

Full Length Research Paper

Utilization of *Blighia sapida* (Akee apple) pod in the removal of lead, cadmium and cobalt ions from aqueous solution

Jimoh, T. O.^{1*}, Buoro, A. T.¹ and Muriana, M.²

¹Department of Chemistry, Federal University of Technology, P. M. B. 65, Minna, Niger State, Nigeria.

²Science Laboratory Technology Department, The Polytechnic, Ibadan, Saki Campus, Oyo State, Nigeria.

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***Blighia sapida* pod was utilized as a low cost adsorbent to remove Pb(II), Cd(II) and Co(II) ions from aqueous solutions. The effect of pH, contact time, initial metal ion concentration, and adsorbent dosage were evaluated using batch adsorption experiment at 32°C. pH dependence study of the biosorption process revealed that maximum pH for Pb(II), Cd(II) and Co(II) ions removal from aqueous solution occurred at 6. Maximum equilibrium was attained at contact time 60 min for the three metal ions. The adsorption capacities of *B. sapida* pod increased as initial metal ion concentration and adsorbent dosage increases. Equilibrium data fitted better to the Freundlich isotherm model than the Langmuir isotherm model. The biosorption study showed that *B. sapida* pod had the potentials for heavy metals removal from aqueous solution.**

Key words: Utilization, *Blighia sapida*, lead, cadmium, cobalt, aqueous solution.

INTRODUCTION

Heavy metal pollution has continued to increase as a consequence of vast expansion of industrialization and urbanization (Jimoh, 2010; Jimoh et al., 2011). These heavy metals have tendency to bioaccumulate in the environment and thus persist to reside inside living tissue with long lasting adverse health effects. Heavy metals are widely used in industrial activities such as metal finishing, electroplating, painting, dyeing, photography, surface treatment and printed circuit board manufacture (Renuga et al., 2010). When these metals are present in significant quantities in the environment they pose serious threat. Therefore measures should be taken to reduce the heavy metal pollution in order to minimize the risk of adverse effects on health and the environment (Nadeem et al., 2009).

Generally water bodies for instance were reported to be the major site of heavy metal deposits due to the fact that streams and rivers flow through agricultural areas

(Okoye et al., 2010). Numerous concerted efforts including the development of chemical processes such as electro-floatation, chemical precipitation exchange, co-precipitation, flocculation and membrane filtration have been developed to reduce hazardous effect of toxic metals. Most of the methods mentioned above were found to be ineffective especially when the heavy metals concentration in the contaminated media are in order of 1 to 100 mg/L (Ahluwalia and Goyal, 2005).

However the recently introduced technique for removing toxic heavy metal is Biosorption. The major advantage of an adsorption system for water pollution treatment includes less investment in terms of initial cost and simple design, easy operation, availability of materials, environmental friendliness when compared to other conventional methods previously mentioned (Markovska et al., 2006).

The agricultural waste material considered in this work was *Blighia sapida* pod. It is an ever green tree belonging to family Sapindaceae and widely distributed in tropical western African countries such as Nigeria, Mali, Ghana, Guinea, Benin, Burkina Faso, Togo, having leathery red and yellow fruits. It is called various names among the

*Corresponding author. E-mail: jimohishola8@gmail.com. Tel: +2348057344464.

tribes in Nigeria. For instance, the Yorubas' in South – western part of the country referred to it as *Ishin*, the Nupes in the North central part of Nigeria called it *Yilanchi*, the Hausas in Northern-western part call it *Gwanja Kusa* and the Igbos' in the eastern part call it *Okpu*. It is important to note that large quantities of *B. sapida* pod is being generated annually without proper disposal system and therefore resulted into environmental pollution. These low value waste produced in huge quantities was being converted into adsorbent that could be utilized to remove toxic metals from aqueous solution, which would be beneficial to the environment at large and also save the cost of purchasing highly expensive activated charcoal. This research was therefore conducted to put into use the *B. sapida* pod waste to remove cobalt, cadmium and lead from aqueous solution.

MATERIALS AND METHODS

Sample collection

The pod of *B. Sapida* fruit was randomly collected at different location within Bida, Metropolis, Niger state around July and August, 2011. The samples were mixed to form a composite sample from where the representative samples were taken for sorption studies.

Preparation of adsorbent

The fresh pod of *B. Sapida* was sun dried for weeks, cleaned, washed with deionized water for several times to remove debris then dried again and grounded to powder form with mortar and pestle. The grounded particle then passed through 300 μm sieve mesh size and it retained in 400 μm was used for the sorption studies.

Sample pretreatment

The fine powder was then washed thoroughly with deionized water for several times to remove all debris, after which they were air dried. The fine powder was sieved through a 300 μm mesh sieve and used for the sorption studied.

Preparation of aqueous solutions

The stock solution was prepared by dissolving 6.87, 13.04 and 1.6 g of analytical reagent (AR) of Cadmium sulphate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$); Mwt (769.51), Cobalt(II)chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$); Mwt (237.93) and lead nitrate [$\text{Pb}(\text{NO}_3)_2$]; Mwt (331.21) in 1000 cm^3 and diluted with deionized water this gave a concentration of 1000 ppm. 100 ppm concentration was further prepared from the 1000 ppm stock solution by pipetting 10 cm^3 of the solution into a measuring cylinder and making up to mark of 100 cm^3 volumetric flask, and then different concentrations of 5, 10, 15, 20, 25 and 30 ppm, solutions were prepared by serial dilution.

