



ADSORPTION KINETICS OF Ni (II) AND Pb (II) IONS FROM AQUEOUS SOLUTIONS BY HUSKS OF *IRVINGIA GABONENSIS*

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ABSTRACT

The ability of an economically cheap biomaterial like bush mango (*Irvingia gabonensis*) husks for adsorption of lead (II) and nickel (II) ions from aqueous solutions was investigated. The effect of contact time on the adsorption of these metal ions was studied in a batch process. The adsorption data were correlated with pseudo first-order, pseudo second-order, Elovich and intra-particle diffusion kinetic models. Results show that pseudo second-order kinetic model correlated the experimental data well. Results further revealed that lead (II) was better adsorbed onto the biosorbent as compared to nickel (II) ions. This study shows that the adsorption process using this biosorbent could be an economical method for the removal of these metal ions from aqueous solutions and may be employed in wastewater treatment.

Key words: Adsorption, Biosorbent, Heavy metals, *Irvingia gabonensis*, Biosorption.

INTRODUCTION

The release of toxic metal ions from several industrial applications viz. electroplating, nickel-cadmium battery production and disposal, fuels and pigments has become a grave environmental problem confronting the world today for water pollution. These metal ions in addition to being toxic, even at low concentrations, are found to be non-biodegradable and gradually accumulate in living tissues over time; thereby, causing health problems in animals, plants and human beings¹⁻³. Exposure to Ni for instance has resulted in several health effects ranging from skin irritations to damage to the lungs, nervous system and mucous membranes^{4,5}. Exposure to lead had been known to cause encephalopathy, seizures and mental retardation particularly in young children⁶⁻⁹. Some heavy metals are also

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known carcinogens. It is, therefore, vital to remove these heavy metal ions from wastewater so as to protect human health and our environment. Agricultural materials being economical and eco-friendly due to their unique chemical composition, availability in abundance, renewability and low cost have offered a viable option for heavy metal remediation¹⁰.

This paper considers the adsorption kinetics of Ni (II) and Pb (II) ions from aqueous solutions by *Irvingia gabonensis* husks. *Irvingia gabonensis* contains several organic compounds of high molecular weight with heteroatoms such as tannins, saponins, alkaloids, anthroquinones and phenols¹¹. These groups of heteroatoms are capable of binding to metal surfaces. Currently, there is no reported work on the kinetics of adsorption of metal ions using this biosorbent by any chemical method. In order to buttress the interest in the use of more eco-friendly, less toxic materials in the adsorption of heavy metal ions from aqueous solutions, we report the kinetics of adsorption of two metal ions, Pb (II) and Ni (II) from their aqueous solutions using the biomaterial, *Irvingia gabonensis* husks.

EXPERIMENTAL

Materials and methods

The bush mango (*Irvingia gabonensis*) fruits were basically sourced from local market, Abakaliki in Ebonyi state of Nigeria. The edible flesh was removed while the husks were extensively washed with distilled water to remove particulate material from their surface. They were cut into small pieces, air-dried and finally oven-dried at 105°C for 12 h in preparation for the adsorption analysis. The oven-dried husks were crushed with manual blender to smaller particles and sieve analysis was performed using the sieve screen to obtain final sample size of 180 µm. Thereafter, 200 g of the screened (180 µm size) adsorbent was further acid treated by soaking it in 500 mL of 0.3 M HNO₃ solution, stirred for 30 min. and allowed to stay for 24 hr. It was then filtered through a filter paper and washed with excess distilled deionised water until a pH of 7.1 was obtained. The rinsed biosorbent was later air-dried for 6 hr. The treatment of the adsorbent with 0.3 M HNO₃ solution was to remove any soluble biomolecules that might interact with the metal ions during the adsorption process and to open-up the micropores of the adsorbent in preparation for the adsorption process. This is also referred as the chemical activation of the biosorbent.

