

Cocoa Pod Husk as a Low Cost Biosorbent for the Removal of Pb(II) and Cu(II) from Aqueous Solutions

^{1,2}Njoku, V.O., ³Ayuk, A.A., ³Ejike, E.E., ³Oguzie, E.E., ³Duru, C.E. and ⁴Bello, O.S.

¹Department of Chemistry, Imo State University, P.M.B. 2000 Owerri, Nigeria

²School of Chemical Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

³Department of Chemistry, Federal University of Technology, P.M.B. 1526 Owerri, Nigeria

⁴Department of Pure and Applied Chemistry, Ladoko Akintola University of Technology, P.M.B. 4000 Ogbomoso, Nigeria

Abstract: Cocoa pod husk, an agricultural waste, was used as biosorbent for Pb²⁺ and Cu²⁺ from aqueous solutions. The percent sorption increased with increasing contact time and initial concentration of metal ions for the two metal ions studied, with higher affinity for Pb²⁺. Equilibrium adsorption for Pb²⁺ and Cu²⁺ at 30 °C was attained after 120 min. The negative standard Gibbs free energy change, ΔG° values obtained confirms the spontaneity of the biosorption process. The higher correlation coefficient, R^2 values (>0.99) and low standard deviation of the pseudo-second-order parameters for the entire sorption period indicates a better prediction of the sorption kinetics than the pseudo-first-order model. The biosorption capacity and hence percent sorption of cocoa pod husk increased with pH attaining maximum values at pH 6. The study on the effect of monovalent and divalent ions on the sorption potential of the biosorbent showed that sorption potential decreased with increase in ionic strength.

Key words: Agrowaste; Biosorption; Heavy metals; Kinetics; Thermodynamic parameters; Wastewater treatment

INTRODUCTION

Environmental contamination by pollutants such as toxic metals is a serious problem due to its incremental accumulation in the food chain and continued persistence in the ecosystem (Jain *et al.*, 2010; Sousa *et al.*, 2010). Electroplating and metal processing, paint, plastics, batteries, mining and ore processing, smelters, tanneries and printed circuit board manufacturers are a few of the industries in which metal-bearing effluents pose a problem to the environment (Njoku *et al.*, 2011; Ofomaja, 2010). The combined effect of environmental pressures, reflected in regulatory status as well as economic considerations make the removal and recovery of heavy metals from industrial effluents an ever-increasing priority (Gupta and Babu, 2009). Such considerations present an extraordinary business opportunity in addition to an exciting scientific challenge.

Biosorption is a promising alternative method to treat industrial effluents, mainly because of the low cost of biosorbents and high metal binding capacity (Salim *et al.*, 2008). Some waste biomass have been reported to effectively sequester heavy metals. These include rice bran (Wang and Qin, 2005), corn chaff (Han *et al.*, 2006), melon seed husk (Okieimen and Onyenkpa, 1989), black gram husk (Saeed and Iqbal, 2003) and hazelnut shells (Cimino *et al.*, 2000).

Biosorbents used for water purification are specific for binding different ions depending on the type of ligands they possess, the relative affinity of ions for the available ligands, and the conditions applied (Sawalha *et al.*, 2009). While the biosorption process could be used even with a low degree of understanding of its metal-binding mechanisms, better understanding will make for more effective and optimized applications (Benhammou *et al.*, 2005). In continuation of the search for diverse and more efficient biosorbents for heavy metals removal from waste waters, cocoa pod husk, a primary agricultural waste and novel biological material, was investigated as biosorbent for the removal of Pb²⁺ and Cu²⁺ ions from aqueous solutions. Lead and copper ions were chosen for this study because of their wide industrial applications and potential pollution impact on living organisms (Nghah and Fatinathan, 2010; Ofomaja *et al.*, 2010). The effects of contact time, pH of solution, initial metal ion concentration and ionic strength on the biosorption process were investigated.

Corresponding Author: Njoku, V. O., Department of Chemistry, Imo State University, P.M.B. 2000 Owerri, Nigeria.
E-mail: viconjoku@yahoo.com

MATERIALS AND METHODS

Preparation of Cocoa Pod Husk:

The cocoa pod husk was obtained from farms in Bendeghe-Afi, Cross River State, Nigeria, where they are generated as primary agricultural waste. These were extensively washed to remove dirt and other particulate matter that might interact with sorbed metal ions and then cut into chips of about 2 cm x 2 cm. These were dried in an oven at 110 °C and ground to powder and sieved with a mesh to maximum particle size of 0.25 mm. The uniform material produced was stored in air-tight, moisture-free containers and subsequently used for biosorption studies. The percentage proximate composition of the husk on dry weight basis was determined according to the methods outlined by Adomako (1972).

