

Full Length Research Paper

Lead (II) and nickel (II) adsorption kinetics from aqueous metal solutions using chemically modified and unmodified agricultural adsorbents

ABIA, A. A.* and ASUQUO, E. D,

Department of Pure and Industrial Chemistry, University of Port Harcourt. P. M. B. 5323, Choba, Port Harcourt, Nigeria.

Accepted 21 August 2006

This paper discusses the kinetics of lead (II) and Nickel (II) ions adsorption from aqueous solutions using chemically modified and unmodified agricultural adsorbents at 28°C, pH 6.2 and 0.01M NaCl ionic strength. The removal of the two metals were found to increase with increase in chemical modification, the sequence being 1.0MOPF>0.5MOPF>UOPF. In addition Nickel (II) had a higher percentage removal than lead (II). The intraparticle diffusion rate constant (K_{id}) were determined to be 63.023 min^{-1} (Ni^{2+}) and 38.212 min^{-1} (Pb^{2+}) for the 1.0MOPF adsorbent. The results show that the intraparticle diffusion model fits the sorption of lead (II) with higher coefficient of determination (r^2) than Nickel (II), thereby indicating that the intra-particle diffusion may be the rate limiting step for Pb^{2+} sorption. The results from this study indicates that a good adsorbent for the removal of Ni^{2+} and Pb^{2+} can be obtained from both chemically modified and unmodified oil palm fruit fibre.

Key words: oil palm fruit fibre, mercaptoacetic acid, intraparticle diffusion, adsorbent, chemical modified and agricultural-by-product.

INTRODUCTION

The problems of our ecosystem are increasing with the advancement in technology. Heavy metal pollution is one of these problems. Toxic heavy metal release into the environment has been increasing continuously as a result of man's industrial activities and technological development. The release of these heavy metal poses a significant threat to the environment and public health because of their toxicity, bioaccumulation in the food chain and persistence in nature (Ceribasi and Yetis, 2001). Lead is a heavy metal that affects the functioning of the blood, liver, kidney and brains of human beings. Lead is a com-

ponent of most industrial and domestic paints. Nickel which causes gastrointestinal irritation and lung cancer is often obtained from Ni/Fe storage batteries. Also, it is used to produce ferrous steel cutlery (Greenwood and Earnshaw, 1993). Due to the magnitude of the problem of heavy metal pollution, research into new and cheap methods of metal removal has been on the increase recently. Several workers have reported on the potential use of agricultural by-products as good substrates for the removal of metal ions from aqueous solutions and wastewaters (Eromosele and Otilolaye, 1994). This process attempts to put into use the principle of using waste to treat waste and becomes even more efficient because these agricultural by-products are readily available and often pose waste disposal problems. Hence, they are available at little or no cost, since they are waste products. This makes the process of treating wastewaters with agricultural by-product adsorbents more cost effective than the use of conventional adsorbents like activated carbon. In addition, there is no need for a complicated regeneration process when using agricultural by products for wastewater treatment (Abia and Igwe, 2005).

*Corresponding authors E-mail: abiauniport2005@yahoo.com.
Phone: 234 – 08036685125.

Abbreviations: a, constant in intraparticle diffusion model depicts adsorption mechanism; C_0 , initial metal ion concentration (mgL^{-1}); C_t , concentration of metal ion at time t (mgL^{-1}); K_{id} , intraparticle diffusion rate constant (min^{-1}); R_{em} , percentage of metal removed; 1.0MOPF, 1.0 M mercaptoacetic acid modified oil palm fruit fibre; 0.5MOPF, 0.5 M mercaptoacetic acid modified oil palm fruit fibre; and UOPF, unmodified oil palm fruit fibre.

