

## KINETICS AND MECHANISM MODELLING OF Pb(II) AND Ni(II) IONS SORPTION FROM AQUEOUS MEDIUM: EVALUATING THE PERFORMANCE OF *Curcuma longa* RHIZOME IN THE TREATMENT OF WASTE WATER.

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### ABSTRACT

In this research *Curcuma longa* Rhizome, an agricultural product, available in large quantity in northern Nigeria, were used as low-cost adsorbent for removal of Pb(II) and Ni(II) ions from aqueous medium. Batch operation was used to study the equilibrium behaviour of *Curcuma longa* rhizome. The effect of solution pH, and contact time on the adsorbent for the removal of Pb(II) and Ni(II) ions were evaluated. To study the adsorption kinetics of Pb(II) and Ni(II) ions onto *Curcuma longa* Rhizome, pseudo-first-order, pseudo-second-order as well as three diffusion models: intraparticle diffusion model (Weber and Morris model), film diffusion model (McKay model) and liquid film Models were used. The sorption kinetics can be described well by the pseudo-second-order model due to the closeness between the  $q_{exp}$  (49.26 mg/g) and  $q_{cal}$  (52.63 mg/g) for Pb(II) and  $q_{exp}$  (57.60) and  $q_{cal}$  (55.56 mg/g) for Ni(II) ions. Moreover, the rate limiting step are liquid film and intraparticle diffusion controlled. In addition, the results suggest that *Curcuma longa* Rhizomes are very effective adsorbent for the removal of Pb(II) and Ni(II) ions from aqueous medium. This will serve as an indicator to consider in the design for waste water treatment plant for heavy metal detoxification using *Curcuma longa* Rhizome.

**Keywords:** *Curcuma longa* Rhizome, heavy metal ions, kinetic study, sorption

### INTRODUCTION

The gravity of water pollution is of great concern to human life as water is the prime necessity of life. Lead and nickel are among the metals of concern because of its toxicity even at low concentrations. When the permissible concentrations are exceeded, these ions exhibit toxic properties and a no biodegradable character [1, 2]. The presence of considerable amounts of heavy metal in industrial wastewater poses serious threat to the environment because the recoveries of heavy metals using conventional chemical methods are not economical [3]. The removal of lead, nickel and other heavy metals from industrial wastewaters is a problem of

increasing concern that has been mostly solved by chemical and physical methods of treatment [4, 5]. However, these methods are not only costly and require trained personnel, but also use chemicals that generate wastes which may be hazardous or toxic [6, 7]. The search for new cost-effective technologies for the removal of heavy metal from wastewaters has therefore been directed towards biosorption which involves the use of either live or dead microorganisms or their derivatives. Biosorption of heavy metal ions using biological materials such as stem, leaf, pod, shell, peels and bark has received greater attention recently due to its advantages over

conventional methods [8]. Some of the advantages include low cost, high efficiency, minimization of sludge production, possibility of regeneration of biosorbent and metal recovery [7,9]. Biosorption is therefore seen as an alternative method that can be categorized as a green technology for heavy metal removal from industrial effluents [10]. Different parts of plants and their related wastes are naturally available as well as inexpensive in comparison to other chemically modified materials. Thus, most of the adsorption studies have been focused on untreated plant materials and their wastes [11, 12]. In this paper, *Curcuma longa* Rhizome powder is selected as the biosorbent for the removal of Ni(II) and Pb(II) ions from aqueous solution. The mechanism of biosorption is influenced by many experimental factors like pH, ionic strength, biomass concentration and temperature. The variability of these factors in rear water systems makes it necessary to know how they influence the sorption capabilities of biomass. The extra information regarding the mechanisms and the influencing factors are highly useful in optimization of experimental conditions. To the best of our knowledge, there is no information in the literature concerning the use of *Curcuma longa* Rhizome, a fact which confirms without doubt the novelty of this work. As part of the study, the basic parameters for carrying out of the adsorption process were determined. The kinetics of the adsorption of the aforementioned ions on the adsorbent was also investigated.

## MATERIALS AND METHODS

### *Preparation of the adsorbent:*

The adsorbent, *Curcuma longa* Rhizome was obtained at National Root Crops Research Institute (NRCRI), Umudike, Abia state, Nigeria. The rhizomes were washed with de-ionized water, crushed with a blender and the juice extracted. The residues were dried and sieved to obtain 0.15 mm mesh size. The sieved samples were soaked in 0.3 M HNO<sub>3</sub>, 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 °C for 2 h and finally stored in a tight plastic container ready for use.

