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Adsorption Kinetics and Mechanism of some Metal (II) Ions from Aqueous Solution using Activated Carbon prepared from Star Apple (*Chrysophyllum albidum*) Pericarp

***Amadi, O. K., Okoro, I. A. and Eze, P. C.**
Department of Chemistry, Michael Okpara University of Agriculture, Umudike, P.M.B. 7267, Umuahia, Abia State, Nigeria
***Correspondence Email:** amadikelvin77@gmail.com

ABSTRACT

In this research white star apple *Chrysophyllum albidum*, an agricultural product, available in large quantity in south region of Nigeria, were used as low-cost adsorbent for removal of metal ions such as Ni(II), Cd(II), Co(II) and Cu(II) from aqueous solution. Batch operation was used to study the equilibrium behaviour of *Chrysophyllum albidum* pericarp. The effects of solution pH, and contact time of adsorbent for the heavy metal ions were evaluated. To study the kinetics of adsorption of Ni(II), Cd(II), Co(II) and Cu(II), pseudo-first-order, pseudo-second-order, Elovich, Macky and Poot and liquid film Models were evaluated. The removal of these metal ions by the biosorbent was found to be dependent on contact time and pH solution. Results showed that the adsorption process was fast and that equilibrium was achieved at 120 min for Ni(II), Cd(II), Co(II) and Cu(II) ions. Results further showed that the optimum solution pH for the study occurred at pH 6.0 with maximum quantity adsorbed of 12.05 mg/g, 12.24 mg/g, 12.43 mg/g and 12.50 mg/g for Co(II), Ni(II), Cd(II) and Cu(II) ions respectively. Adsorption process fitted pseudo-second-order kinetic based on the high correlation coefficient (R^2 values) when compared to other kinetic models. Moreover, maximum adsorption capacities at pH 6.0 for Ni(II), Cd(II), Co(II) and Cu(II) ions are 12.4688 mg/g, 12.3456 mg/g, 12.4224 mg/g and 12.4378 mg/g respectively. The transport mechanism of the process was found to be a combination of intra-particle diffusion and liquid film controlled. In addition, the results will serve as a parameter to consider in the design of wastewater treatment plant for Pb(II), Cd(II) and Ni(II) ions detoxification using *Chrysophyllum albidum*.

Keywords: Activated Carbon, Adsorption Kinetics, Equilibrium, Metal (II) ions, and Mechanisms

INTRODUCTION

Heavy metals have been excessively released into the environment due to rapid industrialization and have created a major global concern. Cadmium, zinc, copper, lead, nickel, mercury and chromium are often detected in industrial waste waters which originates from metal plating, mining activities, smelting battery manufacture, tanneries, petroleum refining , paint manufactures, pigment manufacture, printing and photographic industries etc (Kadirvelu *et al*, 2001a). Unlike organic wastes, heavy metals are non-biodegradable and they can be accumulated in living tissues, causing various diseases and disorders and should be removed before discharge. Thus, all metal bearing wastewater is a pressing environmental concern, therefore the development and putting into practices of cost-effective process for heavy metals removal/recovery is essential in order to minimize the environmental hazard of toxic metal containing effluent.

Various treatment technologies have been developed for the removal of heavy metals from water and waste water, among them are, ion-exchange, electrochemical reduction, evaporation, solvent extraction, reverse osmosis, electro dialysis, electro-flotation, chemical precipitation, membrane filtration, adsorption etc (Demirba *et al.*, 2004).

The effectiveness of the treatment plant can be optimized by adopting any one of the above technique or the appropriate combination of two or more techniques. But most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries (Kobye *et al.*, 2005). Besides high capital and operational cost, conventional methods have inadequate efficiencies at low concentration, particularly in the range of 1-100 mg/L (Davilla *et al.*, 1992; Kapoor and Viraraghavan, 1998). However, research interests into the use of cheaper adsorbents to costly conventional treatment methods have attracted the attention of scientists (Namasivayan and Ranganatham, 1995).

Biosorption is one of the physico-chemical treatment processes found to be effective in removing heavy metals from aqueous solution.

The process is suitable even when the metals ions are present in concentration as low as 1 mg/L (Chong & Volesky, 1995). The removal of heavy metals ions from industrial waste using different adsorbents is currently of great interest. However, in order to minimize processing costs, several recent investigations have focused on the use of low cost agricultural waste materials (Namasivayam and Ranganathan, 1995; Amadi and Okoro, 2019).