Sorption experiment

Effect of pH on adsorption

0.5 g of the sample was added to 30 cm^3 of the aqueous solution at

different pH (1 to 10) in a conical flask. The pH of the solution was adjusted using 0.1 M HCl and 0.1 M NaOH accordingly. The resultant solution with the adsorbent in the flask was shaken with a Gallenkamp shaker and filtered. The filtrate was then analyzed for lead, cadmium and cobalt using Atomic Absorption Spectrophotometer (Perkin Elmer; analyst 200).

Effect of contact time

0.5 g of the sample was mixed with 30 cm^3 solution of the initial concentration of 5 mg/L. The mixture was shaken constantly in an orbit shaker at 420 rpm speed for the time period of 20, 40, 60, 80, 100 and 120 min each. At the end of each contact time period, the mixture was filtered and the concentration of the filtrate was then analyzed for lead, cadmium and cobalt using Atomic Absorption Spectrophotometer (AAS) (Perkin Elmer; analyst 200).

Effect of adsorbent dosage on adsorption

0.5, 1.0, 1.5, 2.0 and 2.5 g of the sample were each separately mixed with 30 cm^3 of concentration 20 mg/l. The mixture was then agitated with a Gallenkamp shaker for 60 min. The resultant solution with the adsorbent in the flask was shaken and filtered. The filtrate was then analyzed for lead, cadmium and cobalt using Atomic Absorption Spectrophotometer.

The effect of initial metal ions concentration

0.5 g of the sample each was separately mixed with 30 cm^3 solution of initial concentration of 10, 15, 20, 25 and 30 mg/L. The mixture were shaken constantly using a Gallenkamp shaker at 6 rpm for 60 min for lead, cadmium and cobalt. At the end of 60 min, the mixture was filtered and the concentration analyzed using Atomic Adsorption Spectrophotometer (Perkin Elmer; analyst 200).

Data analysis

Freundlich model

Freundlich model is used to estimate the adsorption intensity of sorbent towards the adsorbate and is given by the equation below

$$q_e = k_F \cdot C_e^{1/n} \quad (1)$$

Where, q_e is the metal up take in (mg/g); C_e is the equilibrium solute concentration in the fluid (mg/L or mM); N represents Freundlich constant (dimensionless). $1/n$ is a heterogeneity factor, which is a measure of intensity of sorption or affinity of the adsorbate for the adsorbent and is less than 1 if the adsorption process is favorable; k_F is the Freundlich constant, which is a measure of adsorption capacity (mg/g). The Freundlich equation can be linearized as shown:

$$\log q_e = (1/n) \log C_e + \log k_F \quad (2)$$

A plot of $\log q_e$ against $\log C_e$ gives a straight line graph with $1/n$ as slope and $\log k_F$ as intercept.

Langmuir model

It is represented by the expression below

$$q_e = (q_{\max} C_e) / (K_L + C_e) \quad (3)$$

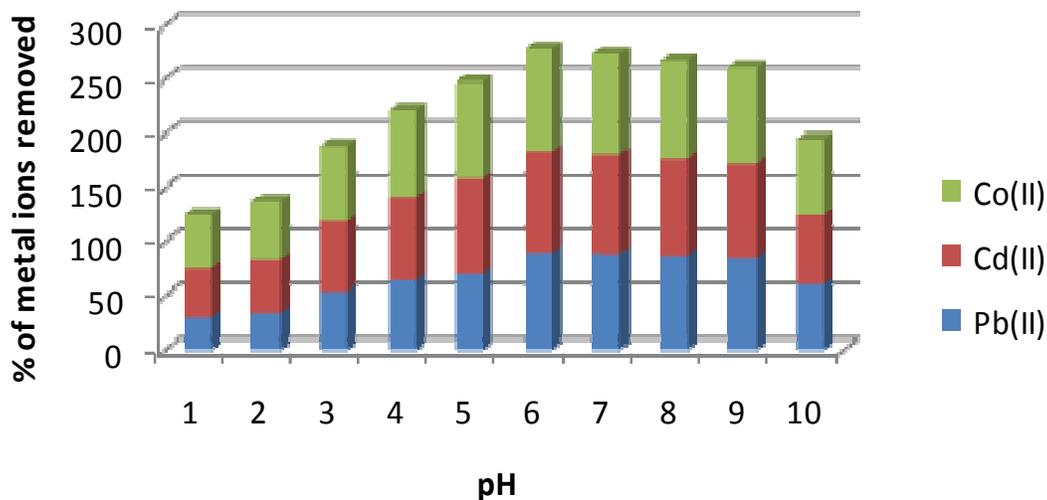


Figure 1. Effect of pH on adsorption of lead, cadmium and cobalt ions.