### *Adsorption Experiments*

Batch adsorption studies for the removal of Ni<sup>2+</sup> and Pb<sup>2+</sup> by *Curcuma longa* Rhizome 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 the solution pH. This was done by introducing 50 cm<sup>3</sup> of each metal ion solution into different 250 cm<sup>3</sup> Erlenmeyer flasks containing 0.05 g of the adsorbent and adjusting the pH of the solutions to 2, 4, 6, 7 and 8. The mixtures were agitated intermittently for 60 min in a rotary shaker and then filtered. The concentration of each filtrate was determined using Perkin Elmer Analysit 200 Atomic Absorption Spectrophotometer. The effect of contact time on adsorption of the metal ions was studied using the same method but at constant adsorbent mass of 0.05 g and constant pH 7 for Pb<sup>2+</sup> and Ni<sup>2+</sup> solutions. However, the time was

varied from 10 to 180 minutes. From the results obtained, percentage removal and the amount absorbed were calculated using equations 1 and 2.

$$\%R = \frac{C_o - C_t}{C_o} \times \frac{100}{1} \quad \text{-----(1)}$$

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

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 at time t (mg/L),  $V$  = volume of metal ion solution used in  $\text{dm}^3$  and  $m$  the dry mass of the adsorbent in (g).

## RESULTS AND DISCUSSION

### *Effect of pH on Adsorption of Metal ion*

Figure 1 shows the role of pH on biosorption of Pb(II) and Ni(II) ions on aqueous solution. It is indicated that percentage removal of Pb(II) and Ni(II) reached a maximum in a slight acidic medium and decreased in slight basic medium. The percentage removal of Pb(II) and Ni(II) increased from 57.93 % and 80.82 % respectively at pH 2 to maximum of 96.37 % at pH 4 for lead and 93.44 % at pH 6 for nickel, but decreased slightly with increasing the pH values to 8. It was found from

the study that the predominant species of Pb(II) and Ni(II) ions occurred at pH 4 and 6 respectively, in agreement with Heidari's report [13]. Therefore, pH 4 and 6 were chosen as the working optimum pH values for the metal ions involved in further experiments. Moreover, in the presence of high concentration of  $\text{H}^+$  ions at pH 2, hydroxonium ions  $\text{H}_3\text{O}^+$  ions would compete with  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  ions for the binding sites, leading to lower percentage removal of these metal ions. However, the decrease in the concentration of  $\text{H}_3\text{O}^+$  ions at pH 4 and 6 lead to decrease in the number of positive charges on the surface of adsorbent which results to reduction in the electrostatic repulsion between the surface of adsorbent and metal ions caused the increased percentage removal to 96.37 % and 93.44 %. Different researchers have reported similar trends [13-14]. But increasing the pH to 5 and 8 for lead and nickel ions respectively would increase the concentration of  $\text{OH}^-$  ions leading to the formation of the predominant species of  $\text{Pb}(\text{OH})_2$  and  $\text{Ni}(\text{OH})_2$ . Due to the low solubility of these compounds at  $30^\circ\text{C}$ , the concentration of metal ions would decrease at pH 8 mainly due to precipitation, and not by adsorption at pH 8 for  $\text{Pb}^{2+}$  and  $\text{Ni}^{2+}$  ions [15].

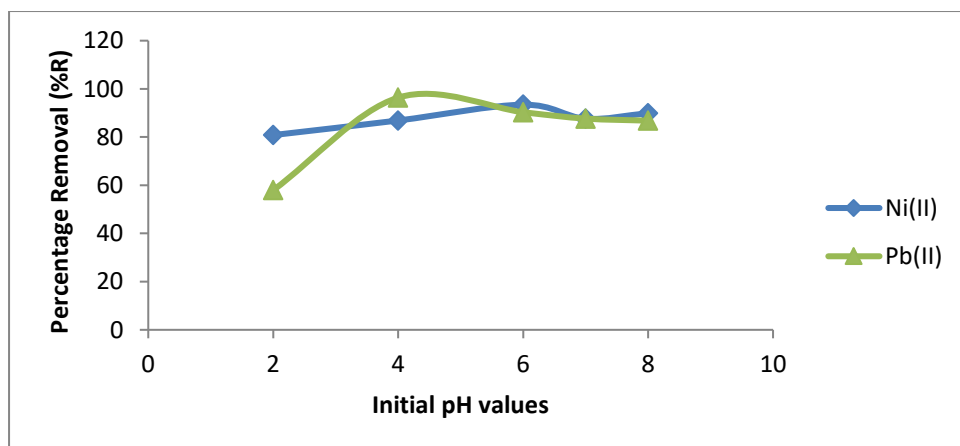


Fig. 1: Effect of pH on sorption of Pb(II) and Ni(II) ions onto *Curcuma longa* Rhizome**Effect of Contact Time on the Adsorption of Metal Ions**

To evaluate the effect of contact time on absorption processes, the amount of metal ions adsorbed (mg/g) measured as a function of time is shown Figure 2. As observed, the amount of ion adsorbed onto the biomass increases rapidly with time for the first 20 min, then gradually until it reaches equilibrium at 60 min. At this point, the amount of the ion desorbing from the adsorbent is in a state of dynamic equilibrium with the amount being absorbed by the

adsorbent. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of ion adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions. This can be explained by the fact that initially, the rate of ion uptake was higher because all sites on the adsorbent were vacant and ion concentration was high, but decrease of adsorption sites reduced the uptake rate [16].

