod husk: a potential biosorbent for Cd^{2+}, Ni^{2+} and $Pb^{2+.}$ *African Journal of Environment and Natural Science Research,* 1, 2, pp. 1-9.

Uchechukwu, O. F., Odoemelam, S. A., Azubuike, O. S., & Eddy, N. O. (2015). Biosorption of Cd2+, Ni2+ and Pb2+ by the shell of *Pentaclethra macrophylla*: equilibrium isotherm studies. *Journal of Science Technology and Environmental Informatics*, 2, 1, pp. 26-35.

Weber, W.J. & Morris J. C. (1963). Kinetics of adsorption on carbon from solution. *Journal Sanit. Div. America Society of Civil Engineering*. 89, pp.31-60.

Yang, X. & Al-Duri, B. (2005). Kinetic modelling of liquid phase adsorption of reactive dyes on activated carbon. *Colloid Interface 287*, 25.

Zhou, X., Xue, X. & Jiang, W. (2011). Study on adsorption of heavy metal ion in metallurgical wastewater by sepiolite. *Proceeding of 2011 2nd International Conference on Environmental Science and Development. IPCBEE*, 4, pp. 100-104.

Conflict of Interest

The authors declared no conflict of interest.