

Adsorption of Iron (III), Lead (II) and Cadmium (II) Ions by Unmodified *Raphia Palm (Raphia hookeri)* Fruit Endocarp

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Abstract: The efficiency of using *Raphia palm* fruit endocarp (nut) to adsorb metal ions from aqueous solution was studied in a batch system using Atomic Absorption Spectrometry (AAS). Equilibrium adsorption isotherms and thermodynamics studies were carried out. The influence of initial metal ion concentration, temperature and particle size was investigated and the results showed that particle size and temperature affected the sorption rate and that the adsorption was fast with a maximum percentage adsorption of 98.7% in 20 min as initial metal ion concentration was increased. Four isotherms; Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin were used to model the equilibrium sorption experimental data. Also, a normalized standard deviation, Δq was used to compare the validity of the isotherm models. The sorption process was found to follow chemisorption mechanism. Thermodynamic parameters were evaluated for the sorption experimental studies. Therefore, these experiments showed that *Raphia palm* fruit endocarp can be effectively used for the removal of iron (III) and lead (II) ions from dilute solutions.

Key words: *Raphia palm* fruit, adsorption, metal ions, isotherms, mechanism, Nigeria

INTRODUCTION

One group of substances of major environmental concern is heavy metals in aqueous media. This concern is due to their toxicity to human and animal lives. The rate at which heavy metal bearing effluents are discharged into the environment and water bodies has been on the increase due to rapid industrialization (Okoye *et al.*, 2010). Generally, water bodies are major sites of heavy metal deposits due to the fact that streams and rivers flow through agricultural areas where pesticides and fungicides may have been used, through industrial districts where there may have been many metal waste deposits and direct discharge of effluents into these water bodies (Malakootian *et al.*, 2009; Okoye *et al.*, 2010).

Much research and advanced development of technologies have been directed towards the remediation and removal of heavy metals from aqueous media as a result of increased concern by environmentalist and governments on the effects of heavy metals and in attempt to protect public health (Son *et al.*, 2004; Karbassi *et al.*, 2007; Shetty and Rajikumar, 2009; Resmi *et al.*, 2010). The conventional methods that have

been used involve the application of unit operation such as chemical reduction, ion-exchange, reverse osmosis, coagulation, nanofiltration and adsorption on silica, alumina and zeolite composites and activated carbon (Steinhauser and Bichler, 2008; Vinodhini and Das, 2010). However, these methods have been proved to have a lot of disadvantages which includes cost of operation and production of post sludge. Among the aforementioned treatment methods, adsorption had been reported as an efficient and economic option (Mahvi, 2008; Malakootian *et al.*, 2009), especially when the source of the adsorbent is economical. Many researchers have reported on the production of activated carbon from economical, natural and agricultural by-products (Onundi *et al.*, 2010; Issabayeva *et al.*, 2008; Okoye *et al.*, 2010).

A recent focus on the removal of metal ions from solution is the use of agricultural and vegetable materials through adsorption. High efficiency and low cost among others are the major advantages of this technique over conventional treatment techniques (Kumar and Kaladharan, 2006). Metal sequestering by biosorbents are reported to occur through the interaction of metals with

some functional groups of the biomass. However, the efficiency of such interactions is dependent on the available binding sites and the binding strength (Vieira and Volesky, 2000). Availability is a major factor in the selection of biomass for adsorption. Examples of naturally available, low cost and efficient materials reported as adsorbents for heavy metals are; palm kernel fibre (Ho and Ofomaja, 2005; Abia and Asuquo, 2006), maize cob and husk (Igwe and Abia, 2005; Igwe *et al.*, 2005; Opeolu *et al.*, 2009), cocoa pod husk (Igwe *et al.*, 2011a), Boiler fly ash (Okoronkwo *et al.*, 2008, 2011), wheat bran (Nameni *et al.*, 2008), Bengal gram (*Cicer arietinum*) husk (Ahalya *et al.*, 2005), tea waste (Mahvi *et al.*, 2005), maize leaf (Babarinde *et al.*, 2006), sawdust (Vinodhini and Das, 2010; Urak *et al.*, 2009), Bamboo root (Babatunde *et al.*, 2009), coconut fibre (Igwe *et al.*, 2008, 2011b) and so on.

One important common ground about these listed adsorbents is that they are all waste by-products which even constitute disposal problems. Thus another advantage of this sorption technique is the use of waste to clean-up another waste hence resulting to environmental sustainability.