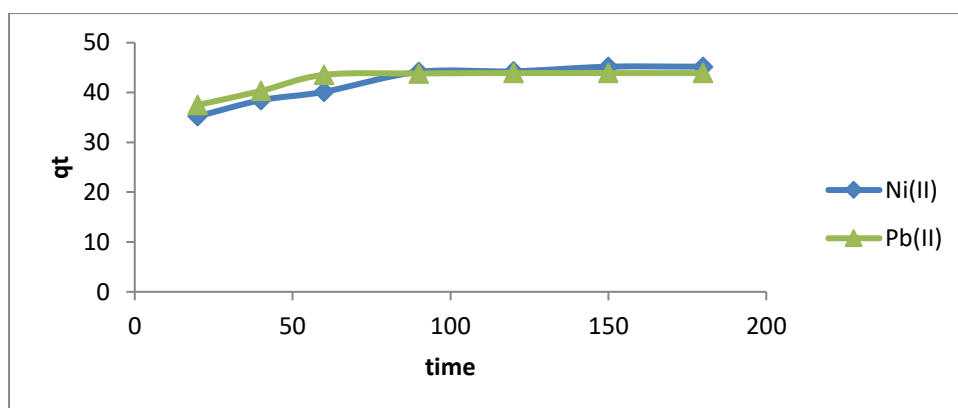


Fig.2. Effect of Contact time on sorption of Pb(II) and Ni(II) ions onto *Curcuma longa* Rhizome  
Pseudo first-order model the Lagergren's rate equation is one of the most widely

**Adsorption Kinetics**

The adsorption kinetics of the metal ions onto *Curcuma longa* Rhizome were analyzed using the Pseudo-First order, Linear Pseudo-second order kinetic model, Elovich model and intraparticle diffusion model. The conformity

between experimental data and the observed data could be used as a parameter to predict the model that best interprete the experimental data. A relatively high  $R^2$  value indicates that the model successfully describes the kinetic of the adsorption process.

**Pseudo first-order model**

used rate equation to describe the adsorption of adsorbate from the liquid phase [17] and is given as:

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

The linear form of equation (3) is given as:

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

The plot of  $\ln(q_e - q_t)$  against time (Figure 3) gives a straight line from which  $k_1$  can be calculated from the slope and  $q_e$  from the intercept. Where,  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed on adsorbent (mg/g) at equilibrium and at time  $t$ (min), respectively,

and  $k_1$  is the rate constant of pseudo first-order kinetics.

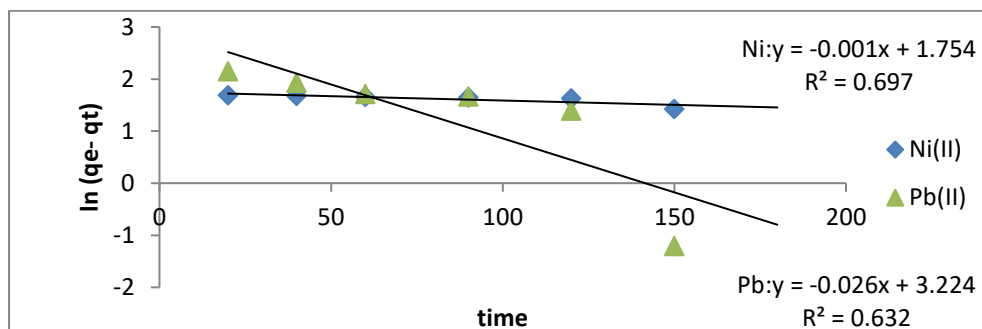


Fig. 3 Pseudo-first order plot of  $\ln(q_e - q_t)$  vs  $t$  for the adsorption of Pb(II) and Ni(II) Ions onto *Curcuma longa* Rhizome

The low  $R^2$  values for Pb(II) and Ni(II) ions are 0.6320 and 0.6970 respectively. The calculated  $q_e$  values for Pb(II) and Ni(II) ions are generally less than their respective experimental values as shown in Table 1 suggesting that pseudo first-order model couldn't interpret the experimental data in the present study.

#### Pseudo Second-Order Model

The pseudo second order relies on the assumption that the rate limiting step of an adsorption process may be chemical reaction involving valence forces resulting from sharing or exchange of electron between adsorbent sites. The pseudo second order adsorption kinetic rate equation is expressed as equation 5 [18].

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

Where  $k_2$  is the rate constant of pseudo second order adsorption ( $\text{g/mg min}^{-1}$ ) for the boundary conditions,  $t = 0$  and  $q_t = q_i$ , the integrated form of the equation becomes

$$\frac{t}{qt} = \frac{1}{h_o} + \frac{t}{q_e} \quad (6)$$

The initial sorption rate,  $h_o$  ( $\text{g/mg min}$ ) as  $t$  approach zero is expressed as

$$h_o = k_2 q_e^2 \quad (7)$$

The plot of  $t/qt$  versus  $t$  using equation (6) gave linear relationship from which  $q_e$  and  $k_2$  were determined from the slope and intercept of the plots respectively. From pseudo second order plot (Figure 4), the pseudo second order kinetic parameters  $k_2$ ,  $q_e$  and  $h_o$  and their  $R^2$  values were computed and presented in Table 1.