Many of the elements that can be considered heavy metals have no known benefits for human physiology. Cadmium accumulates mainly in kidneys and liver, but is also found in skeletal system, muscular system, reproductive system and also in endocrine glands leading to renal dysfunction, hypertension, mutagenesis, and anaemia (Kaewsam and Yu, 2001). Nickel poisoning may cause reduction in cell growth, cancer and nervous system damage (WHO, 1984). Copper has a role as an essential element in human and animal bodies. However, at a higher dose it shows toxic effects, such as kidney and stomach damage, vomiting, diarrhoea and loss of strength (Ravindra *et al*, 2014). Cobalt toxicity causes Beer drinkers (dilated) Cardiomyopathy in acute state and Pneumoconiosis (inhaled) and goitre at chronic state (Mahmood *et al*, 2014).

The present study therefore seeks to examine the kinetic and mechanism potential of the pericarp of *chrysophyllum albidum* as an adsorbent in the removal of Cd(II),Ni(II),Co(II) and Cu(II) ions from aqueous solution.

MATERIALS AND METHODS

Preparation of the Adsorbent

The adsorbent, *Chrysophyllum albidum* was collected from Ama-awom community in lkwuano L.G.A, Abia State Nigeria. The pericarps were carefully removed, washed with de-ionized water, dried and carbonized locally using the method reported by Amadi *et al*, (2018). The carbonized samples were crushed with electrical blender and sieved through to obtain 0.40 mm particle 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 3h. The adsorbent was kept in an oven at 105 ^{O}C for 6 h and finally stored in a tight plastic container. The treatment of the adsorbent with 0.3 M HNO_3 helped in the removal of debris or soluble biomolecules that might interact with the metal ions during sorption. Also, it helps to open the micro pores of the adsorbent, thereby enhancing the surface characteristics of the adsorbent.

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 Ni(II), Cd(II), Cu(II) and Co(II) ions were investigated as a function of pH and contact time. The procedures used to determine the uptake level of metal ions from their various solutions by the adsorption are as reported by Imaga *et al.* (2014). The pH of the metal ion solutions was varied at 2.0, 4.0, 6.0, 7.0 and 8.0 at constant temperature of 30 ^{O}C and constant initial metal ion concentration of 50 mg/L. 20ml portions of the metal ion solutions of 50mg/L initial concentration were introduced into various flasks containing 0.08g of each absorbent. The pH of the solutions was adjusted by using 0.1M HCl or 0.1M NaOH as the case may be. Each mixture was agitated intermittently for 1hr, filtered rapidly and each filtrate was finally determined using atomic absorption spectrophotometer (AAS) Perkin Elmer Analyst 200. The optimum pH was found to be 6.0, and was adopted as the working pH. The effect of contact time on adsorbent of the metal ions was studied at different time intervals, at a temperature of 30 ^{o}C and at an initial concentration of 50 mg/L of each of the metal ions Ni(II), Cd(II), Cu(II) and Co(II). Each 50 ml portions of 50 mg/L of each of the metal ion solution were introduced into different 250 ml Erlenmeyer flasks containing 0.08 g of the adsorbent. The mixtures were shaken intermittently in a rotary shaker SHZ- 82 thermostatic water bath shaker at different contact times (20, 40, 60, 90, 120 and 150 min). At the end of each time, the content of each flask was filtered, centrifuged and the residual concentration of metal ion analysed using atomic absorption spectrophotometer (AAS) Perkin Elmer Analyst 200. 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 equation 1 (Onwu *et al.*, 2014).

$$\% R = \frac{(C_o - C_e)}{C_o} \; x\, 100 \qquad 1$$

While the adsorption capacity, q_t (mg/g) at different times was done using mass balance equation (2);

$$q_t = \frac{(C_o - C_t)V}{m} \qquad 2$$

Where % R = percentage of the metal ion adsorbed, q_t = adsorption capacity in mg/g, Co = initial metal ion concentration in mg/L, Ct = residual metal ion concentration in solution (mg/L), V = volume of metal ion solution used in L and m = the dry mass of the adsorbent in g. The quantity of the various metal ion adsorbed was then calculated using the equations above.

RESULTS AND DISCUSSION

The difference in equilibrium sorption of Cd(II),Ni(II),Co(II) and Cu(II) ions are reported below in accordance with variables like pH and contact time.