Raphia palm tree (*Raphia hookeri*) is commonly found in abundance in the southern part of Nigeria especially the fresh water lowland zones. The objective of this paper is to present the adsorptive potential of raphia palm fruit endocarp on Fe (III), Cd (II) and Pb (II) ions in aqueous solution. The parameters used for this investigation are initial metal ion concentration, temperature and particle size of adsorbent.

MATERIALS AND METHODS

Adsorbent and adsorbate preparation: Raphia palm fruit bunches were collected from the fresh water swamp forest of Ogu village in Yenagoa Local Government Area of Bayelsa State, Nigeria. The fruits were removed from the bunches and left for about a week. The epicarp, mesocarp and endocarp were separated, washed and air dried. The endocarp (nut) was ground by ball mill abrasion after drying in the oven.

Four sizes of ground endocarp were obtained by passing sample through the 75, 150, 300 and 600 μm sieves. The different sample particle sizes were soaked in 0.1M HCl for about 2 days and washed in distilled water until a constant pH was obtained. The washed samples were dried in the oven at 68°C for 2 days. The pretreated samples were stored for adsorption studies. The adsorbates used for this study are iron (III) ions from iron (III) chloride, lead (II) ions from lead (II) nitrate and cadmium (II) ions from cadmium (II) acetate.

Instruments: The instruments used include the following: Barnstead/Labline maxQ 2000 Variable Speed shaker (20-500 rpm), Thermo Electron Corporation PRECISION water bath B.Bran Scientific and Instrument Co. 80-1 Electric Centrifuge, UNICAM Photon Atomic Absorption Spectrophotometer.

Sorption experiment

Effect of particle size: About 0.2 g sample of the 600, 300 and 75 μm sizes Raphia palm fruit biomass was put into tubes. About 10 mL of 40 mg L^{-1} Fe (III), Pb (II) and Cd (II) ion solutions were added to the tubes. Each metal set of tubes were simultaneously subjected to agitation by shaking on a Barnstead/Labline max Q 2000 shaker for 1 h. The mixtures were centrifuged at 3500 rpm for 5 min and decanted. Supernatants were analyzed by flame atomic absorption spectrophotometry.

Effect of initial metal ion concentration: About 0.2 g each of the 600 μm raphia palm endocarp (nut) was put into five tubes. This was followed by the addition of 20, 40, 60, 80 and 100 mg L^{-1} iron (III), lead (II) and cadmium (II) ion concentrations, respectively into the five tubes. The tubes were equilibrated by agitation on a Barnstead/Labline max Q 2000 shaker for 1 h and then centrifuged at 3500 rpm for 5 min. The mixture was decanted and the supernatants were analyzed for metal ion concentration by flame atomic absorption spectrophotometry.

Effect of temperature: About 10 mL of 40 mg L^{-1} of Fe (III), Pb (II) and Cd (II) ion solution were equilibrated for 1 h with 0.2 g sample of 600 μm size of biomass at temperatures of 30, 40, 60 and 80°C, respectively using a Thermo Electronic Corporation Precision water bath. The mixtures were centrifuged at 3500 rpm for 5 min and then decanted. The supernatants were analyzed by flame atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

Sorption capacity: Investigation into particle size effect showed that sorption capacity follows a pattern of dependence. Figure 1 show that there is a general decrease in sorption efficiency as the particle size is increased. Maximum adsorption is peculiar to the sample with the smallest size for all the metal ions except for an outlier for Fe^{3+} at 600 μm . The increased sorption with smaller particle size means that there is higher external surface area available for adsorption with smaller particle at a constant total mass. Similar findings have been reported (Ho *et al.*, 2002; Saueprasearsit *et al.*, 2010).