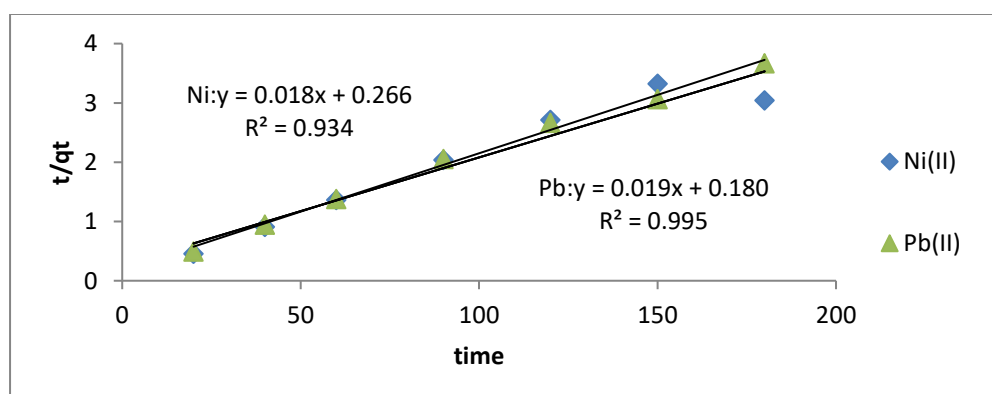


Fig. 4: pseudo-second order plot of  $\ln(q_e - q_t)$  vs  $t$  for the adsorption of Pb(II), Ni(II) Ions onto *Curcuma longa* Rhizome.

Evaluation of the values of the constant in Table 1 using the correlation values  $R^2$  value. The ( $R^2 \geq 0.9340$ ) shows that the pseudo second order kinetic plot gave the best interpretation to the experimental adsorption data. This assertion is based on the selection criterion which States that the closer the  $R^2$  values is to unity, the greater the fitting pattern of that model to the experimental kinetic model. Therefore, the fitting of adsorption data into pseudo second order model means that the rate of occupation of active site is proportional to the square of the number of the unabsorbed sites. Moreover, it is observed that the experimental and the observed values are almost the same for the metal ions under study. The higher the  $k_2$  values, the faster the reaction proceeds and the higher the adsorption rate and this means that the sorption of Pb(II) ion was faster. This suggests that the sorption of Pb(II) and Ni(II) ions by the adsorbent are kinetically controlled as a second order reaction than a first order process, and therefore assumes chemical

sorption as the rate limiting process (Amadi *et al.*, 2020). 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. This was calculated by using the following equation 8 [19]:

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (8)$$

The experimental data for the adsorption of the  $Pb^{2+}$  and  $Ni^{2+}$  ions were also employed to evaluate the controlling mechanism of adsorption processes. The diffusion coefficients for the intra-particle transport of the  $Pb^{2+}$  and  $Ni^{2+}$  ions were calculated using equation 9 [20].

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

where  $r$  is the radius of the adsorbent particle in centimeters and  $D$  is the diffusion coefficient value in  $cm^2 \cdot min^{-1}$ . Estimated  $D$  values (Table 1) correlated with the equilibrium amount of heavy metal ion adsorbed. However, nickel which displayed better adsorption had the lower  $D$  value.

Table 1: Kinetic models' parameters for the adsorption of Pb(II) and Ni(II) ions onto *Curcuma longa* Rhizome. Consider  $r$  to be 0.009 cm.

Adsorption Kinetic models	Parameters	Pb(II)	Ni(II)
Pseudo first-order	$q_{e \text{ exp}}$ (mg/g)	49.26	57.60
	$q_{e \text{ cal}}$ (mg/g)	25.13	5.78
	$k_1$ ( $min^{-1}$ )	0.026	0.001
	$R^2$	0.632	0.6970
Pseudo second-order	$q_{e \text{ exp}}$ (mg/g)	49.26	57.60
	$q_{e \text{ cal}}$ (mg/g)	52.63	55.56
	$k_2$	0.0020	0.00122
	$h_o$ (g/mg min)	5.5679	3.7654

	$t_{1/2}$ (min) D (cm <sup>2</sup> .min <sup>-1</sup> ) R <sup>2</sup>	9.4554 1.7133 x 10 <sup>-7</sup> 0.9950	14.7536 1.0981 x 10 <sup>-7</sup> 0.9340
Elovich	$\alpha$ (mg/g) $\beta$ (g/mg. min) R <sup>2</sup>	5635.412 0.2595 0.8570	1040.41 x 10 <sup>8</sup> 0.6506 0.3760
M & P (intraparticle diffusion)	I <sub>i</sub> k <sub>id</sub> R <sup>2</sup>	35.83 0.965 0.9170	41.08 0.422 0.4850
W & M (intraparticle diffusion)	n <sub>i</sub> k <sub>id</sub> R <sup>2</sup>	0.086 4.118 0.8750	0.033 77.789 0.3830
Liquid Film diffusion	D <sub>F</sub> k <sub>F</sub> R <sup>2</sup>	-3.224 0.001 0.001	-5.222 0.030 0.566

### Elovich Model

Elovich model equation was also used successfully to describe the second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but does not propose any definite mechanism for adsorbate - adsorbent. The equation defining the kinetic principle, assumes that the adsorption implies a multilayer adsorption. In other words, it is another kinetic rate equation which describes the adsorbing surface as heterogeneous in nature. It has extensively been accepted that the chemisorption process can be described by this semi empirical equation 10.