The ability of some agricultural by-products to adsorb heavy metals from wastewater and aqueous metal solutions has been reported in literature and these include: cotton seed hulls, rice straw and sugarcane bagasse (Marshall and Champagne, 1995), shea butter seed husk (Eromosele and Abare, 1998) and cassava fibre (Egila and Okorie, 2002). Also, research by Park et al. (2000) showed that chemical modification of agricultural adsorbents increased the sorption capacity of the adsorbent, thereby increasing the efficiency of the adsorbent. Han (1999) reported the sorption of Ni^{2+} , Cu^{2+} , Zn^{2+} and Cd^{2+} from storm water runoff using sodium sulfite modified kenaf and alfalfa fibres. The increase in sorption capacities of the chemically modified adsorbents was attributed to the effect of the chemical modification process. Furthermore, Eromosele et al. (1996) discovered that shea butter (*Butyrospermum parkii*) seed husk was effective in the removal of iron, zinc and lead ions from aqueous metal solutions and chemical modification of the agricultural adsorbent (husk) greatly enhanced the process.

Oil palm tree (*Elaeis guineensis*) is a member of a small genus of only two species of palms, one specie occurring in Africa and the other in Central and South America. The African oil palm is native to numerous countries in tropical Africa and is found in Southern Nigeria. A by-product of oil palm fruit refining is the oil palm fruit fibre which is used in some localities as source of fuel for heating in the absence of firewood. This paper reports on the study of the kinetics of lead (II) and nickel (II) removal from aqueous metal solutions using unmodified and chemically modified oil palm fruit fibres.

MATERIALS AND METHODS

All the reagents used were of analytical reagent grade and doubly distilled deionized water was used in sample preparation. 1000 mg/l stock solutions of lead (II) from PbCl_2 and nickel (II) from $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ were prepared. From the stock solutions, working solutions of initial concentration (50 mg/l) of each metal were prepared by serial dilution.

Adsorbent preparation

The oil palm fruit fibre was obtained from an oil palm mill in a village near Uyo, Akwa Ibom State, Nigeria. The fibre was deoiled by soaking it in hot deionized water and with detergent for 24 h. It was rinsed in hot deionized water to remove all debris and air dried. The air dried oil palm fruit fibre was ground using a national electric blender. The fibre was screened through a set of sieves (250, 150 and 106 μm). The fibre that passed through the 106 μm sieve was the used for sorption studies.

Activation of adsorbent

The screened fibre adsorbent was further soaked in excess 0.3 M HNO_3 solution for 24 h. It was then filtered through a whatman No

41 filter paper and rinsed with deionized water. The rinsed adsorbent was later air dried for 12 h. The treatment of the adsorbent with 0.3 M HNO_3 solution aids the removal of any debris or soluble biomolecules that might interact with metal ions during sorption. This process is called chemical activation of the oil palm fruit fibre.

Chemical modification of adsorbent

The air dried activated oil palm fruit fibre was weighed and divided into 3 parts. 100 g of the first part labeled "1" was left untreated and called "unmodified oil palm fruit fibre" (UOPF). 100 g of the second part labeled "2" and the third part labeled "3" were acid treated by dissolving it in excess 0.5 M and 1.0 M mercaptoacetic acid (HSCH_2COOH) solution, respectively. The suspension were stirred for 30 min and left to stand for 24 h at 28°C and called 0.5 M modified oil palm fruit fibre (0.5MOPF) and 1.0 M modified oil palm fruit fibre (1.0MOPF), respectively.

After 24 h the mixtures labeled 0.5MOPF and 1.0MOPF were filtered off using whatman No 41 filter paper. The residue in each filter paper was then soaked in 1.0 M hydroxylamine (NH_2OH) for 1 h. After which they were filtered using whatman No 41 filter paper and rinsed with distilled deionized water. The washed residue of 0.5MOPF and 1.0MOPF were air dried. The 3 working adsorbents were stored in air tight plastic containers.

Adsorbent characterization

The three adsorbents, UOPF, 0.5MOPF and 1.0MOPF were characterized by using the following surface properties which include: percentage thiol content (%SH), specific surface area (S_{AA}) and pH point of zero charge (pHpzc).