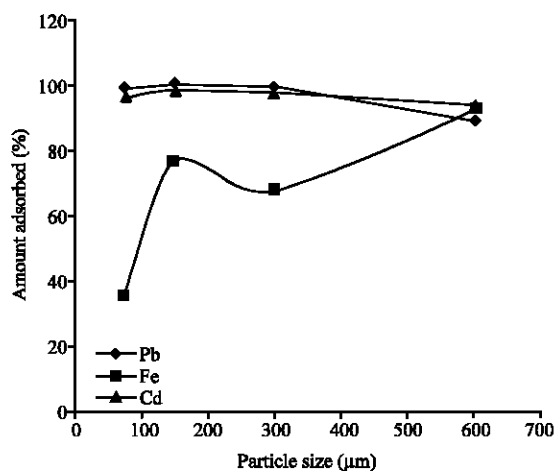


Fig. 1: Amount adsorbed (%) against particle size adsorption of Fe (III), Cd (II) and Pb (II) ions from aqueous solutions using raphia palm fruit endocarp

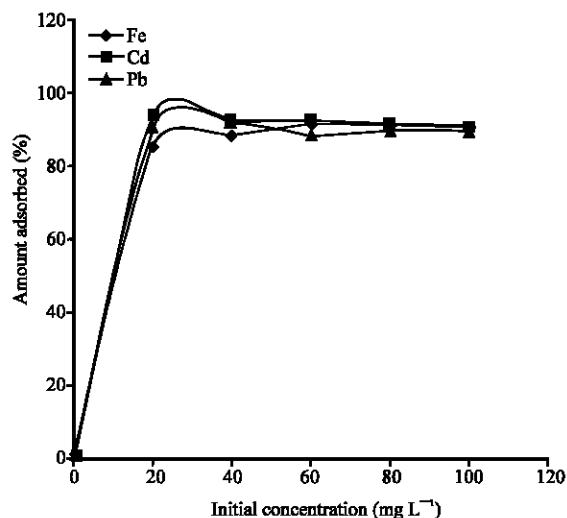


Fig. 2: Amount adsorbed (%) against initial concentration (mg g⁻¹) for adsorption of Fe (III), Cd (II) and Pb (II) ions from aqueous solutions using raphia palm fruit endocarp

The effect of metal ion concentration on adsorption capacity showed that raphia palm endocarp adsorbed Pb²⁺, Fe³⁺ and Cd²⁺ ions. The result of the experimental data for variation in initial metal ion concentration is shown in Fig. 2. From Fig. 2, Cd (II) metal ion was adsorbed more followed by Pb (II) and then Fe (III). Also, the amount of metal ions adsorbed increased with increase in initial metal ion concentration. This is attributed to the increase in the number of metal ions competing for available binding sites on the adsorbent at

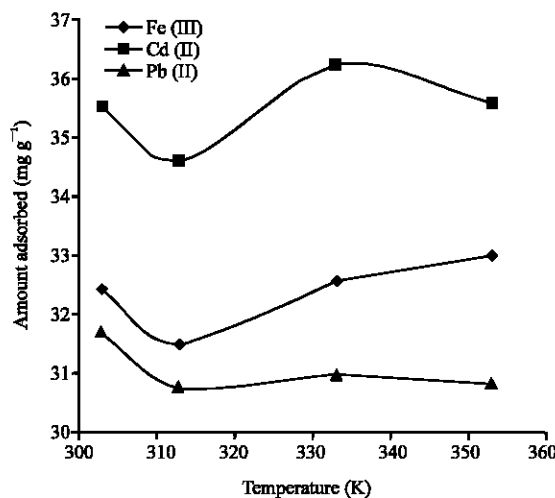


Fig. 3: Amount adsorbed (%) against Temperature (K) for adsorption of Fe (III), Cd (II) and Pb (II) ions from aqueous solutions using raphia palm fruit endocarp

higher concentration levels (Mahvi *et al.*, 2007). The linearity of the plot is also in agreement with other investigations with other biomass (Babarinde *et al.*, 2006; Hashem, 2007). The maximum percentage adsorption of all the metal ions was above 90%.

The effect of temperature on the adsorption on the metal ions in this research is shown in Fig. 3. Temperature effect on metal adsorption follows a nearly similar pattern for Fe and Cd where uptake of the metal ions initially decreases slightly with temperature rise. Then adsorption increases with increase in temperature. The increased adsorption with temperature rise is attributed to acceleration of slow adsorption steps or the creation of some active sites on the adsorbent surface (Hashem, 2007). Increased adsorption at increasing temperature is also ascribed to enhanced mobility of metal ions from bulk solution (Yubin *et al.*, 1998).

The adsorption of Pb²⁺ has a sharp contrast with that of Fe³⁺ and Cd²⁺. The adsorption of lead increased sharply with increase in temperature up to a maximum of 40°C and then decreased with increase in temperature. The decrease in adsorption with increasing temperature, according to Horsfall and Spiff (2005) suggest weak interaction between biomass surface and the metal ions at which point physisorption dominates. The difference in the uptake of the metal ions with temperature may be attributed to the different type of sites on the adsorbent as well as the heat of sorption which depends on the type of metal ions and the heat of sorption at various sorption site (Qaiser *et al.*, 2007).