The equation is generally expressed as:  $\frac{d}{dt} = \alpha \exp(-\beta qt)$  (10)

where  $\alpha$  is the initial rate (mg/g/min) while  $\beta$  is related to the extent of surface coverage and the activation energy for chemisorptions (g/mg). Integrating this equation for the boundary condition  $qt = 0$ ,  $qt = qt$  at  $t = t$ , equation (10) becomes equation 11;

$$qt = \ln(\alpha\beta) + \beta \ln(t) \quad (11)$$

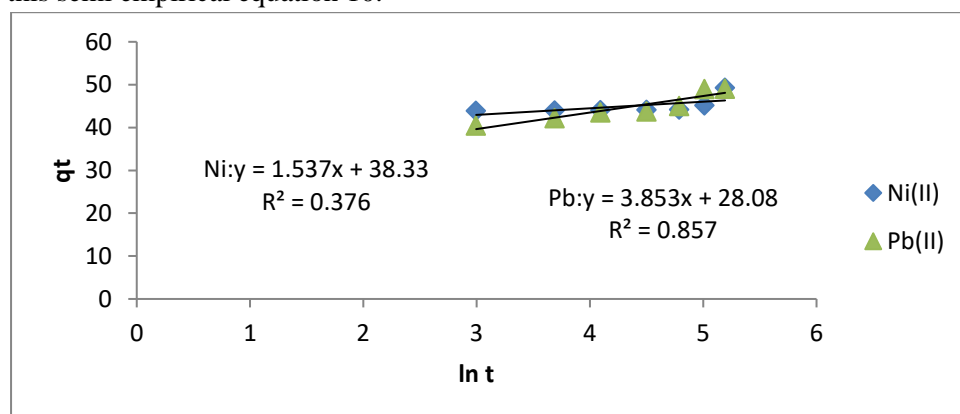


Fig. 5: Elovich plot of  $q_t$  vs  $\ln t$  for the adsorption of Pb(II) and Ni(II) Ions onto *Curcuma longa* Rhizome.

The linear plots of  $qt$  versus  $\ln(t)$  shown above justifies the Elovich model from which the parameters  $\beta$  and  $\alpha$  may be calculated from the



slope and intercept of such plots. The relatively low correlation

coefficient ( $R^2$ ) values showed that the model could not give a good description to the experimental adsorption data.

#### ***Intra particle Diffusion Model.***

Since neither the pseudo first nor the second model can identify the diffusion mechanism, therefore, in order to identify the diffusion mechanism for the sorption process, the kinetic results were analyzed by the intra particle diffusion model, so as to elucidate the diffusion mechanism involved. In this model a graphical method to prove the occurrence of intra particle diffusion and to determine if it is the rate limiting step in the adsorption process was introduced by Webber and Morris:

$$R = k_{id}t^n \quad (12)$$

The logarithmic form is:

$$\ln R = \ln k_{id} + n \ln t \quad (13)$$

Where  $R$  is the percentage of metal ion adsorbed,  $t$  is the contact time in (min),  $n$  is the slope of linear plots, which indicate the adsorption mechanism,  $k_{id}$  is the intra particle diffusion rate constant ( $\text{min}^{-1}$ ) which may be taken as a rate factor. The plot of  $\ln R$  versus  $t$  for adsorption of the metal ion by the adsorbent is shown in Figure 5, from the plots,  $n$  (gradient of the linear plots) and  $k_{id}$  (the intra particle diffusion rate constant in ( $\text{min}^{-1}$ )) were determined from the slope and intercept of the linear plots, respectively and are presented in Table 1.

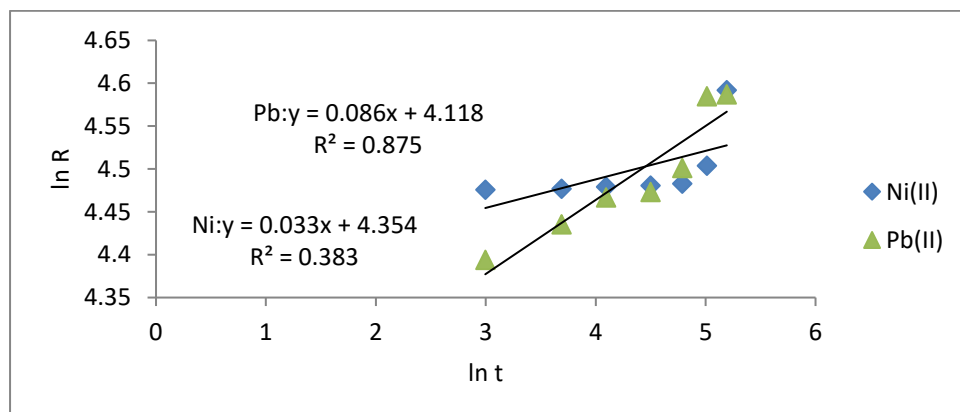


Fig. 6: Morris and Weber plot of  $\ln R$  vs  $\ln t$  for the adsorption of Pb(II) and Ni(II) Ions onto *Curcuma longa* Rhizome.