Effect of pH

The pH of an aqueous solution is an important factor that affects both the availability of metal ions in solution as well as the number of binding sites of the adsorbent (Zouboulis *et al*., 2004). In order to see whether pH plays any role in the biosorption process or not, an experiment was set to study the varying pH to evaluate it's effect on biosorption capacity of carbonized white star apple biomass using a fixed (50 mg/L) concentration of Ni(II), Cd(II), Co(II) and Cu(II) ions (Figure 1). The optimum biosorption occurred at pH 6.0 for the four metal ions. The variation in biosorption of heavy metals at different pH could be due to the differences in the sensitivity of carbonized white star apple biomass to pH. For instance, at a low pH, cell wall ligands tightly bind with the hydronium ions H_3O^+ and hence restrict the approach of metal cations due to repulsive force. While at higher pH values, more ligands like carboxyl, phosphate, imidazole and amino group would be exposed and carry negative charges with a subsequent attraction of metallic ions with positive charge and biosorption onto the cell surface (Pardo *et al*., 2003; Liqiang *et al*, 2015).

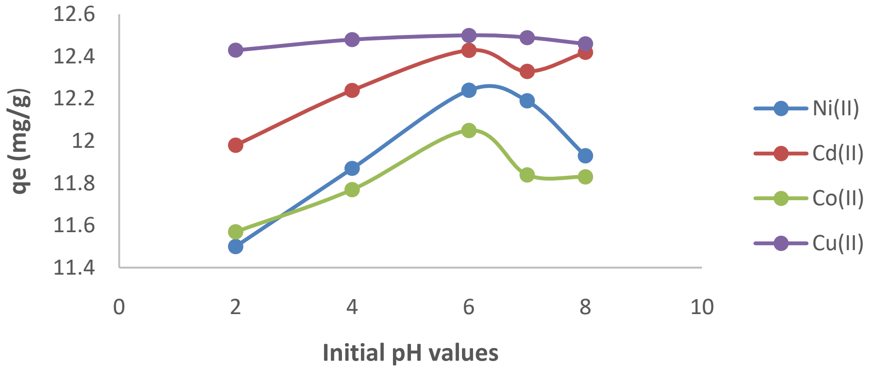

Figure 1: Effect of pH on the adsorption of the metal ions onto carbonized star apple

Effect of Contact Time on Amount of Metal Ion Adsorbed

The amount of metal adsorbed by an adsorbent at a particular time is one of the factors governing the efficiency of adsorption. The variation in the amount of Ni(II), Cd(II), Co(II) and Cu(II) ions adsorbed by carbonized white star apple is shown in Figure 2. The rate of metal ion biosorption was highest in the beginning due to high affinity of free metal ion binding sites on bio sorbent but after few minutes the rate of biosorption slowed and reached to equilibrium. Here, in our experiment, the initial sorption rate was highest for the first 60 min and then gradually increased with lapse of time until saturation at 120 min Therefore, the optimum contact time for the metal ions adsorption was considered to be 120 min. The order of biosorption rate was Co (II) > Ni(II) > Cu(II) > Cd(II). These indicate the equilibrium time at which an equilibrium metal ion concentration is presumed to have been attained. Zoubolis *et al*. (2004)) and Volesky (1990) have also observed that the initial shortest time period of sorption process is important for a high rate of metal sorption. Similar results have also been determined by Gabr *et al*. (2008) for Ni and Pb biosorption onto living and non living cells of Pseudomonas aeruginosa.

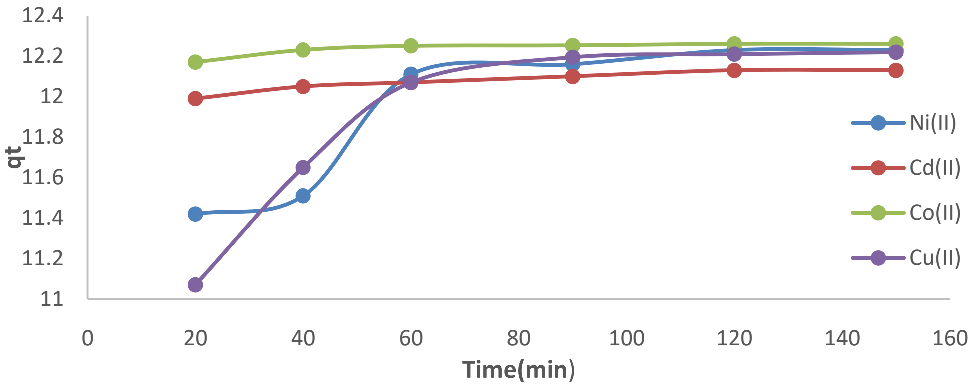

Figure 2: Effect of contact time on the sorption capacity (qt) of metal (II) ions adsorbed onto carbonized star apple