Biosorption studies

All reagents used were of analytical reagent grades and double distilled deionized

water was used in the sample preparation. 100 mg L⁻¹ stock solutions of Ni (II) from NiSO₄·6H₂O and lead (II) from Pb(NO₃)₂ were prepared at a pH 6.0 and temperature of 30°C. From the stock solutions, a working concentration of 50 mg L⁻¹ was obtained by dilution. The concentration of the standard was confirmed using buck scientific Atomic Absorption Spectrophotometer (AAS) model 210 VGP. The pH of the adsorbate solutions was kept at 6.0.

Kinetic adsorption studies were carried out according to the method described by Dermirbas et al.¹² The study was performed for the two metal ions at a pH 6.0, temperature of 30°C and an initial concentration of 50 mg L⁻¹. 50 mL of standard solutions of each of the metal ions was transferred into various 250 mL conical flasks, corked and labelled. Thereafter, 0.2 g of the adsorbent was weighed and put into the different flasks and agitated in a rotary shaker at different contact times (10, 20, 30, 60, 90 and 120 min). At the end of agitation time, the content of each flask was filtered with a filter paper, centrifuged and the residual concentration of each of the metal ions analyzed using the Atomic Absorption Spectrophotometer (AAS). The amount adsorbed was then calculated by difference. Blank solutions were also prepared and analyzed.

RESULTS AND DISCUSSION

Effect of contact time

The retention of the metal ions Ni (II) and Pb (II) onto the *Irvingia gabonensis* husk was observed to increase with increasing contact time for the fixed initial concentration and adsorbent mass. Fig. 1 shows that the initial adsorption rate increased rapidly and that optimal adsorption occurred within 120 min and after which, the concentrations of the metal ions became almost constant. This maximum adsorption within 120 min may be explained by the fact that for the adsorption process at the initial period, a large number of vacant sites were available for the adsorption of these metal ions and the process decreased gradually due the saturation of these surface active sites and repulsive forces between the solute molecules (adsorbates) and bulk phase. A similar conclusion was given by Saravanane et al.¹³ in their study on the efficiency of chemically modified low cost adsorbents for the removal of heavy metals from wastewater.

Adsorption dynamics

The study of adsorption dynamics explains the rate of adsorption of metal ions and

this rate apparently controls the residence time of adsorbate removal at the solid-solution interface. In a bid to establish the adsorption rate and the mechanisms of the adsorption of the metal ions Ni (II) and Pb (II) onto the biosorbent, the following kinetic models were applied to the experimental adsorption data viz., pseudo first-order, pseudo second-order¹⁴, Elovich equation^{15,16} and intra-particle diffusion^{17,18} models.

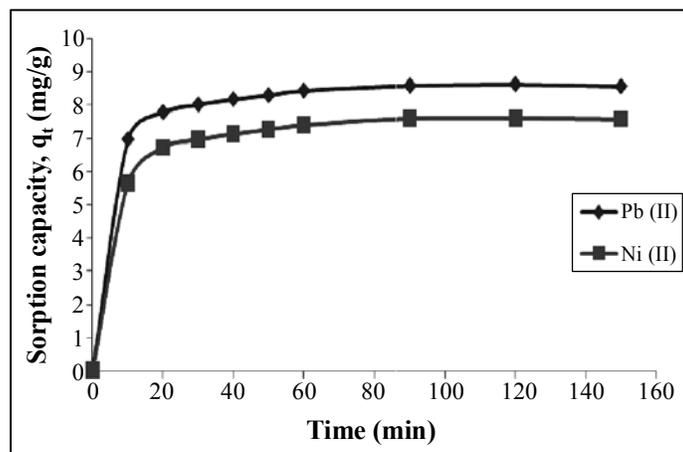


Fig. 1: Effect of contact time on the adsorption the metal ions by the adsorbent

The conformity between the experimental data and the model-predicted values is expressed by the correlation coefficients (R^2 values close or equal to 1). A high R^2 value indicates that the model successfully describes the kinetics of the metal ion adsorption. The different kinetic models are described as follows:

The pseudo first-order model

The integrated pseudo first-order equation is generally given as –

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \quad \dots(1)$$

Where q_e and q_t are the adsorption capacities at equilibrium and at a time, t and k_1 is the pseudo first-order rate constant while t is the contact time for the adsorption process. The plots of $\log(q_e - q_t)$ vs. t yielded linear relationship from which the rate constant, k_1 was determined from the slope of the linear plot. Fig. 2 shows the linear plot for the pseudo first-

order model. The pseudo first-order constants and the correlation coefficients (R^2 values) are shown in Table 1.