Sorption isotherm: The extent of adsorption was estimated using the Langmuir, Freundlich, Dubinin-Radushkevich (D-R) and Temkin adsorption isotherms. Adsorption isotherm is the basic requirement for designing any adsorption system. Isotherm express the relation between the amounts of adsorbate removed from liquid phase by unit mass of adsorbent at constant temperature (Shokoochi *et al.*, 2009).

The Langmuir model represents one of the first theoretical treatments of non-linear sorption and suggests that uptake occurs on a homogeneous surface by monolayer sorption without interaction between adsorbed molecules.

In addition, the model assumes uniform energies of adsorption onto the surface and no transmigration of the adsorbent (Boukhiar *et al.*, 2008a, b). The Freundlich isotherm is originally empirical in nature but was later interpreted as biosorption to heterogeneous surfaces or surfaces supporting sites of varied affinities and has been used widely to fit experimental data (Oubagaranadin *et al.*, 2007).

The D-R isotherm is reported to be more general than the Langmuir and Freundlich isotherms; it helps to determine the apparent energy of adsorption, the characteristic porosity of the adsorbent towards the adsorbate and does not assume a homogeneous surface or constant sorption potential (Akcay, 2006). The Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic as implied by the Freundlich equation. The linearised Langmuir equation applied to the data is (Langmuir, 1918):

$$\frac{1}{q_e} = \frac{1}{b q_{\max} C_e} + \frac{1}{q_{\max}} \quad (1)$$

Where:

- q_e = Amount of metal ion adsorbed (mg g^{-1}) at equilibrium
- q_{\max} = Maximum amount of metal ion adsorbed (mg g^{-1})
- C_e = Final concentration of metal ion in solution (mg g^{-1})
- b = Equilibrium or Langmuir constant for adsorption (L g^{-1})
- $q_{\max} b$ = obtained from the intercept and slope of the plot of $1/q_e$ against $1/C_e$ respectively

The Freundlich isotherm equation is defined as:

$$q_e = K C_e^{1/n} \quad (2)$$

The linear form applied to the experimental data is:

$$\log q_e = \log K_f + n \log C_e \quad (3)$$

where, K_f and n are Freundlich constants. The Dubinin-Radushkevich isotherm equation is given as (Dubinin and Radushkevich, 1947):

$$q_e = q_m \exp(-\beta \epsilon^2) \quad (4)$$

The linear form of the equation is given as:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (5)$$

Where:

- q_e = The equilibrium solid phase concentration
- q_m = The theoretical saturation capacity
- ϵ = The Polanyi potential given as:

$$\epsilon = RT \ln(1 + 1/C_e) \quad (6)$$

β is a constant related to the adsorption energy by the Eq. 7:

$$E = (2\beta)^{-1/2} \quad (7)$$

The sorption mean free energy is the energy required to transfer one mole of the sorbate from infinity in solution to the surface of solid. The magnitude of the sorption mean free energy E is widely used for estimating the type of adsorption (Mufazzal *et al.*, 1999; Abusafa and Yucel, 2002; Mahramanlioglu *et al.*, 2002; Erdem *et al.*, 2004). The Temkin isotherm equation as given by Malkoc and Nuhoglu (2007) is:

$$q_e = RT / b (\ln(AC_e)) \quad (8)$$

$$q_e = B \ln A + B \ln C_e \quad (9)$$

where, $B = (RT/b)$; q_e (mg g^{-1}) and C_e (mg L^{-1}) are the amount adsorbed at equilibrium and the equilibrium concentration, respectively. Also T is the absolute temperature (K) and R is the universal gas constant. The constant b is related to the heat of adsorption (Pearce *et al.*, 2000; Akkaya and Ozer, 2005). The isotherm plots for the sorption of the metal ions are shown in Fig. 4 for Fe (III), Fig. 5 for Cd (II) and Fig. 6 for Pb (II) ion. The isotherm constants were obtained from the intercepts and slopes of the respective plots and are shown in Table 1.