Kinetic Modelling

Quantification of the changes in sorption of metals with time requires the use of appropriate kinetic model. The kinetic models Pseudo first and Second order and Elovich models were employed to investigate the kinetics of sorption of the divalent metal ion by the adsorbents.

Pseudo-First Order Model

The pseudo-first order adsorption kinetic rate equation (3) expressed as;

$$In(q_e-q_t)=Inq_e-k_1t \qquad 3$$

Where, qe is the equilibrium biosorption capacity in mg/g, qt is the sorption capacity at any time, t in mg/g , k_1 is the pseudo-first order rate constant in $gmg^{-1}.min^{-1}$. A plot of log(qe-qt) against t was made and values of k_1 and q_{cal} were obtained from the slope and intercept respectively (Figure 3). The k_1, q_{cal} and R^2 values are presented in table 1. The variation in the rate should be proportional to the first power of concentration and rate of adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the adsorption process as displayed by Cu(II) ion whose pseudo first order equation fits well for the first 90 min and thereafter the data deviate from the theory. Despite the high correlation coefficient (R^2) values for the metal ions, the disparities between the observed and calculated values of qe indicate the non-applicability of pseudo first-order model in the present study.

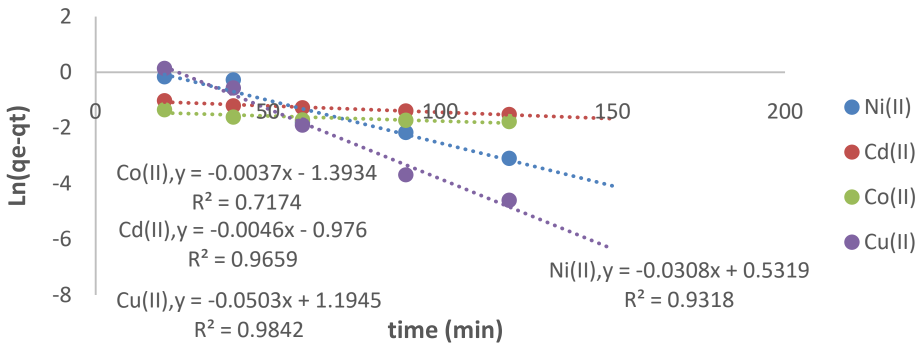

Figure 3: Pseudo-first order plot of ln(qe-qt) vs time for the adsorption of the metal ions onto carbonized white star apple

Pseudo-Second Order Model

The pseudo-second order adsorption kinetic rate equation (4) is expressed as;

$$\frac{dq_t}{d_t} = k_2(q_e-q_t) \qquad 4$$

Where k_2 (g/mg/min) is the rate constant of pseudo-second order adsorption, qe and qt (mg/g) respectively, are the sorption capacity at equilibrium and at time t. For the boundary conditions t = 0 to t = t and qt = qt, the integrated form of the above equation (5) becomes;

$$\frac{1}{q_e-q_t} = \frac{1}{q_e} + k_2t \qquad 5$$

This is the integrated rate law for a pseudo-second order reaction. This has a linear form;

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}\,t \qquad 6$$

Where h_o can be regarded as the initial rate as (t/qt) hence h_o(mg/g/min)

$$h_o = k_2q_e^2 \qquad 7$$

The equation becomes: $\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e}\,t$ 8

A plot of $\frac{t}{q_t}$ versus t gives a linear relationship from which the equilibrium capacity qe and k_2 can be determined from the slope and intercept of the plot respectively (Figure 4) (Theivarasu and Mylsamy, 2010). The linear plot of t/qt versus t show good agreement between experimental and calculated values Table 1. The correlation coefficients for the pseudo second order kinetics model are greater than 0.9996, which led to the assumption that pseudo second order kinetics model provided better correlation for the bio-adsorption of these heavy metals.