Determination of thiol content

The extent to which the mercaptoacetic acid incorporated the thiol (SH) group into the 0.5MOPF and 1.0MOPF adsorbents was determined by the method described by Okieimen et al. (1988). 0.5 g of 0.5MOPF and 1.0MOPF adsorbents were weighed into two 250 cm^3 Erlenmeyer flasks. To each flask, 20 ml of 0.5 M iodine solution was added. The flasks were agitated on a shaker (EFLI – Mk-3 model) for 10 min and then allowed to settle. The unreacted iodine was back titrated with 0.1 M sodium thiosulphate until the colour of the solution turned yellow. Thereafter 2 ml of starch solution was added and then the solution turned blue. The titration with sodium thiosulphate was continued until the solution finally became colourless indicating end point. The titre values were recorded and the degree of thiolation was calculated.

Determination of specific surface area

The specific surface areas of the three adsorbents (U OPF, 0.5 M OPF and 1.0 M OPF) were determined using the methylene blue absorption test (MBT) method described by Santamarina et al. (2002). 2.0 g of each adsorbent was dissolved in 200 ml of deionized water and 10 ppm of the methylene blue solution was added to the adsorbent suspension and agitated in a shaker for 2 h. Thereafter, it was kept for 24 h to reach equilibrium, after which 10 ml aliquot was taken and centrifuged. The centrifuged aliquot was then analysed in a UNICAM-8700 UV/visible spectrophotometer to

Table 1. Surface Characteristics of Adsorbents).

Parameter	UOPF	0.5MOPF	1.0MOPF
Specific Surface Area (m^2g^{-1})	248.42	289.83	331.23
Thiol content (% SH)	-	1.35	2.83
pHpzc	7.1	6.4	6.0

determine the amount of methylene blue absorbed. Also, 20, 30, 40, 50, 60 and 70 ppm solutions of methylene blue were then added sequentially and the previous steps repeated. For the 1.0 M OPF adsorbent, 80 ppm solution of methylene blue was also used. A graph of concentration of methylene blue added versus the amount of absorbed methylene blue was used to identify the point of complete cation replacement. The specific surface area was calculated from the amount of absorbed methylene blue at the optimum point of cation replacement as follows:

$$\text{Specific surface area} = \frac{m_{MB} \times A_v \times AMB}{319.98} \times \frac{1}{ms}$$

m_{MB} = Amount of methylene blue absorbed at the point of complete cation replacement

M_s = Mass of adsorbent

A_v = Avogadro's number, 6.02×10^{23}

AMB = Area covered by one methylene (assumed to be 130\AA^2)

Determination of pH point of zero charge

The pH point of zero charge (pHpzc) of each of the adsorbents (UOPF, 0.5MOPF and 1.0MOPF) was carried out as described by Onyango et al. (2004). 50 ml of 0.01 M NaCl solutions were placed in different closed Erlenmeyer flasks and corked. The pH of each solution in each flask was adjusted to values of 2, 4, 6, 8, 10 and 12 by adding 0.1 M HCl or 0.1 M NaOH solutions. Then 0.5 g of UOPF adsorbent was added and agitated in a shaker for 1 h and allowed to stay for 48 h to reach equilibrium at 28°C. The zeta potential (mV) of each solution was then determined. For 0.5MOPF and 1.0MOPF adsorbents, the pHpzc was also determined using the above method. A graph of zeta potential (mV) versus initial pH was used to determine the pH point of zero charge of each adsorbent.

Kinetics of metal sorption

Kinetic sorption studies for lead (II) and Nickel(II) were carried out for each adsorbent (UOPF, 0.5MOPF and 1.0MOPF) at pH 6.2, temperature 28°C, initial concentration 50 mg/L and ionic strength 0.01 M using NaCl. 100 ml of standard solutions of each metal was transferred into various 250 cm^3 Erlenmeyer flask corked and labeled. Then 0.5 g of each adsorbent was weighed into the different labeled flasks and agitated in a shaker for the different contact times (10, 15, 20, 30, 45, 60, 90 and 120 min). After each agitation time, the content of each flask was then filtered using whatman No 41 filter paper. The residual concentration of 20 ml of the filtrate of each metal solution was analyzed using UNICAM 919 solar atomic absorption spectrophotometer (AAS). Blank solutions were also prepared and analysed.