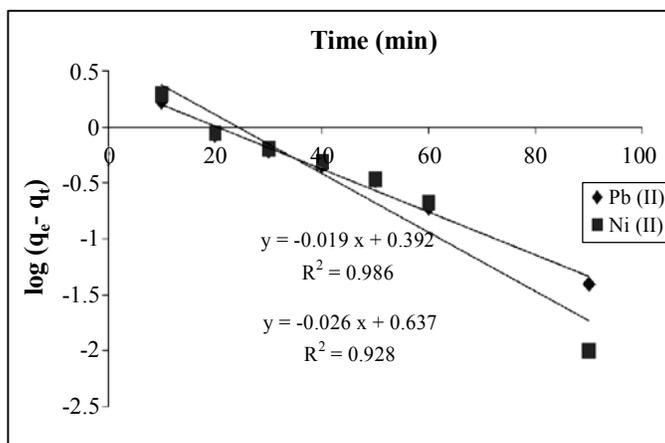


Fig. 2: Pseudo-first order plot of $\log (q_e - q_t)$ vs t for adsorption of the metal ions onto the *Irvingia gabonensis* husks

Pseudo second-order kinetic model

The integrated pseudo second-order model is usually given as –

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

where $h_0 = k_2 q_e^2$ is usually described as the initial adsorption rate as t approaches zero. The pseudo second-order model was applied in this analysis and a plot of t/q_t vs t gave linear plots, which allowed the evaluation of q_e , k_2 and h_0 . According to Ho et al.,¹⁹ if the plots are linear, then the rate-determining step of the adsorption process may be described as chemisorption. Fig. 2 is pseudo second-order plot indicating high correlation coefficients (R^2 values > 0.990). The high R^2 values suggest that the pseudo second-order kinetic model can describe the adsorption of the metal ions on the adsorbent in this study. Therefore, the possibility of chemical adsorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate correlates the data, if the rate-limiting step is assumed.

Table 1 shows the pseudo second-order rate constant, k_2 and and the initial adsorption rate, h_0 , of the adsorption of the metal ions. These parameters were calculated

from the intercept and slope of the linear plot of t/q_t versus t . The values for the pseudo second-order rate constants were found to increase for the adsorption of the metal ions in the order – Ni (II) < Pb (II) showing that there was a greater adsorption of the Pb (II) ions by the biosorbent as compared to the Ni (II) ions.

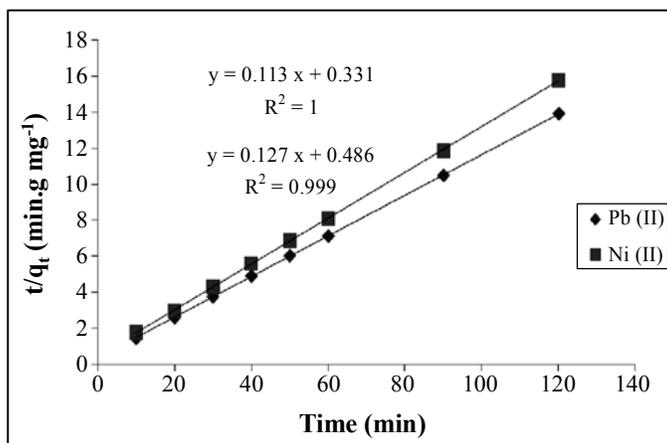


Fig. 3: Pseudo-second order plot of t/q_t vs t for adsorption of the metal ions on the *Irvingia gabonensis* husks