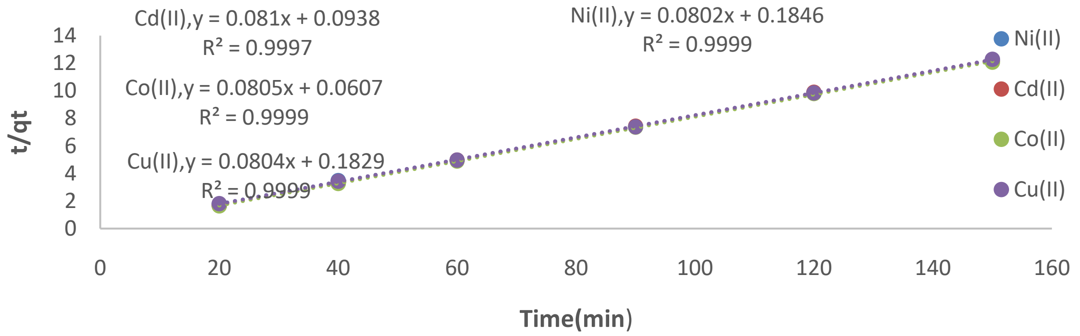

Figure 4: Pseudo-second order plot of t/qt vs t for the adsorption of the metal ions onto carbonized white star apple

Elovich Isotherm Model

Elovich model equation was also used successfully to describe the second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism for adsorbate–adsorbent interaction. It has extensively been accepted that the chemisorption process can be described by this semi-empirical equation given below (Amadi *et al.*, 2020). The linear form of this equation is given by Yakout and Elsherif (2010):

$$q_t = \frac{1}{\ln(\alpha\beta)} + \frac{1}{\beta \ln t} \qquad 9$$

Where α is the initial adsorption rate (mg/g min), and the parameter β is related to the extent of surface coverage and activation energy for chemisorption (g/mg).The Elovich coefficients could be computed from the plots qt versus $\frac{1}{\ln t}$. The initial adsorption rate, α, and desorption constant, β, were calculated from the intercept and slope of the straight-line plots of qt against lnt in Equation 9. Table 1 presents the kinetic constants obtained from the Elovich equation. The application of the simple Elovich equation for the present kinetic data suggests that Elovich equation was unable to describe properly the kinetics of the Ni(II), Cd(II), Co(II) and Cu(II) ions on the carbonized star apple. Moreover, the experimental data did not give a good correlation for these results especially for Ni(II), Co(II), Cd(II) and Cu(II) ions.

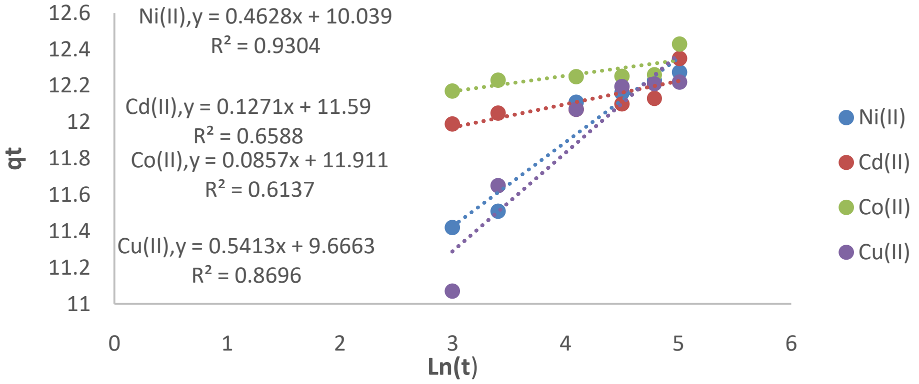

Figure 5: Elovich model for the adsorption of metal ions onto carbonized star apple

Adsorption Mechanisms

Liquid Film Diffusivity Model

The kinetics of adsorption of metal ions on various adsorbents may be controlled by several independent processes such as bulk diffusion, external mass transfer, film diffusion, chemical reaction, and intra particle diffusion. Itodo *et al.* (2010) used the linear driving force concept and developed a simple relationship:

$$\ln(1-\alpha_e) = -K_p t + D_F \qquad 10$$

Here $\alpha_e = q_t/q_e$ is the fractional attainment of equilibrium and K_p (min^{-1}) is the rate constant.