Data analysis

The amount of Pb^{2+} and Ni^{2+} adsorbed (a_t) in mg/L from each metal solution by the various adsorbents at time t was computed by using the following equation:

$$a_t = C_o - C_t \quad (1)$$

The percentage of each metal removed from the aqueous solutions by the adsorbents (% R_{em}) was computed using equation 2:

$$\% R_{em} = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

Where C_o and C_t are the initial metal ion concentration and metal ion concentration at time t respectively in mg/L.

Adsorption dynamics

Adsorption kinetics of Pb^{2+} and Ni^{2+} sorption on the three adsorbents was evaluated using the intraparticle diffusion model (Weber and Morris, 1963; Srivastava et al., 1989; Demirbas et al., 2004) below:

$$R = K_{id} (t)^a \quad (3)$$

Which can be linearised to

$$\log R = \log K_{id} + a \log t \quad (4)$$

Where R is the percent of metal adsorbed, t is the contact time, a is a constant that depicts the adsorption mechanism and K_{id} is the intraparticle diffusion rate constant.

If the mechanism of adsorption fits the intraparticle diffusion model, then a plot of $\log R$ against $\log t$ will yield a straight line with a slope (a) and an intercept of $\log K_{id}$.

RESULTS AND DISCUSSION

Characterization of adsorbents

The characteristics of the three adsorbents unmodified oil palm fibre (UOPF), 0.5 M modified oil palm fibre (0.5MOPF) and 1.0 M modified oil palm fibre (1.0MOPF) which include percentage thiol content (%SH), specific surface area (S_{AA}) and pH point of zero charge (pHpzc) are presented in Table 1.

Specific surface area of adsorbents: The specific surface area (S_{AA}) of an adsorbent is the ratio of its surface area to its mass (Santamarina et al., 2002). From the experiment using the methylene blue method for the determination of specific surface area of each adsorbent, values of 248.42, 289.83 and 331.23 m^2g^{-1} for UOPF, 0.5MOPF and 1.0MOPF, respectively, were obtained. The results show a trend in which, the specific surface area of the adsorbents increased with chemical

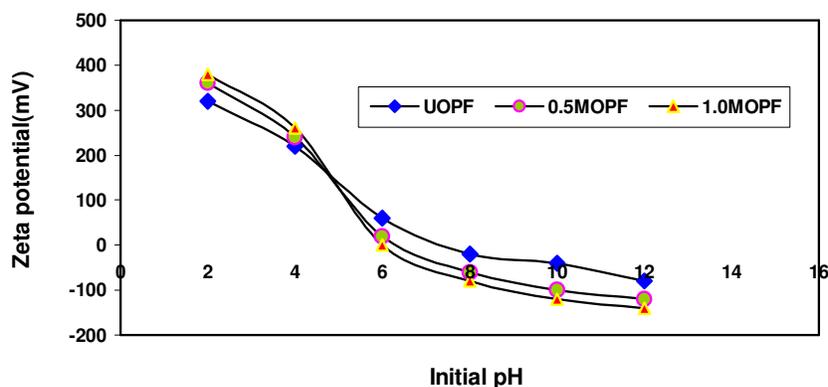


Figure 1. Determination of pH point of zero charge (pHpzc) of adsorbents (UOPF, 0.5MOPF and 1.0MOPF).

modification. Furthermore, increasing the concentration of mercaptoacetic acid also increased the specific surface area which followed the trend $UOPF < 0.5MOPF < 1.0MOPF$. It has been reported that the surface area has a great effect on the sorption capacities of adsorbents (Qadeer and AKhtar, 2005).