From Table 1 the high  $R^2$  value observed for Pb(II) ion than Ni(II) ions shows that the adsorption of Pb(II) ion into the micro pores of adsorbent may be mostly controlled by intra particle diffusion.

#### ***McKay and Poot intraparticle diffusion model***

In this model, it is assumed that the mechanism for metal ion removal by adsorption on a sorbent material takes through four steps (i) migration of metal ions through the surface of the adsorbent through bulk diffusion, (ii) diffusion of the metal ions through the



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 surface of material by chemical reaction via ion exchange, complexation and/or chelation. The adsorption process is a diffusive mass transfer process when the rate can be expressed in terms of the square root of time (t). The intra particle diffusion model is expressed as follows [21].

$$q_t = k_i t^{1/2} + I. \quad (14)$$

Where  $q_t$  is the fraction uptake (mg/g) at time (t),  $k_i$  is the intra particle diffusion rate constant (mg/g min<sup>1/2</sup>) and I is the intercept (mg/g). A plot of  $q_t$  versus  $t^{1/2}$  (Figure 7) will give  $k_i$  as slope and I as intercept and results are presented in Table 1. The I represent the effect of boundary layer thickness. The smaller the intercept length, the less the adsorption boundary layer controlled.

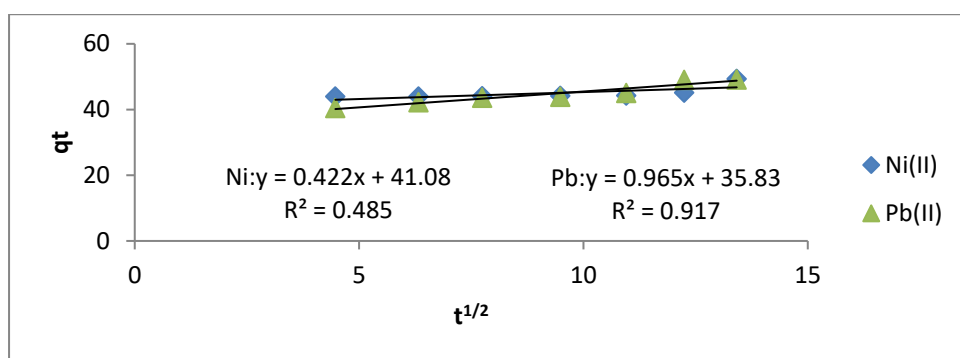


Fig. 7: McKay and Poot plot of  $q_t$  vs  $t^{1/2}$  for the adsorption of Pb(II) and Ni(II) Ions onto *Curcuma longa* Rhizome.

but careful observation infer that data points can be better presented by double linear with difference in slope ( $k_i$ ) and intercept I. In these first straight lines, the gradual increases (for a long time period) in slopes signify that the metal ions are transported to the external of the *Curcuma longa* Rhizome through film diffusion and its rate is very slow. After that, metal ions are entered into the *Curcuma longa* Rhizome by intra particle diffusion through pore, which is represented in the second straight lines. Both the lines do not pass through the origin that concludes that both film diffusion and intra particle diffusion are simultaneously occurring during the adsorption of these metal ions onto *Curcuma longa* Rhizome [22].

#### Liquid Film Diffusion 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 and others [23] used the linear driving force concept and developed a simple relationship:

$$\ln(1-a_e) = -k_p t + D_f. \quad (15)$$

$$\text{Hence } a_e = q_t / q_e. \quad (16)$$

is the fractional attainment of equilibrium and  $k_p$  is the rate constant.

A plot of  $\ln(1-a_e)$  versus time (t) yields the  $k_p$  the rate constant (min<sup>-1</sup>) as the slope of the graph and a dimensionless constant  $D_f$  as intercept. The diffusion rate constant  $k_p$  and the

linear driving force  $D_f$  (diffusion parameter) obtained from the slope and intercept of the plots are presented in Table 1. If a plot of  $\ln(1-a_e)$  against  $t$  is a straight line, then adsorption is controlled by particular diffusion and the diffusion of the metal ions, but if it is not a straight line, then it suggests that the sorption process is film diffusion controlled. 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 [16]. The  $R^2$  value of Pb(II) and Ni(II) ions suggests that the diffusivity model does not entirely support their adsorption using *Curcuma longa* Rhizome. Figure 8 shows that Pb(II) and Ni(II) is particle diffusion controlled (linear graph). Since sorption is particle diffusion controlled (plot is linear), it could be affected by four (4) processes [24]. The mechanism of sorption depicted to be particle diffusion-controlled means that intra-particle mass transfer resistance is rate limiting [23]. This means that in the presence of a mixture of the metal ions, the metal ions compete for the adsorption site