The results of these studies show that unmodified raphia palm fruit endocarp is effective for remediation and recovery of metal ions in solution. The high percentage adsorption, the R^2 values of the Langmuir, Freundlich D-R and Temkin isotherms as well as the low values of the separation factors (Horsfall *et al.*, 2004), show that the

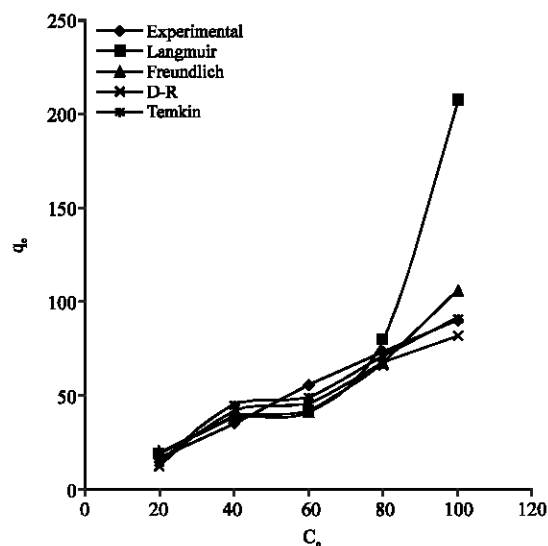


Fig. 4: Isotherm plots for adsorption of Fe(III) ions from solutions using raphia palm fruit

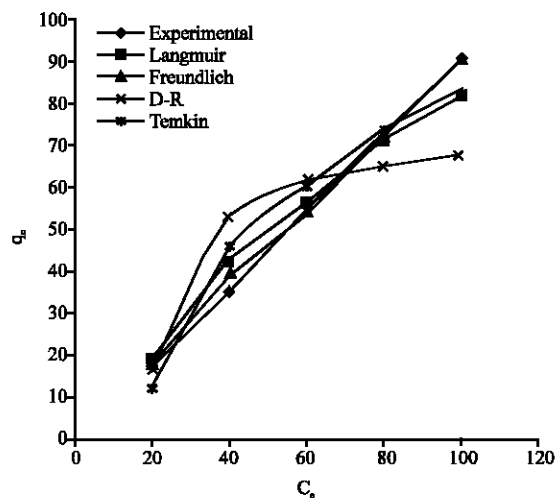


Fig. 5: Isotherm plots for adsorption of Cd (II) ions from aqueous solutions using raphia palm fruit

biomass is a good adsorbent. To further quantify the adsorption properties of the Langmuir isotherm, a dimensionless separation factor (S_F) was used. The separation factor S_F was applied to the data to establish the favourability of the adsorption isotherm. This is given as (Ho *et al.*, 2002; Horsfall *et al.*, 2004):

$$S_F = 1/(1 + bC_0) \quad (10)$$

The values of the Langmuir dimensionless separation factor (S_F) are shown in Fig. 7. The favourability of the

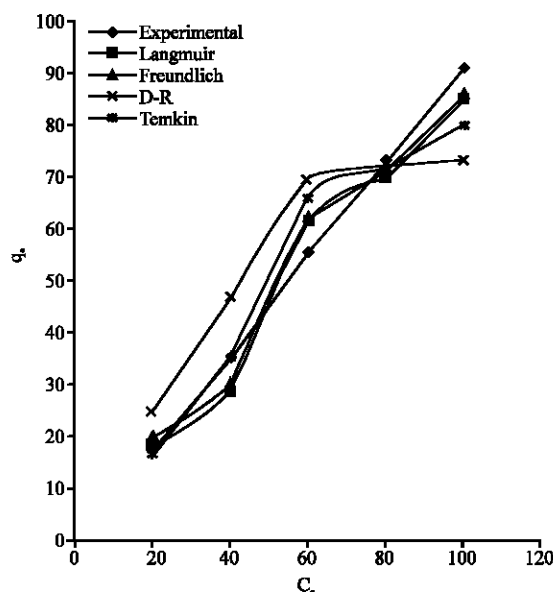


Fig. 6: Isotherm plots for adsorption of Pb (II) ions from aqueous using raphia palm fruit endocarp

Table 1: Isotherm constants for adsorption of Fe (III), Cd (II) and Pb (II) ions from aqueous solutions using Raphia palm fruit endocarp