Preparation of Metal Solutions:

Analytical grade chemicals were used throughout the study. Stock solutions of Pb²⁺ and Cu²⁺ were prepared from lead nitrate (Pb(NO₃)₂) and copper nitrate (Cu(NO₃)₂) respectively using deionized water. In each case, stock solution of 1000 mg dm⁻³ was prepared and from these, fresh dilutions were made to the needed concentration using deionized water to obtain working solutions for specific biosorption studies. Nitrate salts were preferred to facilitate solubilization and to eliminate metal precipitation often associated with opposing anions (Ma and Tobin, 2004).

Biosorption Experiments:

Batch biosorption experiments were conducted for each metal by contacting 0.5 g of biosorbent with 0.1 dm³ solutions containing metal ions of desired concentrations at 30 °C and fixed pH values. The suspensions were then placed in a waterbath shaker (Kottermann 3392) at 150 revs min⁻¹ for a period corresponding to the desired contact time to achieve equilibrium. After this, the suspensions were passed through filter papers and the resultant filtrates were analyzed to determine the concentration of the residual metal ions using atomic absorption spectrophotometry (AAS; Unicam Solar 969). The percent sorption of metal ions onto cocoa pod husk was calculated for each sample using the following expression:

$$\% \text{ sorption} = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i is the initial metal ion concentration in mg dm⁻³ and C_e is the equilibrium metal ion concentration in mg dm⁻³.

RESULTS AND DISCUSSION

Proximate Composition of Cocoa Pod Husk:

The percentage proximate composition of cocoa pod husk on dry weight basis as determined are presented in Table 1 and shows that cocoa pod husk is a lignocellulosic fibre.

Biosorption Kinetics:

Batch biosorption kinetics tests were performed by collecting 0.02 dm³ of each sample at 0, 5, 15, 30, 60, 90, 120, 150 and 180 min. Initial metal ion concentrations of 80 mg dm⁻³ for the two metal ions studied, cocoa pod husk concentration of 5 g dm⁻³ and temperature of 30 °C were maintained. Fig. 1 shows the plots of the percent sorption of metal ions biosorbed (mg g⁻¹) versus contact time, for Pb²⁺ and Cu²⁺ ions. Metal uptake was rapid for both Pb²⁺ and Cu²⁺ ions for the first 30 min and thereafter proceeded at a slower rate and finally attained equilibrium implying saturation of the biosorbent at about 120 min. The equilibrium biosorption time for the batch experiments were thus fixed at 150 min. The biosorption capacity of cocoa pod husk at equilibrium was 13.76 and 11.58 mg g⁻¹ for Pb²⁺ and Cu²⁺ ions respectively.

According to Low and Lee (1990), the initial sorption of metal ions could be attributed to ion exchange of the surface functional groups on the biosorbent, followed by a gradual uptake of metal ions on inner surfaces of the biosorbent. The higher sorption capacity observed for Pb²⁺ ion could be attributed to its smaller hydrated radius (187 pm) compared to that of Cu²⁺ ion (210 pm), which increases its accessibility to the sorption active sites (Tondi *et al.*, 2009).

Table 1: Proximate composition of cocoa pod husk.

Moisture Content (%)	Crude Protein (%)	Ash Content (%)	Fat Content (%)	Crude Fibre (%)	Carbohydrate (by difference) (%)	Crude Fibre (59.34%)		
						Lignin (%)	Cellulose (%)	Hemicellulose (%)
10.50	2.09	9.02	1.53	59.34	17.52	24.24	26.38	8.72

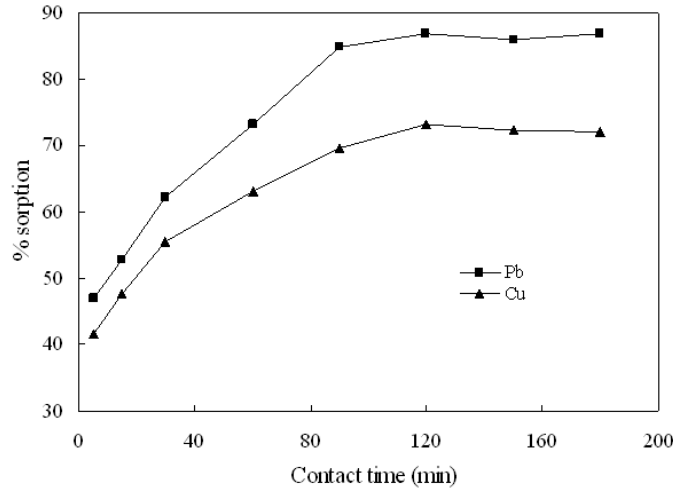


Fig. 1: Effect of contact time on percent sorption of Pb(II) and Cu(II) ions onto cocoa pod husk.