Elovich equation

The Elovich equation is expressed as^{15,16} –

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \quad \dots(3)$$

Where α is the initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$) and β is the desorption constant (g mg^{-1}) during any one experiment. The equation is simplified by applying the boundary conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at time $t = t$ and this yields –

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad \dots(4)$$

A plot of q_t vs $\ln(t)$ (Fig. 4) displays the Elovich plot, from which β was determined from the slope and α was determined from the intercept of the linear plots. The lower R^2 values show that the Elovich model may not be the appropriate model for the interpretation of the adsorption data.

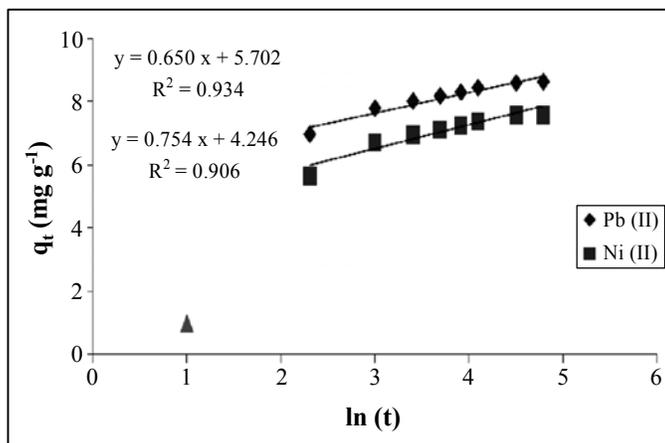


Fig. 4: Elovich plot of q_t vs $\ln(t)$ for the adsorption of the metal ions by the adsorbent

Intra-particle diffusion model

The intra-particle diffusion model is expressed as^{17,18} –

$$R = k_{id} (t)^a \quad \dots(5)$$

A linearized form of the equation is followed by –

$$\log R = \log k_{id} + a \log (t) \quad \dots(6)$$

where R is the percent metal ions adsorbed at different times, t is the contact time (min), a depicts the adsorption mechanism and is determined from the slope of the linear plots, k_{id} is the intra-particle diffusion rate constant (min^{-1}), which may be considered as a rate factor i.e., amount of the metal ions adsorbed per unit time. A plot of $\log R$ vs $\log(t)$ displays the intra-particle diffusion plot (Fig. 5), from which a was determined from the slope of the linear plot, while the intra-particle diffusion constant, k_{id} was determined from the intercept as shown in Table 1. The lower R^2 values obtained from the particle-diffusivity plot show that the adsorption process is not particle-diffusion controlled. Hence, the time for metal ions uptake is independent on the initial metal ion concentration.

A comparison of the kinetic models-pseudo first-order, pseudo second-order, Elovich and intra-particle diffusivity models was assessed using the R^2 values to determine the best fit. As shown in Table 1, the correlation coefficients (R^2 values) for the four models confirmed that pseudo second-order provides the best description of the kinetics of the metal ions adsorption with R^2 values greater than 0.990.

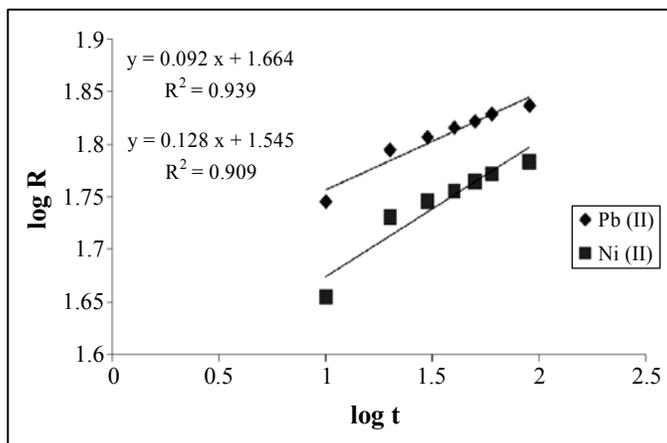


Fig. 5: Intra-particle diffusion plot of log R vs log (t) for the adsorption of the metal ions by the biosorbent