If a plot of ln(1- αe) against (t) is a straight line, then the adsorption is controlled by particle diffusion, suggesting that the diffusion of the metal ions to the adsorbent surface is independent of the initial concentration of the metal ions. However, if the plot is not a straight line, then the adsorption process becomes film-diffusion controlled. The fractional attainment at 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 this two different mechanism cannot be sharply demarcated (Itodo *et al.*, 2010). The diffusion rate constant K_p and the linear driving force D_F (diffusion parameter) obtained from the slope and intercepts of the plots are presented in table 1. Figure 6, shows that Co(II) and Cd(II) are particle diffusion controlled(linear graph) while Ni(II) and Cu(II) ions are film diffusion controlled (non linear graph). The mechanism of sorption depicted to be particle diffusion controlled means that intraparticle mass transfer resistance is rate limiting (Igwe and Abia, 2006). This means that in the presence of a mixture of the metal ions, the metal ions compete for the adsorption sites on the adsorbent. This competition affected the diffusion properties of the metal ions, hence decreased the adsorption capacity of the metal ions. The R^2 values confirm this. Therefore, the ease with which metal ion successfully reaches the adsorption site faster affects the adsorption capacity, this ease among other things depends on the ionic radii of the metal ions competitions for adsorption sites (Igwe *et al.*, 2005). Consequently, in an adsorption process, the metal ions from the bulk solution should move through the thin liquid film surrounding the adsorbent. The thin film may produce a diffusion barrier for the metal ion to penetrate before they arrive at the binding sites on the adsorbent. This suggests that the metal ion must overcome this film barrier to be adsorbed at the sites on the adsorbent. This mechanism is consistent with the fact that the rate of diffusion of the metal ion also affects adsorption rate.

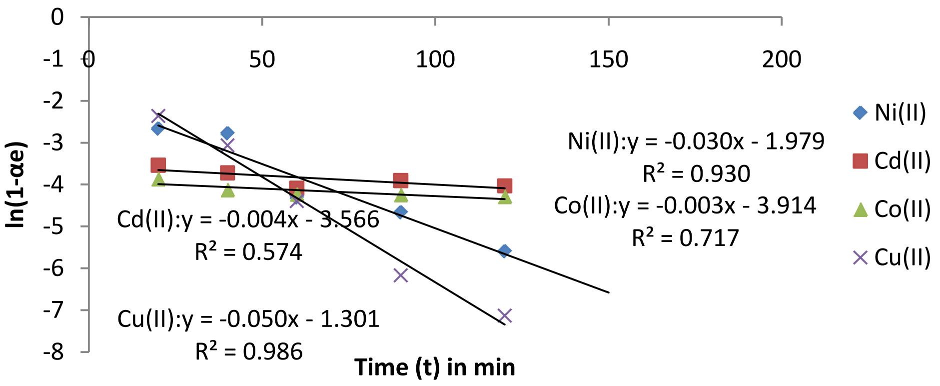

Figure 6: Liquid Film Diffusivity Model for the adsorption of metal ions onto carbonized star apple

Intra Particle Diffusivity Model (Mckay and Poot)

Intra particle diffusivity equation for description of sorption kinetics was explored using the intra-particle diffusivity model given below (Hassan *et al.*, 2012):

$$q_t = k_{id} t^{1/2} + C \qquad 11$$

Where, k_{id} is the rate of sorption controlled by intra particle diffusivity ($mgg^{-1}min^{-1(1/2)}$), C depicts the boundary layer thickness. This model predicts that the plot of qt versus $t^{1/2}$ should be linear with k_{id} and C as slope and intercept respectively if intra particle diffusivity is involved in the sorption process. Intra particle diffusivity is the rate controlling step if the line passes through the origin. According to Itodo *et al.* (2010), the intraparticle diffusivity plot, for sorption mechanism assumes an intraparticle diffusivity model if the following conditions are met: (i) High R^2 values to ascertain applicability. (ii) Straight line which passes through the origin for the plot area qt versus $t^{1/2}$. (iii) Intercept $C < 0$. The deviations from condition i, ii and iii above as shown in Figure 7, shows that the mode of transport is affected by more than one process. The intercept C values are very high $C > 10$ for the metal ions. Higher values of k_{id} illustrate an enhancement rate of adsorption, also, larger k_{id} values illustrate better adsorption which is related to improved bonding between adsorbate and adsorbent particles (Itodo *et al.*, 2010). From the assertion above, the values of k_{id} are relatively very low showing that there is no enhancement rate of adsorption which illustrates no adsorption and no better bonding between adsorbate and adsorbent particles. From the results in Table 1, it shows that none of these conditions (i, ii and iii) listed above were met suggesting that the intraparticle diffusivity model adsorption mechanism does not favour the adsorption of Ni(II), Cd(II), Co(II) and Cu(II) ions with the carbonized star apple.