The transient behaviour of the metal sorption process was analysed by fitting the data obtained after the pseudo-first- and pseudo-second-order kinetic models. This is on the assumptions that sorption is a pseudo chemical reaction and that the measured metal concentrations are equal to cell surface concentrations (Chojnacka, 2005). Sorption rate could then be determined by the first- and second-order reaction rate equations. The two sorption kinetic models are based on the Ritchie equation (Eq. 2), where a number of surface sites, n , are occupied by each metal ion (Vilar *et al.*, 2006).

$$r_{ads} = \frac{dq}{dt} = k_n (q_e - q)^n \tag{2}$$

where r_{ads} is the rate of biosorption and k_n is the associated rate constant.

Lagergren Pseudo-First-Order Kinetics:

The pseudo-first-order kinetic model has been widely used to predict metal ion sorption kinetics and is given by (Sivaraj *et al.*, 2001):

$$\frac{dq}{dt} = k_1 (q_e - q) \tag{3}$$

where q_e (mg g^{-1}) is the solid phase concentration of the metal ions at equilibrium, q (mg g^{-1}) the average solid phase concentration of metal ions at contact time t (min) and k_1 (min^{-1}) is the pseudo-first-order rate constant. The simplified linear expression of first-order equation can be given by:

$$\log(q_e - q) = \log(q_e) - \frac{k_1 t}{2.303} \tag{4}$$

Thus the rate constant k_1 (min^{-1}) could be obtained from the plot of $\log(q_e - q)$ versus t as shown in Fig. 2. The values of k_1 are presented in Table 2 and shows a decrease in the order $\text{Pb}^{2+} > \text{Cu}^{2+}$.

Ho Pseudo-Second-Order Kinetics:

The kinetic data were further analysed using Ho's pseudo-second-order kinetics, which is represented by (Ho, 2003):

Table 2: Pseudo-first-order rate constants for sorption of Pb(II) and Cu(II) ions onto cocoa pod husk.

Metal ions	k_1 (min ⁻¹)	R ²	S.D.
Pb(II)	0.0343	0.944	0.516
Cu(II)	0.0212	0.952	0.612

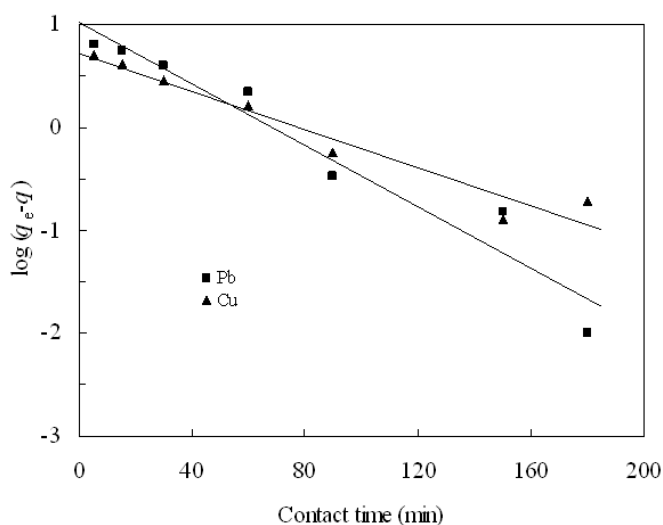


Fig. 2: Pseudo-first-order kinetics for the sorption of Pb(II) and Cu(II) ions onto cocoa pod husk.

$$\frac{dq}{dt} = k_2 (q_e - q)^2 \tag{5}$$

where k_2 (g mg⁻¹) is the pseudo-second-order rate constant. Pseudo-second-order rate model is based on the assumption that chemical sorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate is the limiting step (Ho and McKay, 1999). The linear form of the Ho pseudo-second-order equation is:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{6}$$

t/q should change linearly with time t if the sorption process obeys the pseudo-second-order rate equation. Thus, a plot of t/q versus t gives a straight line and the values of the constants k_2 (g mg⁻¹) and q_e (mg g⁻¹) can be calculated. Equation (5) can be inverted to obtain:

$$\frac{q}{t} = \frac{k_2 q_e^2}{1 + k_2 q_e t} = \frac{h}{1 + k_2 q_e t} \tag{7}$$

where h can be regarded as the initial sorption rate as q/t when t approaches 0. Hence,