Degree of chemical modification of adsorbents: The degree of chemical modification of the adsorbent was examined using the percentage thiol (%SH) content of the chemical modified adsorbents. Since the adsorbents were modified using mercaptoacetic acid [$CH_2(SH)COOH$], the efficiency of the modification process was analysed by the amount of the thiol on the adsorbent surface. From Table 1, the percentage of thiol in the chemically modified adsorbent increased with increase in concentration of the modifying agent. That is for 0.5MOPF, the % thiol was 1.35 while for 1.0MOPF the value was 2.83%. The values here are comparable with those obtained for acid treatment of maize cob meal (Okieimen et al., 1988). Here, the mercaptoacetic acid incorporated thiol group onto the maize cob meal adsorbent and the percentages were 1.7 and 3.3, respectively, for 0.5M and 1.0 M thioglycolic acid modified adsorbents. We had previously observed that the incorporation of thiol (SH) groups onto an adsorbent surface increases the sorption properties of the adsorbent by increasing the number of binding sites (Abia et al., 2003)

pH point of zero charge (pHpzc) of adsorbents: The results of the determination of the pH point of zero charge (pHpzc) of the three adsorbents is recorded in Table 1. Figure 1 shows the plot of zeta potential against initial pH for the determination of this property for the three adsorbents. There exist a relationship between pHpzc and adsorption capacity of an adsorbent; which is that cations adsorption on any adsorbent will be favourable at pH value higher than the pHpzc. While anions adsorption will be favoured at pH values lower their adsorbent pHpzc (Nomanbhay and Palanisamy, 2005). The chemical modification of the adsorbents

surface with mercaptoacetic acid reduced the pHpzc of the adsorbents from 7.1 for UOPF to 6.4 for 0.5MOPF and to 6.0 for 1.0MOPF. In a similar study, Krishnan and Anirudhan (2003) reported the decrease in pHpzc of steam activated sulphurised carbon prepared from sugarcane bagasse pith from 5.8 to 5.5, 4.7 and 4.3, respectively, by the loading of 2.3, 6.8 and 8.9% sulphur content. In this study, it can be stated that the thiol (SH) group in the mercaptoacetic acid used in the chemical modification of the oil palm fibre adsorbents caused the reduction of the pHpzc. This is due to its increased negative charge contribution to the adsorbent surface.

Sorption kinetics

Kinetics of metal sorption governs the rate, which determines the residence time, and it is one of the important characteristics defining the efficiency of an adsorbent (Krishnan and Anirudhan, 2003). Sorption kinetics can be controlled by several independent processes that could act in series or in parallel, such as bulk diffusion, external mass transfer (film diffusion), chemical reaction (chemisorption) and intraparticle diffusion (Ho et al., 2000). Figure 2 represents the variation in lead ion adsorption with contact time, while Figure 3 indicates the variation of Nickel (II) ion with time. From the figures, it can be determined that the adsorption of both metals were quite rapid initially, however the adsorption rate becomes slower with passage of time up to 120 min. Also the percentage removal of Nickel (II) ion was higher than that of lead (II) ion. The initial faster rate of removal of each metal ion may be due to the availability of the uncovered surface area of the adsorbents, since adsorption kinetics depends on the surface area of the adsorbent (Qadeer and Akhtar, 2005). The variation in percentage removal of the two metals by the three adsorbents (UOPF, 0.5MOPF and 1.0MOPF) are indicated in Figures 4, 5 and 6. There was slight increase in the percentage of each adsorbents, the sequence of increase in percentage of each metal adsor-

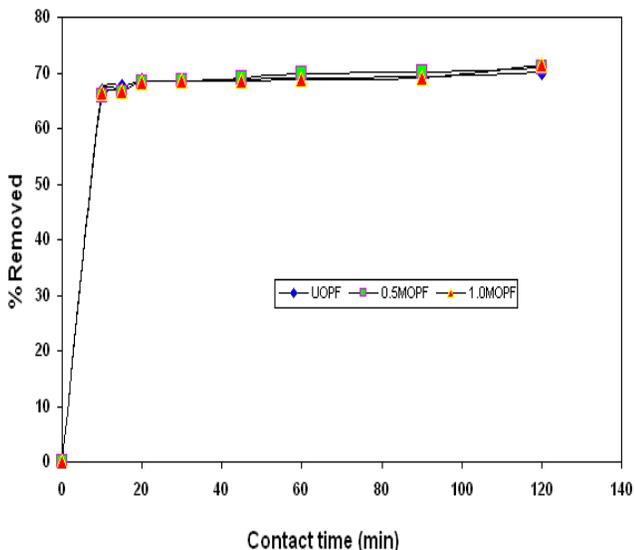
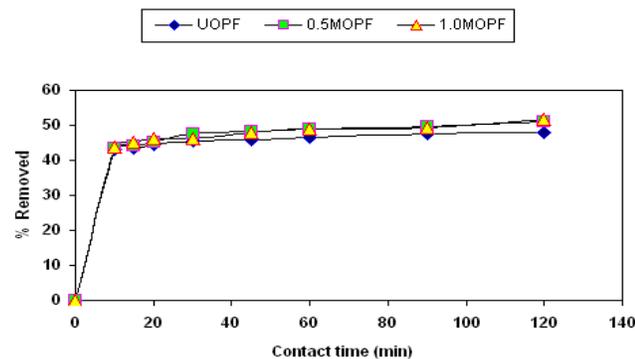