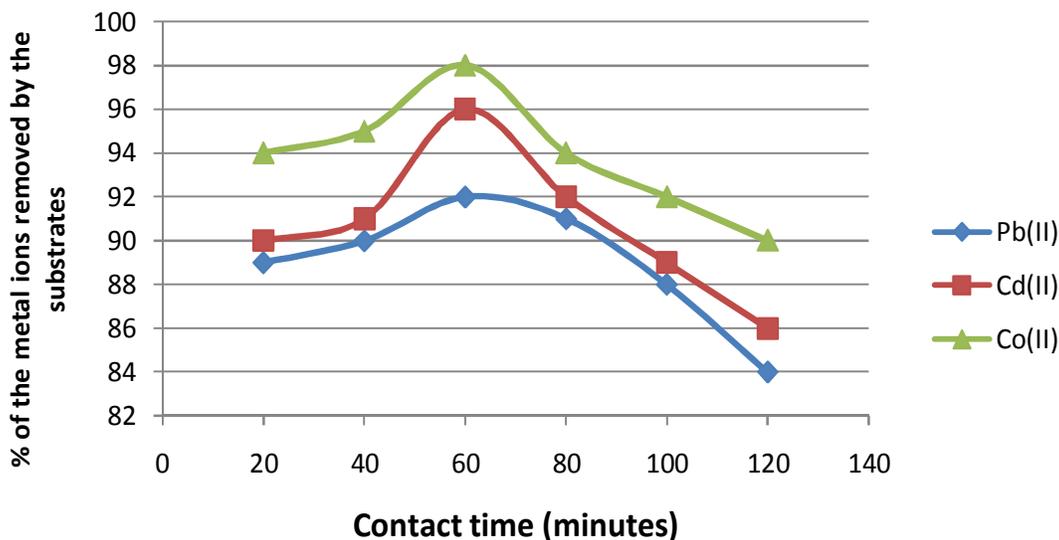


Figure 2. Effect of variation of contact time on adsorption of lead, cadmium and cobalt ion by the sample.

Where, q_e is the metal up take (mg/g), q_{max} is the Langmuir maximum metal uptake (mg/g), C_e is the equilibrium concentration of the adsorbate, (mg/L or mM); k_L is the Langmuir's constant and is related to the measure of affinity of the adsorbate for the adsorbent (L/mg or mM). For correlation purposes, the equation is rearranged as shown:

$$1/q_e = 1/k_L \cdot q_{max} (1/C_e) + 1/q_{max} \cdot C_e \quad (4)$$

A plot of $1/q_e$ against $1/C$ gives a straight line plot with a slope $1/k_L \cdot q_{max}$ and an intercept of $1/q_{max}$.

RESULTS AND DISCUSSION

From Figure 1, pH 1 to 5 indicated low removals of metal

ions while maximum adsorption at pH 6, which later decreased when the pH was increased to 10 for the three metal ions.

Figure 2 revealed that as the contact time increased from 20 to 120 min, the amount of metal ions removed also increased, this trend was consistent up to 60 min contact time when equilibrium was attained. Further increase of contact time beyond 60 min; generally result in decrease in the amount of Pb(II), Cd(II) and Co(II) ions. Figure 3 indicated the adsorbent dosage results. It was observed that an increase in the dosage of adsorbent from 0.5 to 2.5 g yield corresponding increase in the amount of metal ions that is adsorbed unto the surface of the adsorbent. It was also observed that for the different

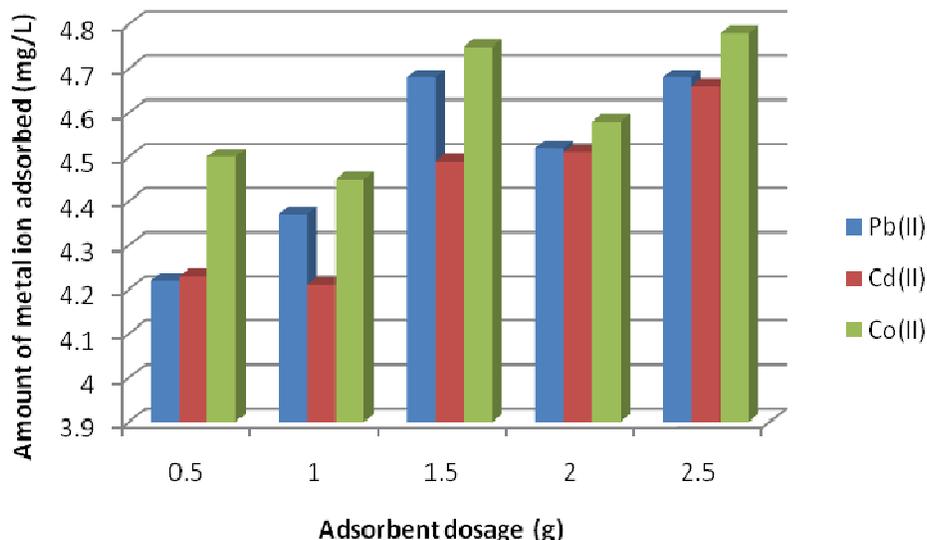


Figure 3. Effect of *Blighia sapida* dose on adsorption of lead, cadmium and cobalt ions.