Isotherms/Constants	Fe (III)	Cd (II)	Pb (II)
Langmuir			
q_{max}	-16.3500	153.8500	500.0000
b	-0.0800	0.1200	0.0200
R^2	0.9321	0.9888	0.9562
Δq (%)	33.1000	8.9300	6.8500
Freundlich			
n	0.6900	1.3000	1.1600
K_F	3.9800	16.1700	11.6700
R^2	0.9222	0.9965	0.9531
Δq (%)	8.8100	4.3000	6.7400
Dubinin-Radushkevich			
β	4.0×10^{-6}	6.0×10^{-7}	1.0×10^{-6}
q_D	104.4800	69.9500	77.4000
E	353.5500	912.8700	707.1100
R^2	0.9461	0.8380	0.9310
Δq (%)	24.5200	13.3600	13.9400
Temkin			
A	0.4200	1.2200	0.8200
B	64.7700	33.9500	37.8300
R^2	0.9556	0.9339	0.9187
Δq (%)	8.3600	6.9800	7.0500

isotherm is guided by the following: the isotherm is unfavourable if $S_F > 1$; linear if $S_F = 1$; favourable if $0 < S_F < 1$ and irreversible if $S_F = 0$.

From the values of S_F it could be seen that the isotherm was favourable for the adsorption of Cd (II) and Pb (II) metal ions on raphia palm fruit endocarp but showed negative values for the adsorption of Fe (III) ion which did not correspond to any of the guidelines. For the Freundlich isotherm, the K_F values were higher for Cd (II) ion followed by Pb (II) ion and then Fe (III) ion. The n

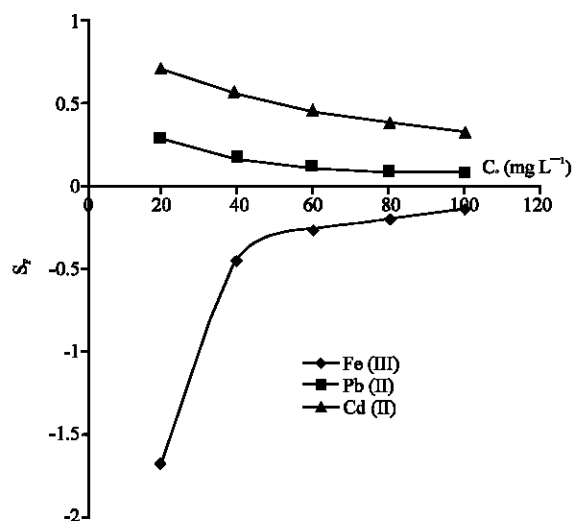


Fig. 7: Langmuir dimensionless separation factor for adsorption of Fe (III), Cd (II) and Pb (II) ions from aqueous solutions using raphia palm fruit endocarp

values for the Freundlich isotherm were higher for Cd (II) ion (1.30) followed by Pb (II) ion (1.16) and then Fe (III) ion (0.69). The values for Cd (II) and Pb (II) were >1 but <10 while the value for Fe (III) ion was <1 . According to Kadirvelu and Namasivayam (2000), n values between 1 and 10 shows easy separation beneficial adsorption.

This also indicates high affinity of the adsorbent to the metal ions (Hashem, 2007). Therefore, this means that the adsorption of Cd (II) and Pb (II) ions were favourable by the Freundlich isotherm. The values of n have also been reported to be related to the distribution of bonded ions on the sorbent surface (Ahalya *et al.*, 2005).

From the D-R isotherm, the apparent energy ($E/kJmol^{-1}$) of adsorption was 912.87 for Cd (II) ion; 707.11 for Pb (II) ion and 353.55 for Fe (III) ion. The apparent energy of adsorption shows if the sorption process follows physisorption, chemisorption, ion-exchange mechanism, etc.

It has been reported that physisorption processes usually have adsorption energies $<40 kJ mol^{-1}$ and above this value sorption is of chemisorption mechanism (Horsfall *et al.*, 2004). If the mean biosorption energy (E) value is between 8.0 and 16.0 $kJ mol^{-1}$, the biosorption process follows chemical ion-exchange and if $E < 8.0 kJ mol^{-1}$, the biosorption process is of a physical nature (Lodeiro *et al.*, 2006; Sari *et al.*, 2007). Therefore from the results of this research shown, it could be shown that the sorption process was of chemisorption mechanism for adsorption of the metal ions on raphia palm