Figure 3. % removed versus contact time for Nickel (II) ion.

bent is: UOPF < 0.5MOPF < 1.0MOPF. This may be attributed to the increase in the number of functional groups on the modified adsorbents (0.5MOPF and 1.0MOPF), since chemical modification of an adsorbent tends to increase the adsorption capacity of the adsorbent (Abia et al., 2002).

Furthermore, Nickel (II) ion was adsorbed at a faster rate with higher percentage removal than lead (II) ion. This may be explained by considering the ionic radii of the two metals; Ni^{2+} (0.72Å) and Pb (1.20Å). Since Ni^{2+} ions has a smaller ionic radius, it is possible that Ni^{2+} ions diffuse faster through the adsorbent pores faster than the bulkier Pb^{2+} ions. According to Atkinson et al. (1998), during sorption of metal ions, the ions of smaller ionic radii tend to move faster to potential adsorption sites.

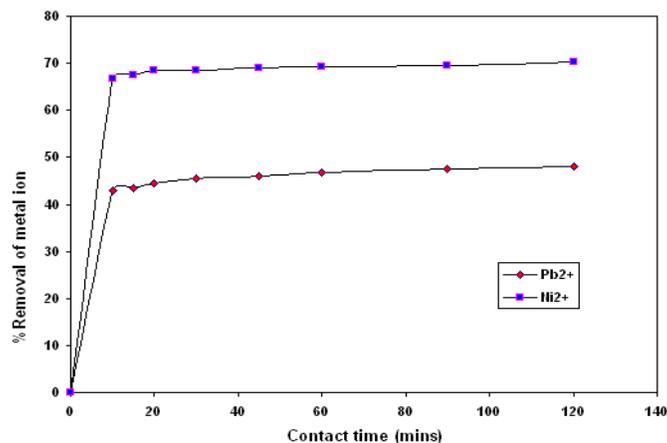


Figure 4. % Removal of Pb^{2+} and Ni^{2+} Vs Contact time for UOPF adsorbent.

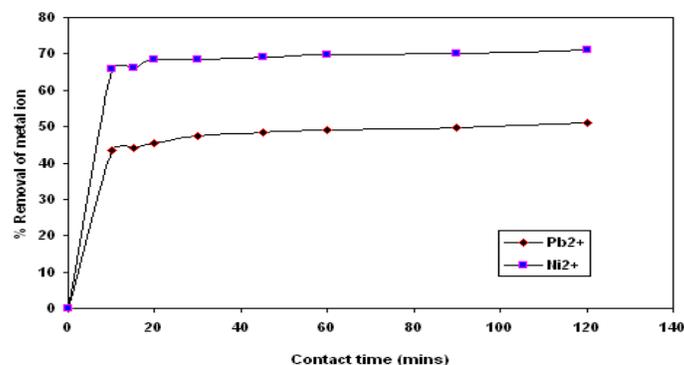


Figure 5. % Removal of Pb^{2+} and Ni^{2+} Vs Contact time for 0.5MOPF adsorbent.