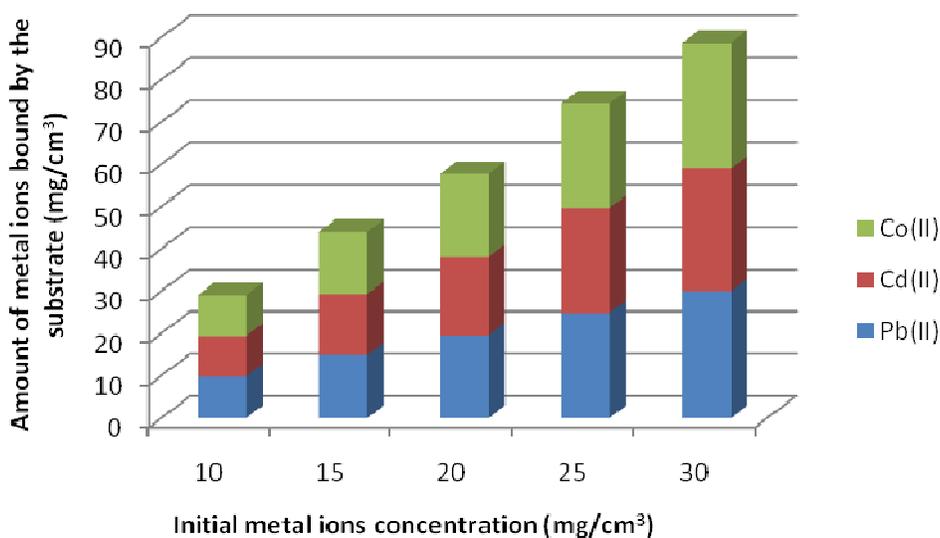


Figure 4. Effect of initial metal ions concentration on lead cadmium and cobalt ions.

adsorbent dosage, Co(II) ion had the highest amount adsorbed than lead and cadmium ion (Co>Pb>Cd).

Figure 4 showed that as the initial metal ion concentration increases, the amount of metal ion bound also increased. Comparing the three metal ions it was observed that at the concentration of 10 mg/L, Pb(II) ion had the highest amount of metal ion adsorbed than Cd(II) and Co(II) ions (Pb>Co>Cd). At 20 mg/L, Co(II) ion had the highest removal than lead and cadmium (Co>Pb>Cd). At 25 and 30 mg/L, Cd (II) ion had the highest removal than lead and cobalt. The trend of adsorption was Cd>Co>Pb. Table 1 indicated the

Freundlich constant for lead (II) was 1.633, the slope 1/n adsorption intensity was 0.981 while the correlation regression coefficient was 0.997. The K_F for cadmium (II) was 1.845, the slope 1/n, adsorption intensity was 1.018 while the correlation regression coefficient was 0.996. The K_F for cobalt (II) was 1.999, the slope 1/n, adsorption intensity was 1.041 while the correlation regression coefficient was 0.997.

Table 2 revealed the Langmuir constant for lead (II) was 0.135, the maximum amount of adsorption Q_{max} 0.381 while the correlation regression coefficient was 0.214. The K_L for cadmium (II) was 0.639, the Q_{max} was

Table 1. Freundlich adsorption isotherm constant associated with the adsorption of lead, cadmium and cobalt ions by *Blighia sapida* pod.

Metal	K_F	1/n	N	R^2
Pb (II) ion	1.633	0.981	1.019	0.997
Cd (II) ion	1.845	1.018	0.982	0.996
Co (II) ion	1.999	1.041	0.961	0.997

Table 2. Langmuir adsorption isotherm constant associated with the adsorption of lead, cadmium and cobalt ions by *Blighia sapida* pod.

Metal	Q_{max} (mg/g)	K_L	R^2
Pb (II) ion	0.381	0.135	0.214
Cd (II) ion	0.209	0.639	0.011
Co (II) ion	0.293	-2.188	0.147

0.209 while the correlation regression coefficient was 0.011. The K_L for cobalt (II) was -2.188, the Q_{max} was 0.293 while the correlation regression coefficient was 0.147.

Effect of pH on adsorption

The adsorption behavior of Pb(II), Cd(II) and Co(II) ion was studied from the aqueous solution at different pH values. pH is one of the principal factors influencing the adsorptive capacities of metal ions on agricultural wastes. The effect of pH on heavy metal adsorption from aqueous solutions was reported by several researchers (Igwe and Abia, 2005; Oboh and Aluyor, 2008; Saima et al., 2008; Nadeem et al., 2009; Egila et al., 2010; Onwu and Ogah, 2010; Saravanakumar and Kumar, 2011) in all cases it was found that removal of heavy metal ions was pH dependent. For this reason, the pH solution was varied from 1 to 10 for the three investigated metal ions. It is clear that Pb (II) ion was effectively adsorbed in the pH range 4, 5 and 6 with the highest percentage removal at pH 6 while for cadmium (II) and cobalt (II) ion, maximum removal also occurred at pH 6. Similar trends were reported by Onwu and Ogah (2010) and Egila et al. (2010). The increase in the amount of metal ion adsorbed due to the increase in pH may be explained on the basis of a decrease in competition between proton (H^+) and the positively charged metal ion at the surface sites and by decrease in positive charge near the surface resulting in a lower repulsion of the adsorbing metal ion.