Table 1: The adsorption kinetic model rate constants for the adsorption of the metal ions on the *Irvingian gabonensis* husks

Metal ions	Pseudo first-order		Pseudo second-order			Elovich model			Intra-particle diffusion		
	k_1	R^2	k_2	h_0	R^2	β	A	R^2	k_{id}	a	R^2
Pb (II)	4.42 x 10^{-2}	0.9863	3.86 x 10^{-2}	3.02	1.000	1.54	4189	0.9349	46.20	0.0925	0.9392
Ni (II)	6.06 x 10^{-2}	0.9282	3.32 x 10^{-2}	2.06	0.9999	1.33	209	0.9060	35.13	0.1285	0.9099

Therefore, the fitting of the adsorption data into pseudo second-order model means that the rate of occupation of active sites is proportional to the square of the number of unoccupied sites. The data obtained indicate that lead (II) ions were better adsorbed than nickel (II) ions. This trend may be explained by the fact that metal ions form aquo complexes, when dissolved in water²⁰. The aquo complex is of the form $[M(H_2O)_x]^{n+}$, where M denotes the metal ion, n^+ the net charge on the complex and x the coordination number. The relative uptake levels of these two metal ions are nearly inversely dependent on their hydration energies. Ni^{2+} with ionic radius 0.072 nm has hydration energy of $-1592 \text{ kJ mol}^{-1}$ while Pb^{2+} with ionic radius of 0.12 nm has hydration energy of $-1480 \text{ kJ mol}^{-1}$. Since the displacement of water molecules from the aquo ion is the basis of adsorption dynamics, the stability of the aquo ion may therefore play a role in the adsorption process. The aquo ion

stability, as can be assessed from the hydration energies of the metal ions was found to be dependent on the size of the ion. It could be concluded from the variation of ionic size with hydration energy, that an ion with a relatively large size (and low hydration energy) will attach less strongly to the water molecules than an ion with a smaller size (and of course relatively higher hydration energy). This suggests that an ion with a large size will displace the water molecule from the aquo complex very easily and interact more strongly with the active sites of the substrate than that with a smaller size. This may have contributed to the greater adsorption of Pb (II) ions than Ni (II) ions.

CONCLUSION

The effect of contact time on the adsorption of these metal ions showed that the adsorption process increases with increase in contact time, reaching equilibrium in about 120 min. Kinetic adsorption show that the process fitted best into pseudo second-order kinetic model, indicating that the rate-rate limiting step of the process could be by chemical reaction. Results from the current study shows that *Irvingia gabonensis husks* could be used for the removal of Pb (II) and Ni (II) ions from aqueous solutions.

REFERENCES

1. R. Kumar, T. N. Abraham and S. K. Jain, The Removal of Cadmium Ions from Aqueous Solution using Silica Support Immobilized with Hydroxyacetophenone-3-thiosemicarbazone, Proceedings of 2nd Int. Conf. Environ. Sci. Dev., IPCBEE, **4**, 48-52 (2011).
2. G. Crini, Recent Developments of Polysaccharide-based Materials used as Adsorbent in Wastewater Treatment, Prog. Polym. Sci., **30**, 38-70 (2005).
3. R. Salim, M. M. Al-Subu and E. Sahrhage, Uptake of Cadmium from Water by Beech Leaves, J. Environ. Sci. Health A, **27**, 603-627 (1992).
4. M. A. Oliver, Soil and Human Health: A Review, Eur. J. Soil Sci., **48**, 573-592 (1997).
5. M. E. Argun, S. Dursun, C. Ozdemir and M. Karatas, Heavy Metal Adsorption by Modified Oak Sawdust, Thermodynamics and Kinetics, J. Harzad. Mater., **141**, 77-85 (2007).
6. K. Schumann, The Toxicological Estimation of the Heavy Metal Content (Cd, Hg, Pb) in Food for Infants and Small Children Z. Ernährungswiss, **29**, 54-73 (1990).