fruit endocarp. Several other researchers have reported on the mean sorption energy being $<8 kJ mol^{-1}$ depicting physical sorption (Horsfall *et al.*, 2004) between 8-16 $kJ mol^{-1}$ showing chemical ion-exchange (Sari *et al.*, 2007; Shah *et al.*, 2009) and above 40 $kJ mol^{-1}$ showing chemisorption mechanism (Ozacar *et al.*, 2008). The favourable application of the Langmuir, Freundlich, D-R and Temkin isotherms to sorption experimental data have been reported by several researchers (Shokoochi *et al.*, 2009; Boukhiar *et al.*, 2008a; Abdel-Ghani *et al.*, 2009; Boukhiar *et al.*, 2008b; Okoye *et al.*, 2010; Rafati *et al.*, 2010).

Thermodynamics of the sorption process: In order to describe the thermodynamic behaviour of the sorption of Fe (III), Cd (II) and Pb (II) ions onto raphia palm fruit endocarp from aqueous solutions, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were evaluated. The sticking probability model was also calculated and used to deduce the activation energy for the sorption process and to ascertain whether the sorption process was of physisorption or chemisorptions mechanism. It was also used to confirm the probability of the metal ion remaining on the surface of the adsorbent. The distribution coefficient (K_d) or equilibrium constant was calculated using the equation below:

$$K_a = q_e / C_e \quad (11)$$

The enthalpy (ΔH°) and entropy (ΔS°) for the sorption process was evaluated using the equation:

$$\ln K_a = \Delta S^\circ / R - \Delta H^\circ / RT \quad (12)$$

The plot of $\ln K_a$ against $1/T$ is shown in Fig. 8. ΔS° and ΔH° were calculated from the values of the intercepts and slopes of the plots for the respective metal ions. The values of enthalpy (ΔH°) and entropy (ΔS°) obtained are shown in Table 2.

The values of ΔH° are negative for Fe (III) and Pb (II) but positive for Cd (II) ion. A negative value for ΔH° shows that the sorption process was exothermic while positive value depicts endothermicity. The endothermicity of the heat of sorption may be due to the removal of water molecules from the solid/solution interface and from the sorbing cations. This is a dehydration process of the cations and it requires energy (Shah *et al.*, 2009). This energy of dehydration supersedes exothermicity of the ions getting attached to the surface. This suggests the

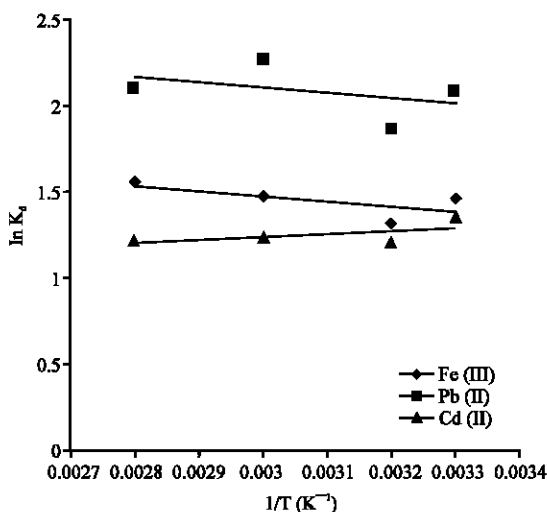


Fig. 8: Vant Hoff plot for adsorption of Fe (III), Cd (II) and Pb (II) ions from aqueous solutions using raphia plan fruit

Table 2: Values of ΔH° , ΔS° , E_A and sticking probability function (S^*) for adsorption of Fe (III), Cd (II) and Pb (II) ions using Raphia palm fruit endocarp

Constants (kJ/mol/K)	Fe (III)	Cd (II)	Pb (II)
ΔH°	-2560.4600	1459.1900	-2506.9200
ΔS°	19.1900	5.8900	24.9000
E_A	2094.8000	-1143.5100	2229.3200
S^*	0.0900	0.3400	0.0500
R^2 (Vant Hoff)	0.4633	0.3712	0.1626
R^2 (Sticking probability)	0.4747	0.3733	0.1647

Table 3: Values of ΔG° for adsorption of Fe (III), Cd (II) and Pb (II) ions using Raphia palm fruit endocarp at various temperatures