on the adsorbent. This competition affects the diffusion properties of the metal ions, hence decreases the adsorption capacity of the metal ions. The  $R^2$  values confirmed this. Thus, the metal ion that successfully reaches the adsorption site faster depends on the above factors and also on the ionic radii of the metal ions competition among the metal ions for adsorption sites clearly affected the adsorption capacity [24]. 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 ions to penetrate before they arrive at the binding site 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. This conclusion was also arrived at by Abia and Asuquo [25] in their study on  $Pb^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$  and  $Cr^{2+}$  with oil palm fibre.

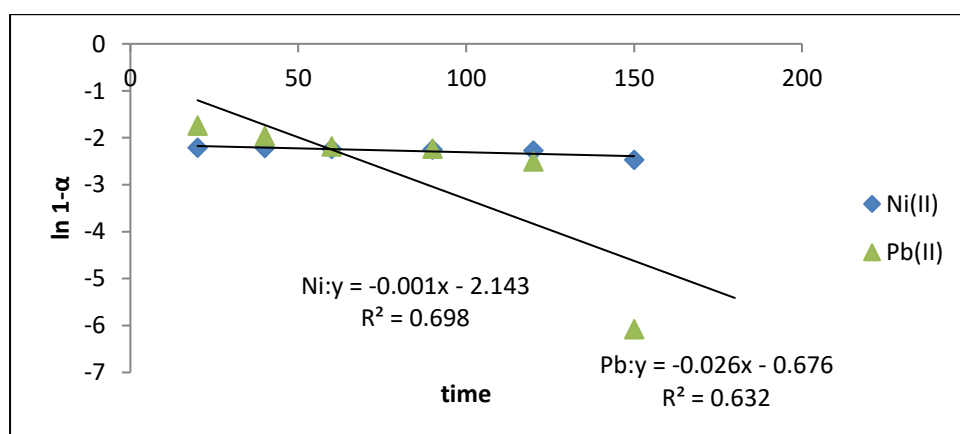


Fig. 8; Liquid film diffusivity model for adsorption of Pb(II) and Ni(II) ions adsorption onto *Curcuma longa* Rhizome.

## CONCLUSION

This study has shown that *Curcuma longa* Rhizomes are good materials for fast and efficient sorption of (Pb(II) and Ni(II)) ions from aqueous solution. The adsorption of these sorbates was found to be dependent on pH and contact time. The pH of 6.0 and 4.0 were recorded as the optimum for maximum adsorption of Ni(II) and Pb(II) ions respectively by the adsorbent. Results from pseudo second order kinetics studies showed that the affinity of the metal ions sorption for the adsorbent was in the order Ni(II) > Pb(II) due to the 55.63 mg/g and 52.56 mg/g quantities adsorbed respectively. The adsorption process was found to follow pseudo second order kinetics. The transport mechanism was found to be film-diffusion and intra particle diffusion controlled. A contact time of 60 min was sufficient for attainment of equilibrium for the sorption.

## REFERENCES

- 1 T. A. Saleh, and V.K Gupta. (2012). Column with CNT/magnesium oxide composite for lead (II) removal from water. *Environ. Sci. Pollut. Res.* 19, 1224–1228.
- 2 M. Jain, G. V, Kumar, K. Kadirvelu, (2013).. Removal of Ni(II) from aqueous system by chemically modified sunflower biomass. *Desalin. Water Treat.* 52, 5681–5695.
- 3 O.K. Amadi<sup>1</sup>, F.K. Ekuma<sup>1</sup>, C. M. Ngwu<sup>1</sup> and C. H. Nwankwo<sup>1</sup>.(2020). Kinetic studies on biosorption of Pb(II), Cd(II) and Ni(II) ions from aqueous solution by activated ceasar weed (*Urena lobata*) bark, *J. Chem Soc. Nigeria*, 45(1), 63 – 69
- 4 F. K. Onwu, T. A., Abia, A. C.. and 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): 471-480.
- 5 L.Klapiszewski, P, Bartczak, M., Wysokowski, M., Jankowska, K., Kabat, KT, Jesionowski, ., (2015). Silica conjugated with kraft lignin and its use as a novel ‘green’ sorbent for hazardous metal ions removal. *Chem. Eng. J.* 260, 684–693.
- 6 M. Wawrzekiewicz, and Z. Hubicki, (2011). Remazol Black B removal from aqueous solutions and wastewater using weakly basic anion exchange resins. *Cent. Eur. J. Chem.* 9, 867–876.
- 7 K. P. Senthil, S. Ramalingam, K. S., Dinesh A., Murugesan, T. Vidhyadevi, and S. Sivanesan. (2011). Adsorption behavior of nickel(II) onto cashew nut shell: equilibrium, thermodynamics, kinetics, mechanism and process design. *Chem. Eng. J.* 167, 122–131.
- 8 M. Himani, R. C. Priyadarshi, D. B. Pulakananda, and K. G. Bhattacharyya (2020). Kinetics of Aqueous Cu(II) Biosorption onto Thevetia peruviana Leaf Powder, *ACS Omega*, 5, 13489–13502
- 9 H. Medhi, K. G. Bhattacharyya, (2015). Kinetics of Cu(II) Adsorption on Organo-Montmorillonite. *J. Surf. Sci. Technol.* 31, 150–155.
- 10 J.Wang, and C. Chen, (2009). Biosorbents for heavy metals removal and their future. *Biotechnology Advances*, 27, 195 – 226
- 11 S. Abadian, A. Rahbar-Kelishami, P Norouzbeigi, M. Peydayesh, M. (2015) Cu(II) adsorption onto Platanus orientalis leaf powder: kinetic, isotherm, and thermodynamic studies. *Res. Chem. Intermed.* 41, 7669–7681.
- 12 R. M. Alia, H. A. Hamada, M. M. Hussein, and G. F. Malash. (2016).