7. A. C. I. Anusiem, F. K. Onwu and S. P. I. Ogah, Adsorption Isotherms studies of Ni (II), Cd (II) and Pb (II) Ions from Aqueous Solutions by African White Star Apple (*Chrysophyllum Albidium*) Shell, Int. J. Chem., **20(4)**, 265-274 (2010).
8. E. C. Lima, F. J. Krug and M. A. Z. Aruda, Direct Determination of Lead in Sweet Fruit-Flavored Powder Drinks by Electrothermal Atomic Absorption Spectrometry, Spectrochim. Acta B, **53**, 601-611 (1998).
9. E. C. Lima, J. L. Brasil and A. H. D. P. Santos, Evaluation of Rh, Ir, Ru, W-Rh, W-Ir and W-Ru as Permanent Modifiers for the Determination of Lead in Ashes, Coals, Sediments, Sludges, Soils and Freshwaters by Electrothermal Atomic Absorption Spectrometry, Anal. Chim. Acta, **484**, 233-242 (2003).
10. M. Bansal, D. Singh, V. K. Garg and P. Rose, Use of Agricultural Waste for the Removal of Pb (II) and Cd (II) Ions from Aqueous Solutions: Equilibrium and Kinetic Studies, Int. J. Environ. Sci. Engg., **1(2)**, 108-115 (2009).
11. A. I. Babatunde, O. Ogundele, O. T. Oyelola and O. K. Abiola, The Inhibitive Effect of *Irvingia Gabonensis* Extract on the Corrosion of Aluminium in 1.0 M HCl Solution, Adv. Appl. Sci. Res., **3(6)**, 3944-3949 (2012).
12. E. Demirbas, M. Kobya, E. Senturk and T. Ozkan, Adsorption Kinetics for the Removal of Chromium VI from Aqueous Solutions on the Activated Carbons Prepared from Agricultural Wastes, Water SA, **30(4)**, 532-539 (2004).
13. R. Saravanane, T. Sundararajan and S. Sivamurthyreddy, Efficiency of Chemically Modified Low Cost Adsorbents for the Removal of Heavy Metals from Wastewater, A Comparative Study, Indian J. Environ. Hlth., **44**, 78-81 (2002).
14. Y. S. Ho, G. McKay, D. A. J. Wase and C. F. Foster, Study of the Sorption of Divalent Metal Ions onto Peat, Adsorp. Sci. Technol., **18**, 639-650 (2000).
15. S. H. Chien and W. R. Clayton, Application of Elovich Equation to the Kinetics of Phosphate Release and Sorption on Soils, Soil Sci. Soc. Am. J., **44**, 265-268 (1980).
16. D. L. Sparks, Kinetics of Reaction in Pure and Mixed Systems in Soil Physical Chemistry, Edited by Sparks, D. L., CRC Press, Boca Raton Florida, 83-145G (1986).
17. S. K. Srivastava, R. Tyagi and N. Pant, Adsorption of Heavy Metal Ions on Carbonaceous Material Developed from the Waste Slurry Generated in Local Fertilizer Plants, Water Res., **23**, 1161-1165 (1989).
18. W. J. Weber and J. C. Morris, Kinetics of Adsorption on Carbon from Solution, J. Sanit. Div. Am. Soc. Civ. Eng., **89**, 31-60 (1963).

19. Y. S. Ho, D. A. J. Waste and C. F. Forster, Batch Nickel Removal from Aqueous Solution by Sphagnum Moss Peat, *Wat. Res.*, **29**, 1327-1332 (1995).
20. A. A. Abia, M. Jr Horsfall and O. Didi, Studies on the use of Agricultural Bi-Product for the Removal of Trace Metals from Aqueous Solution, *J. Appl. Sci. Environ. Mgt.*, **6(2)**, 89-95 (2002).

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