When alkalinity increased that is from pH value of 7 to 8, there was further decrease in the rate of adsorption by *B. sapida* for Pb(II), Cd(II) and Co(II) ions in aqueous solution. This could be as a result of decrease in the degree of protonation of the adsorbent functional group (Saima et al., 2008). The minimum percentage adsorption observed at pH low pH may be due to the

ligands on the cell walls that were closely associated with the hydroxonium ions thereby causing the surface of the adsorbents to be positively charged, but when the pH was increased, the hydroxonium ions were gradually dissociated and the positively charged metal ions were associated with the free binding sites on the adsorbent. This result also suggests that H^+ ion concentration on the substrate affects the amount of metal ions adsorbed (Ajmal et al., 2000). Therefore it is plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H_3O^+), thereby preventing the metal ions from approaching the binding sites of the adsorbent (Wong et al., 2003; Saeed et al., 2003). In contrast as the pH increases, more negatively charged surface becomes available thus enhancing greater metal ion removal.

Effect of contact time on removal of the cobalt, cadmium and lead ion on adsorption

The influence of contact time on lead, cadmium and cobalt ions removal from aqueous solution is illustrated in Figure 2. The rate of metal uptake level was rapid within 60 min for the three metal ions which were independent of the metal ion concentration, additional increase in time resulted in a decrease in the amount of metal ions adsorbed. This implied that the binding sites on the adsorbent were exhausted and further shaking resulted in desorption or the adsorption sites became saturated to maximum uptake capacity. Similar trends was observed for the biosorption of Pb(II) ion (Wuyep et al., 2007), Co(II) ion (Egila et al., 2010) and Cd(II) ion (Mataka et al., 2010). At each contact time, more of cobalt (II) ion was being removed than cadmium (II) and lead (II) ion. This could be plausibly due to the fact that cobalt with smaller ionic radii was able to diffuse through the pores of the pod than lead and cadmium, although they both reached

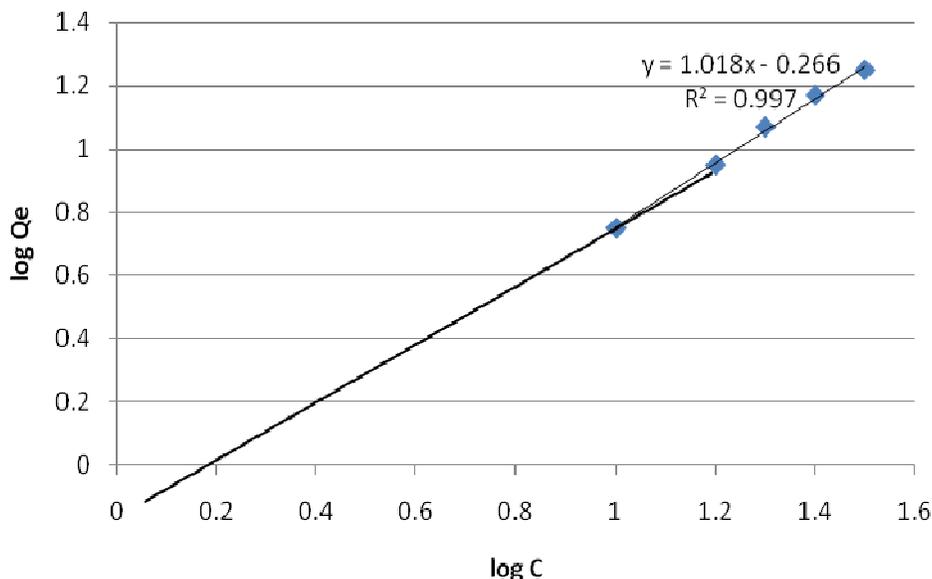


Figure 5. Freundlich adsorption isotherm plot of cobalt (II) ion.

equilibrium at the same time of 60 min. Therefore, in a mixture of the adsorbent and metal ion, the metal ion competes for the adsorption sites on the adsorbent. This competition could affect ions. Hence, equilibrium time is one of the important parameter for an economical wastewater treatment system. The adsorptive capacities of lead, cobalt and cadmium sorption at equilibrium were 0.280, 0.290 and 0.280 mg/g, corresponding to a removal percentage of about 92.20, 95.20 and 92.40%, respectively at 60 min contact time.

Effect of initial metal ion concentration

The result of the effect of initial metal ion concentration shows the relationship between concentrations and the amount of metal ion bound at fixed adsorbent dosage of 0.5 g. The increase in the initial metal ion concentration led to increase in the amount of metal ion bound. At low concentration, adsorption sites took up the available metal more quickly or due to the availability of the uncovered surface area of the adsorbents, since adsorption kinetics depends on the surface area of the adsorbent (Akhtar and Qadeer, 2005). However, at higher concentration, metal ions needed to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a lower rate. The trend of adsorption was Cd>Co>Pb. It is generally expected that as the concentration of the adsorbate increases, the metal ions removed should increase according to Okeimen and Onyenkpa (2000) and Elaigwu et al. (2009). The results showed that the amount of the metal ion bound by *B. sapida* pod depended on the metal ions type and the concentration of the metal ions.