Kinetic modeling

Kinetic equations have been developed to explain the transport of metals onto various adsorbents. These equations include the pseudo-first order equation (Lagergren, 1898), the pseudo-second order (Ho and McKay, 1998), the Elovich equation (Chien and Clayton, 1980) and the intraparticle diffusion model (Weber and Morris, 1963; Srivastava et al., 1989; and Demirbas et al., 2004). These Kinetic models are only concerned with the effect of the observable parameters on the over all rate of sorption (Ho, 2006). However, for this study the intraparticle diffusion model was chosen to analyse the rate of sorption of Pb^{2+} and Ni^{2+} on the three adsorbents (UOPF, 0.5MOPF and 1.0MOPF).

Figures 7 and 8 present the intraparticle diffusion kinetic model for lead (II) and nickel (II) ions, respectively. Linear regression (r^2) is frequently used to determine the best fitting kinetic model for metal sorption. In this study,

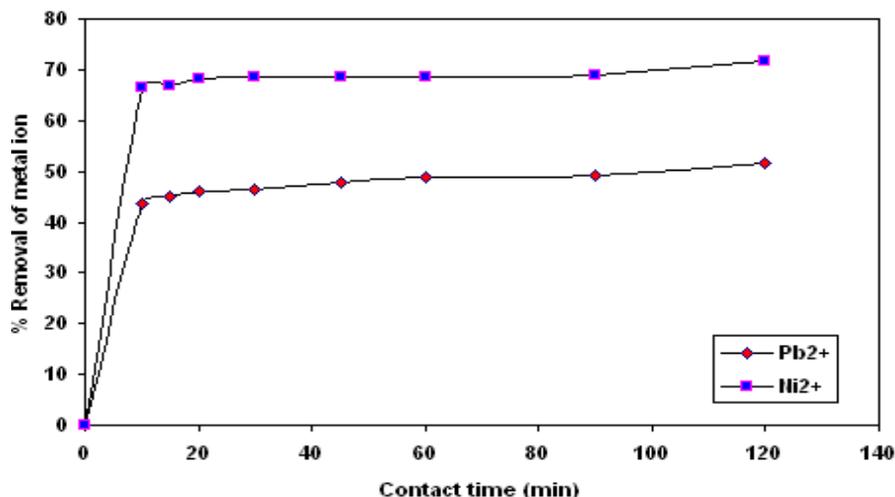


Figure 6. % Removal of Pb²⁺ and Ni²⁺ Vs Contact time for 1.0MOPF adsorbent.

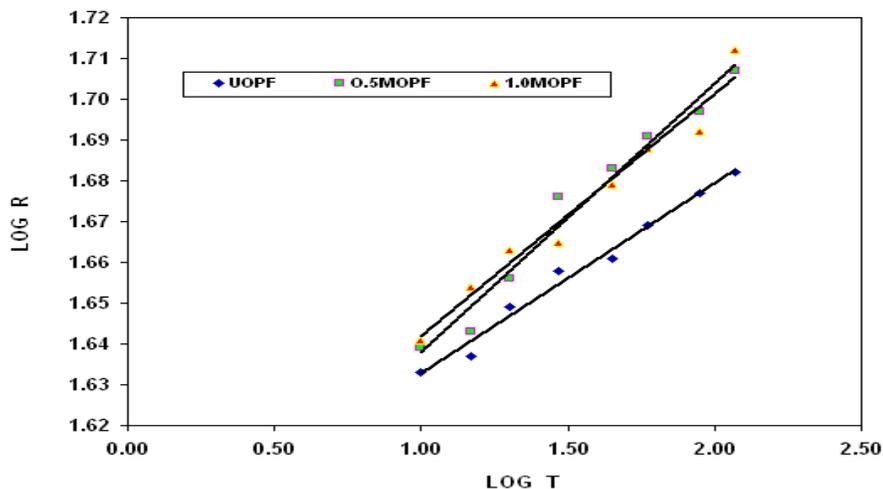


Figure 7. Intra particle diffusion kinetic model for lead (II) ion.

a comparison of the kinetics of Ni (II) and Pb (II) ions was evaluated using the intraparticle diffusion model. The coefficient of determination (r^2) was used as the fitting parameter.