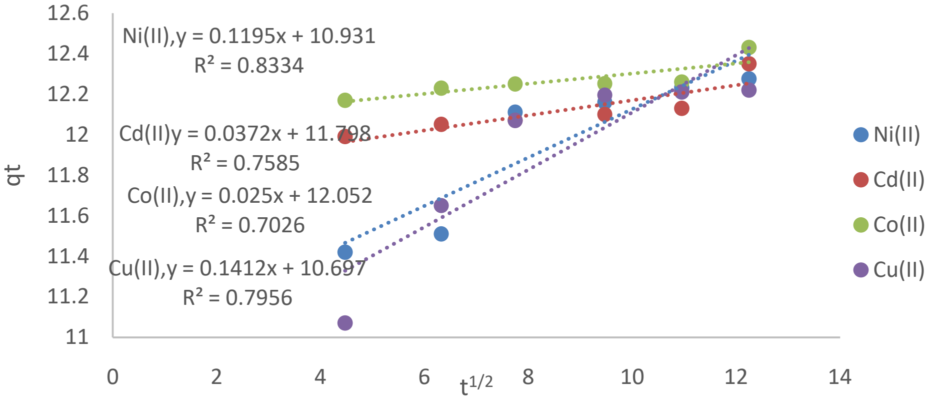

Figure 7: Mckay and Poot Intraparticle diffusion model for the adsorption for Ni(II), Cd(II), Co(II) and Cu(II) ions adsorption onto carbonized star apple

Table 1: Kinetic models' parameters for the adsorption of Ni(II), Cd(II), Co(II) and Cu(II) ions adsorption onto carbonized star apple

Adsorption Kinetic models	Parameters	Ni(II)	Cd(II)	Co(II)	Cu(II)
Pseudo First-Order	q_e (mg/g)	1.70	0.38	0.25	3.30
	K_1 (min^{-1})	0.03	0.01	0.004	0.05
	R^2	0.93	0.97	0.72	0.98
Pseudo Second-Order	qe (mg/g)	12.46	12.35	12.42	12.44
	K_2	0.03	0.07	0.11	0.04
	h_o(g/mgmin)	5.41	10.66	16.47	5.47
	R^2	0.99	0.99	0.99	0.99
Elovich	α (mg/g)	12×10^8	5×10^{38}	1.9×10^{59}	3×10^7
	β(g mgmin)	2.16	7.87	11.67	1.85
	R^2	0.93	0.66	0.61	0.87
Mckay and Poot intraparticle diffusion	C	10.93	11.80	12.05	10.70
	K_i	0.12	0.04	0.03	0.14
	R^2	0.83	0.76	0.70	0.80
Liquid Film Diffusion	D_F	-1.98	-3.57	-3.91	-1.30
	K_F	3×10^{-2}	4×10^{-3}	3×10^{-3}	5×10^{-2}
	R^2	0.93	0.57	0.72	0.99

CONCLUSIONS

This study has shown that carbonized star apple pericarp are good materials for effective and efficient sorption of Co(II), Cu(II), Cd(II) and Ni(II)) ions. Adsorption of these sorbates was found to be dependent on contact time. Maximum sorption occurred within the first 60 min while equilibrium contact time was reached for Ni(II), Cd(II), Co(II) and Cu(II) ions. The equilibrium contact time was reached for cobalt after 120 minutes but 100 minutes of agitations for nickel, cadmium and copper. The work supports an enhanced rate of adsorption which is linked to improved bonding. Deviation from validity test for transport mechanism is an indication that intraparticle transport is not the only rate limiting step. Estimations based on fractional attainment of equilibrium (αe) revealed that sorption is more of particle diffusion controlled (transport of the sorbate through the sorbent-sample interphase onto the pores of the sorbent) than liquid film diffusion controlled. Moreover, adsorption process undergoes pseudo-second-order kinetic as proved by the high value of R^2 (correlation coefficient) and that pH 6 recorded the highest adsorption values.

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