Effect of dosage on adsorption

The result of the effect of dosage on the removal of Pb(II), Cd(II) and Co(II) ions from aqueous solution is shown in Figure 3. The dosage of substrate employed was found to influence the efficiency of the adsorption process. The rate of metal uptake capacity of the adsorbent increases with the increase in dosage. This is as a result of increase in the number of active sites available for the metal ions. This could also be due to increase in electrostatic interaction between the substrate and the adsorbate. The higher the electrostatic interaction between the adsorbent and the metal ions, the higher the metal uptake level. According to this finding, *B. sapida* pod is more effective in removing cobalt ion than lead and cadmium ion. This could be plausibly due to the fact that cobalt with smaller ionic radii was able to diffuse through the pores of the pod than lead and cadmium. The trend of adsorption was Co>Cd>Pb. The results therefore shows that the adsorption of cations with large ionic radii would less likely compared with smaller ionic radii. This is in line with what was reported by Abia and Asuquo (2007) and Mataka et al. (2010) that during sorption of metal ions, ions of smaller ionic radii tend to move faster to potential adsorption than the heavier one.

Equilibrium modelling

The equilibrium of the biosorption process of this study was described by fitting the experimental data with models which are used to represent the equilibrium adsorption isotherm. The results obtained were tested using Freundlich and Langmuir isotherms and were presented in Figures 4 to 10 and Tables 1 and 2.

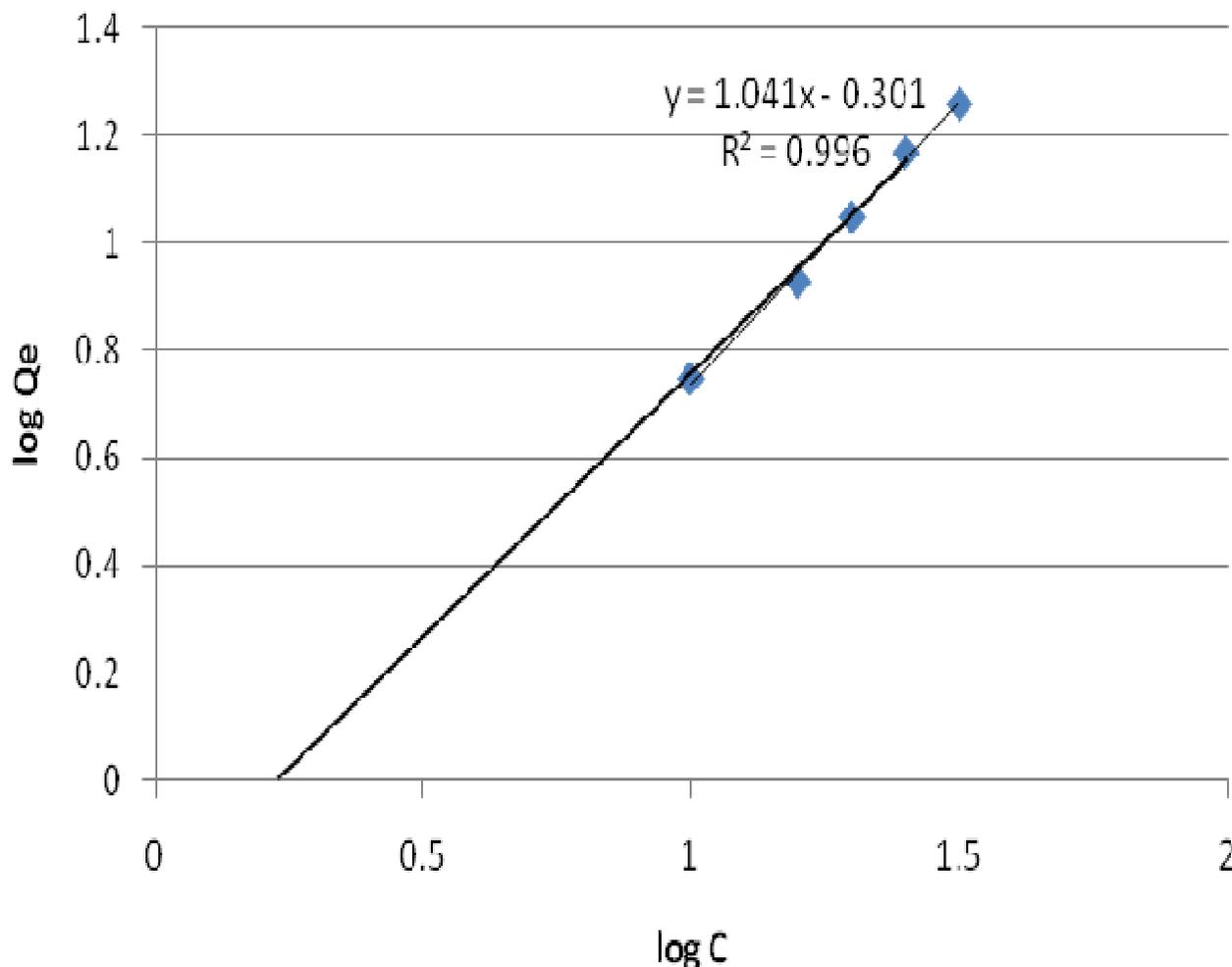


Figure 6. Freundlich adsorption isotherm plot of cadmium(II) ion.