Table 2 presents the values of the parameters calculated from the linearised form of the intraparticle diffusion model equation. Comparing the r^2 values for nickel (II) and lead (II) ions, it can be stated that sorption of lead (II) ions on the three adsorbents, to a certain extent, can be explained using the intraparticle diffusion model. The adsorption of lead (II) can be described by this model than nickel (II) ion. Since sorption of Nickel (II) cannot be described very well by the intraparticle diffusion model. It therefore means that intraparticle diffusion is not the rate limiting step for the sorption of nickel (II) ion unto the three adsorbents. However, for sorption of lead (II) ion, intraparticle diffusion may be the

rate-limiting step since it obeys the intraparticle diffusion model. It has been reported by earlier workers that the sorption of Cr (iv) follows the intraparticle diffusion model (Demirbas et al., 2004).

Conclusion

This study indicated that a good adsorbent for the removal of Ni²⁺ and Pb²⁺ can be obtained from oil palm fruit fibre. Chemical modification of the adsorbents increased the percentage removal of each of these metals. The adsorption of Ni²⁺ was higher than that of Pb²⁺. The Kinetics of the adsorption of both metals were rapid in the initial stage followed by a slow rate. The adsorption data indicated the applicability of the intraparticle diffusion model for Pb²⁺ removal. However,

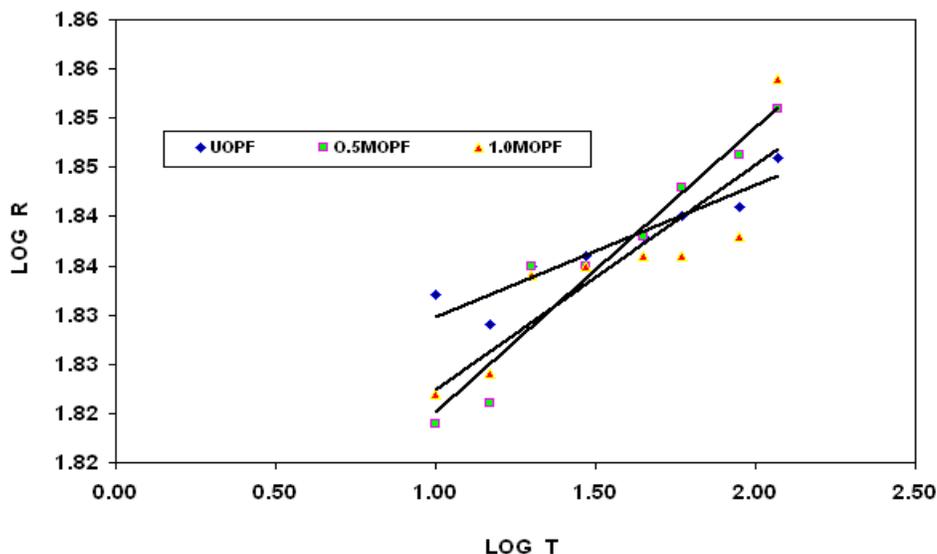


Figure 8. Intra particle diffusion kinetic model for nickel (II) ion.

Table 2. Intraparticle Diffusion Model Rate Constants for Ni²⁺ and Pb²⁺ on UOPF, 0.5MOPF and 1.0MOPF.

Adsorbent	K _{id} (min ⁻¹)		a		r ²	
	Ni ²⁺	Pb ²⁺	Ni ²⁺	Pb ²⁺	Ni ²⁺	Pb ²⁺
UOPF	65.539	38.565	0.013	0.046	0.891	0.984
0.5MOPF	61.844	37.307	0.028	0.066	0.932	0.974
1.0MOPF	63.023	38.212	0.022	0.059	0.792	0.966

the kinetics of Ni²⁺ sorption did not follow the intraparticle diffusion model. In view of the above, it can be argued that sorption of nickel can perhaps be more correctly described by other models. Hence subsequent studies will involve the use of other kinetic models like the pseudo-second order, pseudo first order and Elovich to explain the sorption of nickel on the oil palm fibre adsorbents.

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