- Potential of using green adsorbent of heavy metal removal from aqueous solutions: Adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecol. Eng.* 91, 317–332.
- 13 H. Y. Heidari, Z. Mehraban, and H. Heikkinen, (2013) Selective Adsorption of Pb(II), Cd(II), and Ni(II) Ions from Aqueous Solution Using Chitosan-MAA Nanoparticles. *International Journal of Biological Macromolecules*, 61, 251- 263. <http://dx.doi.org/10.1016/j.ijbiomac.2013.06.032>
  - 14 W. Li, L. Zhang, J. Peng, N. Li, S. Zhang, and S. Guo. (2008) Tobacco Stems as a Low Cost Adsorbent for the Removal of Pb(II) from Wastewater: Equilibrium and Kinetic Studies. *Industrial Crops and Products*, 28, 294-302.
  - 15 L. Giraldo, and J. C. Moreno-Piraján, (2008) Pb<sup>2+</sup> Adsorption from Aqueous Solutions on Activated Carbons Obtained from Lignocellulosic Residues. *Brazilian Journal of Chemical Engineering*, 25, 143-151.
  - 16 O. K. Amadi, F. K. Ekuma, I. A. Okoro, and C. C. Aleruchi. (2019). Kinetics studies of sorption of Pb(II), Cd(II) and Ni(II) ions from aqueous solution using functionalized calopo (*Calopogonus mucunoides*) seed pod. *J. Chem Soc. Nigeria*, 44(6), 1183 - 1190
  - 17 S. Lagergren, and K. Svenska. (1898). About the Theory of So-Called Adsorption of Soluble Substances, *Vetenskapsakad Handl.*, 24(2), 1- 39.
  - 18 Y. S. Ho, and G. Mickay. (2000). The kinetics of sorption of divalent metal ions onto sphagnum moss peat water research, 34 (3): 735-742
  - 19 S. Shallari, C. Schwartz, A. Hasko, J. L. Morel. (1998). Heavy metals in soils and plants of serpentine and industrial sites of Albania. *Sci. Total Environ.*;19209:133–142.
  - 20 O.K. Amadi<sup>1</sup>, F.K. Ekuma<sup>1</sup> and B. N. Uche (2021). Bioremediation of Ni<sup>2+</sup>, Cd<sup>2+</sup> and Pb<sup>2+</sup> from aqueous solution using chemically modified *Newbouldia Leavis* seed pod. Kinetics and Intraparticle Diffusivities. *J. Chem. Soc. Nigeria*, 46(2) 0217 – 0224
  - 21 W.J. Weber, and J. C. Morris. (1963). Kinetics of adsorption on carbon from solution. *Journal Sanit. Div. American Society of Civil Engineering*. 89:31-60.
  - 22 B. Norrooz, G. A. Sorial, H. Bahrami, and M. J. Arami. (2007). Hazard Mater, B139, 167-174.
  - 23 A. U. Itodo, F. W. Abdulrahman, L. G. Hassan, S. A. Maigandi. and H. U. Itodo, (2010). "Intraparticle Diffusion and intra particulate Diffusivities of Herbicide on Derived Activated Carbon". <http://www.sciencepub.net/researcher>, 74-86.
  - 24 J. C. Igwe. E. C. Nwokennaya, and A. A. Abia. (2005). The role of pH in heavy metal detoxification by biosorption from aqueous solution containing chelating agents. *African Journal of Biotechnology*. 4 (10): 1109-1112.
  - 25 A. A. Abia and E. D. Asuquo. (2007). Kinetics of Cd<sup>2+</sup> and Cr<sup>3+</sup> sorption from aqueous solutions using Mercaptoacetic acid modified and unmodified oil palm fruit fibre (*Elaeis guineensis*) Adsorbents. *Tsinghua Science and technology* 12(4):485-492