The Freundlich isotherms presented highest adsorption capacity value K_F of 1.633, 1.845 and 1.999 for Pb (II), Cd (II) and Co (II) ions respectively. Also the adsorption onto *B. sapida* pod obtained from this isotherm gave a higher adsorption intensity $1/n$ (0.981, 1.018, 1.041 for Pb(II), Cd(II) and Co(II) ions). The correlation coefficient R^2 values for the three investigated metal ions were 0.997, 0.996 and 0.997 as predicted using Freundlich isotherm model. On the contrary, the Langmuir constants representing the maximum adsorption capacity ($q_{max} = 0.381$ mg/g) was higher for lead compared to that of cadmium and cobalt ions ($q_{max} = 0.209$ and 0.293 mg/g). The correlation coefficient R^2 , value for lead, cadmium and cobalt are 0.214, 0.011 and 0.147, respectively. Since the Freundlich isotherm gave the highest correlation regression coefficient values for R^2 as 0.997, 0.996 and 0.997 for lead, cadmium and cobalt ions, it implies that the adsorption capacity and intensity estimation was based on the Freundlich isotherm. Hence, the metal ion uptake by *B. sapida* pod gave a better

adsorption capacity using Freundlich adsorption isotherm.

More so, the values obtained for lead, cadmium and cobalt ions from Freundlich and Langmuir isotherms, indicated that the biomass used had greater affinity for Pb(II) ion because the correlation coefficient R^2 of Pb(II) ion is higher than that of Cd(II) and Co(II) ions. This observation is probably as a result of lead (II) ions having larger ionic radii (1.33\AA) than cadmium (0.97\AA) and cobalt (0.68\AA). Another plausible reason for this trend in adsorption could also be ascribed to size of hydrated lead ion when compared with that of cadmium and cobalt which become smaller and so the mechanism of the uptake of metal ions was affected by steric hindrance. Similar trend was observed in the study of *Sargassum* biomass as an adsorbent for Pb(II) (Yan and Vijayaraghavan, 2001), the result indicated that the maximum metal uptake for Pb(II) ion was 214 mg/g. However the result showed that Freundlich isotherm fitted better for Pb(II) ion, Cd(II) and Co(II) ions biosorption by

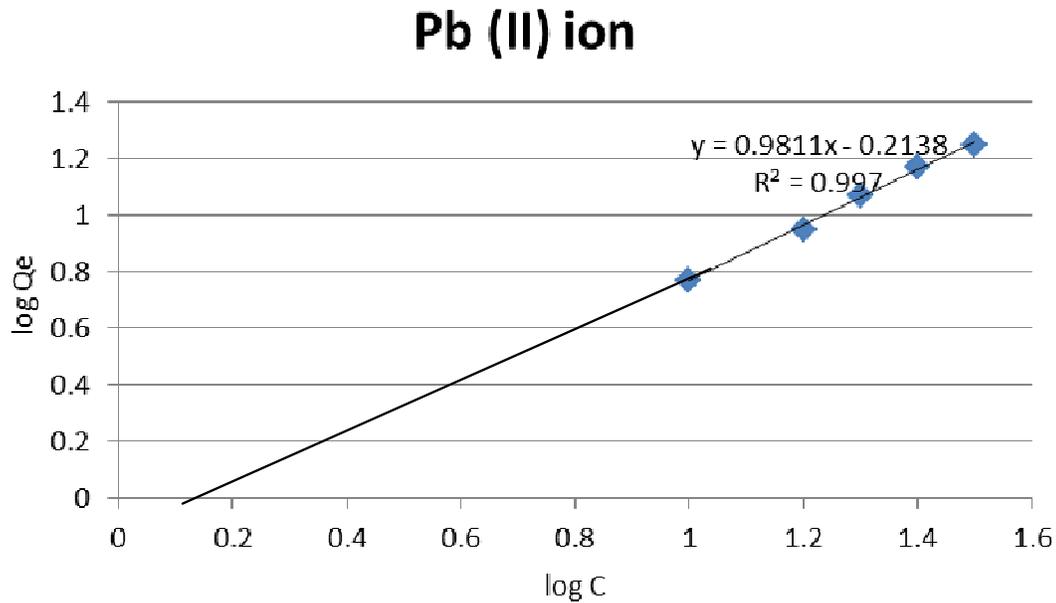


Figure 7. Freundlich adsorption isotherm plot of lead (II) ion.