Temperature (K)	ΔG° (J/mol/K)		
	Fe (III)	Cd (II)	Pb (II)
303	-3670.39	-5217.14	-3380.69
313	-3411.59	-4827.23	-3129.69
333	-4072.56	-6256.95	-3416.41
353	-4554.88	-6113.28	-3562.90

possibility of strong bonding between sorbet and sorbent. The standard Gibbs free energy (ΔG°) for the sorption process are all negative (Table 3). The negative values obtained for the Gibbs free energy (ΔG°) indicates that the sorption process is spontaneous in nature and also feasible. Similar findings have been reported (Shah *et al.*, 2009; Malkoc and Nuhoglu, 2007). Sari *et al.* (2007) reported the decrease in ΔG° values with increase in temperature which shows a decrease in feasibility of biosorption at higher temperatures. The potential sticking probability equation is given by a modified Arrhenius type equation related to surface coverage as given (Horsfall and Spiiff, 2005):

$$S^* = (1 - \theta) \exp - E_A / RT \quad (13)$$

Where:

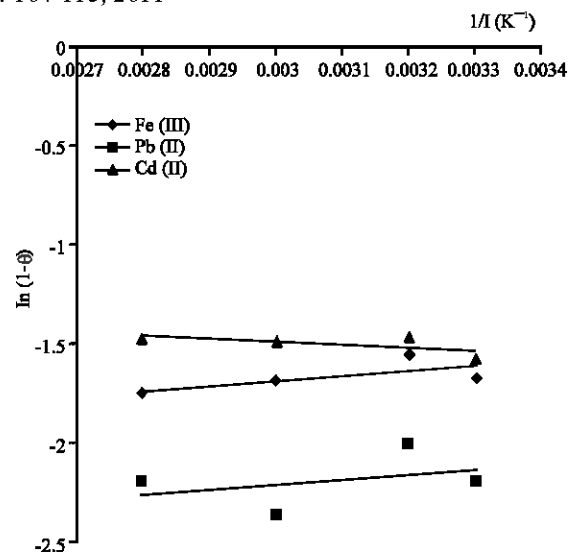


Fig. 9: Sticking probability plot for adsorption of Fe (III), Cd (II) and Pb (II) ions from aqueous solutions using raphia palm fruit

Table 4: The potential sticking probability relationship between sorbate and sorbent

Values of S^*	Potential sticking probability
$S^* > 1$	Adsorbate unsticking to adsorbent no sorption
$S^* = 1$	Linear sticking relationship between adsorbate and adsorbent-possible mixture of physiosorption and chemisorptions
$S^* = 0$	Indefinite sticking of adsorbate to adsorbent chemisorptions mechanism predominant
$0 < S^* < 1$	Favourable sticking of adsorbate to adsorbent physiosorption mechanism predominant

S^* = The potential sticking probability

E_A = The activation energy for the reaction

R = The molar gas constant

T = Absolute temperature and θ is given by the equation:

$$\theta = 1 - (C_e / C_o) \quad (14)$$

where, C_o and C_e are the initial and equilibrium metal ion concentrations, respectively. The value of S^* evaluated at different temperatures are also show in Table 2, through a plot of $(1 - \theta)$ against $1/T$ (Fig. 9). The guidelines for the potential sticking probability relationships are shown in Table 4. From the values of S^* on Table 2 and the guidelines in Table 4, it could be seen that the system falls within category number 4. This means that there is favourable sticking of the metal ions to the adsorbent. This also means that physiosorption mechanism is the predominant mechanism.

The activation energy of any reaction process depicts the energy barrier which the reactants must overcome before any reaction could take place. High activation energy means that fewer molecules will have enough energy to react hence decrease in reaction rate.

From this study, the activation energy (E_a) of the metal ion also shown on Table 2 is lowest for Cd^{2+} followed by Fe^{3+} and highest for Pb^{2+} . This confirms the trend of adsorption of the metal ions on raphia palm fruit endocarp.

CONCLUSION

The results of this study showed that unmodified raphia palm nut endocarp is efficient for the adsorption of Fe^{3+} , Pb^{2+} and Cd^{2+} ions from aqueous media. From the percentage adsorption reported, it was observed that Cd was the most adsorbed (98.7%), followed by Pb (91.98%) and Fe (91.16%) in 20 min. The adsorption of the metals was temperature dependent, with optimal temperatures of 303 K for Pb, 333 K for Cd and 353 K for Fe. The separation factors (<1) and the negative ΔG values show that the reaction was favourable, feasible and spontaneous. The mechanism of sorption was found to be chemisorption mechanism.

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