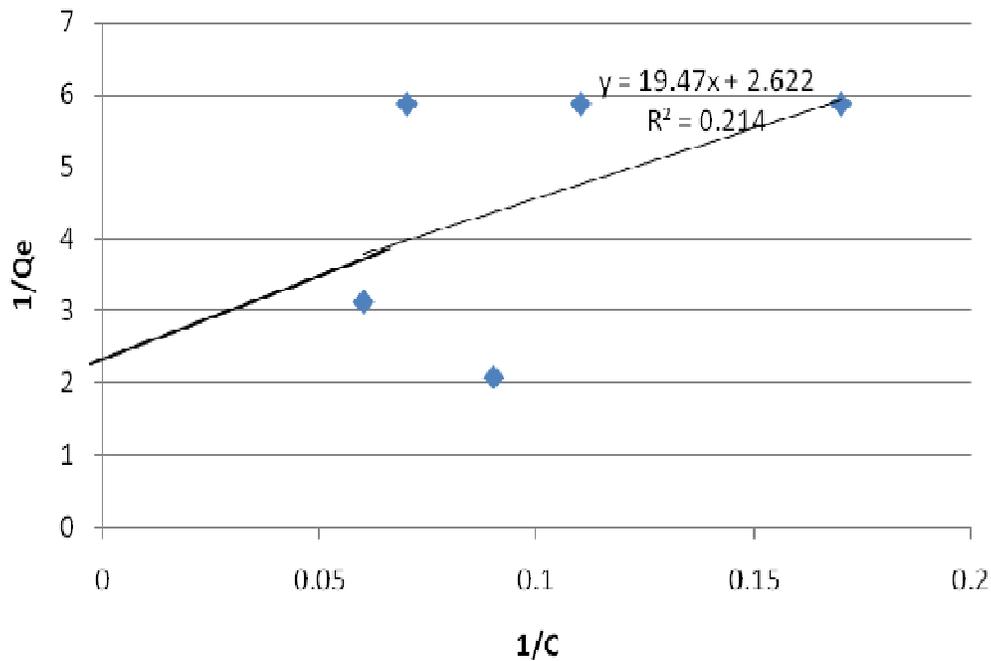


Figure 8. Langmuir adsorption isotherm plot of lead (II) ion.

B. sapida pod than the Langmuir isotherm.

Conclusion

This study showed that a good adsorbent for the removal

of Pb(II), Cd(II) and Co(II) ions from aqueous solution could be obtained from *B. sapida* pod. Batch experiments conducted revealed that the adsorption of Pb(II), Cd(II) and Co(II) ions was pH, time, adsorbent dosage and also initial metal ion concentration dependent. The binding of the three investigated metal ions unto *B. sapida* pod

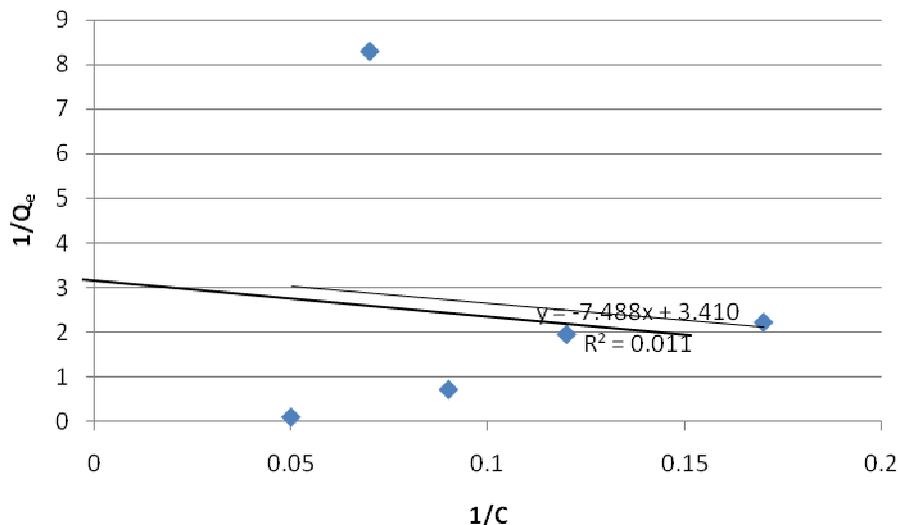


Figure 9. Langmuir adsorption isotherm plot of cadmium (II) ion.

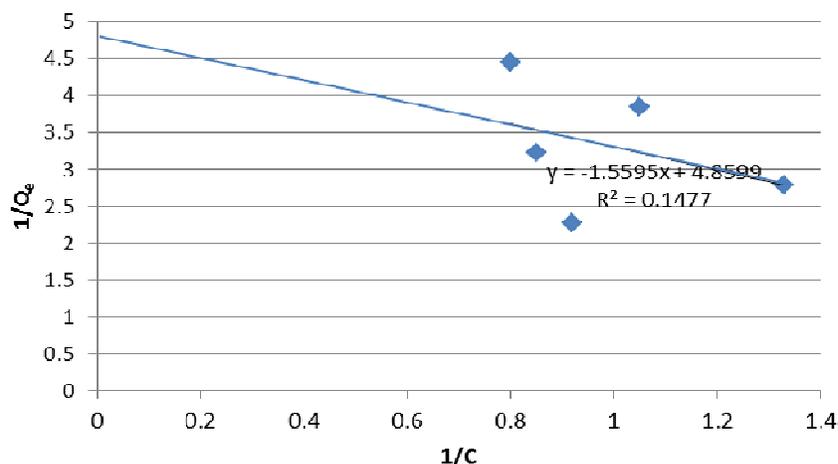


Figure 10. Langmuir adsorption isotherm plot of cobalt (II) ion.

occurred in 60 min. The equilibrium data obtained fitted the Freundlich isotherm results more than that of the Langmuir isotherm. Therefore, Lead (II), cadmium (II) and cobalt (II) ions on adsorption were more of the multiple layer adsorption than a monolayer adsorption. *B. sapida* pod (a waste) being inexpensive and readily available, could serve as a cost effective means for removing metal ions from contaminated water or effluents.

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