$$h = k_2 q_e^2 \tag{8}$$

Fig. 3 shows the plots of t/q versus t . The initial sorption rate h , pseudo-second-order rate constant k_2 , amount of metal ions sorbed at equilibrium q_e , and the corresponding linear regression correlation coefficient R^2 values are given in Table 3. It was observed that the R^2 values in the case of the pseudo second-order were higher than those for the pseudo-second-order and this confirms that the sorption process follows a pseudo-second-order mechanism (Kumar and Porkodi, 2007). This is in line with the findings of Oo *et al.* (2009). Better data fit with the pseudo-second-order model implies a marked chemisorption contribution to the metal uptake process and a similar observation was reported by Ho (2003) for copper ions onto tree fern adsorbent. Chemical sorption can occur by the polar functional groups of lignin or cellulose, which include

Table 3: Pseudo-second-order rate constants for sorption of Pb(II) and Cu(II) ions onto cocoa pod husk.

Metal ions	k_2 (g mg ⁻¹)	h (mg g ⁻¹)	q_e predicted (mg g ⁻¹)	R ²	S.D.
Pb(II)	0.00654	1.42167	14.74926	0.9969	0.266
Cu(II)	0.00995	1.46864	12.15067	0.9980	0.256

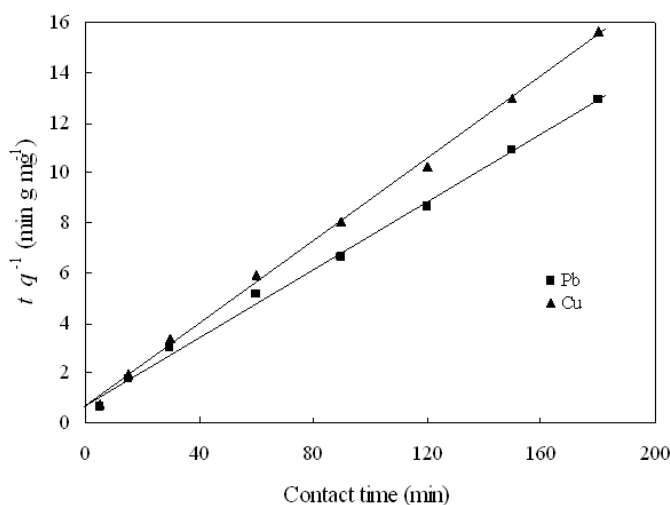


Fig. 3: Pseudo-second-order kinetics for the sorption of Pb(II) and Cu(II) ions onto cocoa pod husk.

alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers as chemical bonding agents (Vadivelan and Kumar, 2005). From Table 3, it was also observed that the predicted equilibrium sorption capacity q_e increased in the order $Cu^{2+} < Pb^{2+}$, while the pseudo-second-order rate constant k_2 increased in the opposite order.

Effect of Solution pH on Biosorption:

Solution pH is an important process parameter in sorption, since it is responsible for protonation of metal binding sites, metal speciation and degree of ionization in solution. The effects of pH on the amount of Pb^{2+} and Cu^{2+} ions biosorbed were analyzed over the pH range 1–7. The pH was adjusted using 0.1 M NaOH and 0.1 M HCl solutions.

Fig. 4 reveals that the biosorption capacity and hence percent sorption of cocoa pod husk increased sharply with pH from 1 to 5 attaining maximum values at pH 6, which seems to be most favourable for biosorption of Pb^{2+} and Cu^{2+} ions onto cocoa pod husk. The effect of solution pH on biosorption could be related to the active sites and also the chemistry of the solute in solution. The structure of cocoa pod husk is cellulose based, and the surface of cellulose in contact with water is negatively charged (Han *et al.*, 2006). Dissolved metal ions are positively charged and will undergo attraction on approaching the anionic husk structure. At lower pH, the overall surface charge on the adsorbent biosorbent will be relatively positive, which will inhibit the approach of positively charged metal cations, consequently reducing metal ion binding on the biosorbent surface. The H^+ ions compete effectively with the metal cations causing a decrease in biosorption capacity. As pH is raised, the biosorbent surface becomes increasingly negatively charged thereby supporting more metal cation uptake due to electrostatic forces of attraction. This is supported by the experimental data, which displays improved biosorption capacities at higher pH values until the optimum value. This is in accordance with the findings of Davis *et al.* (2000) that the rise in pH, usually results in an increase in the metal ion sorption but at the same time decreases its solubility. Similar results were obtained by Ho and Ofomaja (2006). The pH trend suggests ion exchange between H^+ and metal ions (represented as M^{2+}) at the surface of the biosorbent in the biosorption process. For a biosorbent having carboxyl functional groups, this has been shown by Goel *et al.* (2005) to correspond to:



Effect of Initial Concentration of Metal Ions:

Equilibrium experiments were carried out by contacting 0.5 g cocoa pod husk particles with metal ion solutions of initial concentrations ranging from 5–100 mg dm⁻³ under pre-determined optimized conditions of 150 min shaking time and pH 6. The experiments were performed at temperature of 30 °C. Fig. 5 shows the

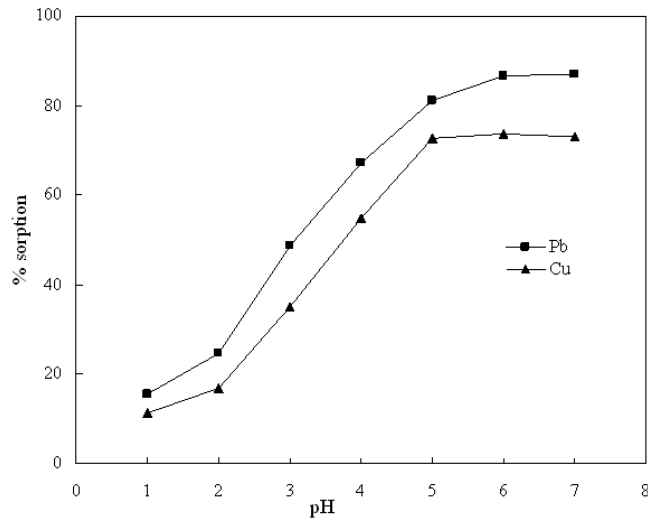


Fig. 4: Effect of pH on percent sorption of Pb(II) and Cu(II) ions onto cocoa pod husk.

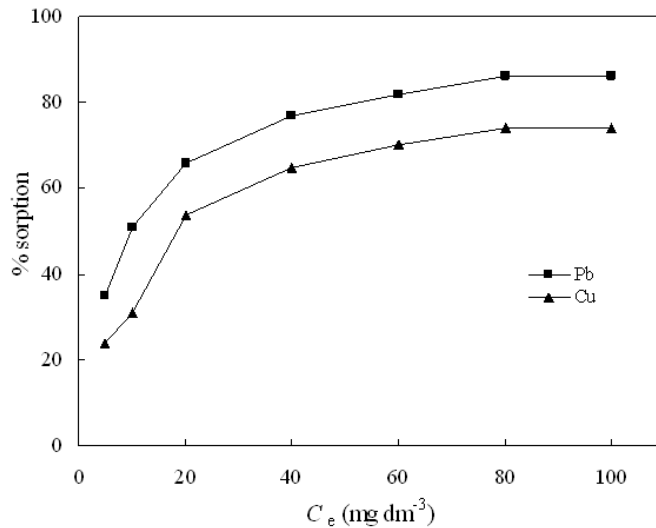


Fig. 5: Effect of initial concentration on percent sorption of Pb(II) and Cu(II) ions onto cocoa pod husk at 30 °C.

effect of the initial concentration of metal ions on the percent sorption of Pb^{2+} and Cu^{2+} ions by cocoa pod husk at 30 °C. The results show an increase in the biosorption capacity and hence percent sorption as the initial metal ion concentration increased. This could be due to the increase in the concentration gradient, which acts as a driving force (Han *et al.*, 2006). The percent sorption was optimized at about 80 mg dm⁻³, when equilibrium was attained. This could be attributable to the saturation of the available binding sites on the biomass, resulting from increased competition for the fixed number of binding sites on the biomass by more and more metal ions, leading to a reduction in the complexation of the metals with the biomass.

Thermodynamic Parameters:

Assuming, according to Henry’s law, that the activity coefficients are unity at low concentrations, the apparent equilibrium constant (K_c) of the biosorption can be defined as (Namasivayam and Ranganathan, 1993):

$$K'_c = \frac{C_{ad,e}}{C_e} \quad (10)$$

where $C_{ad,e}$ is the metal ion concentration on the biosorbent at equilibrium (mg dm^{-3}) and C_e is the equilibrium concentration of the metal ion in solution (mg dm^{-3}). The value of K'_c could be obtained using the lowest experimental metal ion concentration (Namasivayam and Ranganathan, 1993). The change in Gibbs free energy, ΔG° (kJ mol^{-1}) for the biosorption of Pb^{2+} and Cu^{2+} onto cocoa pod husk can then be calculated as follows:

$$\Delta G^\circ = -RT \ln K'_c \quad (11)$$

where T is the absolute temperature (K) and R the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$).

Table 4 shows the values of K'_c and ΔG° obtained for this study. The higher K'_c value for the biosorption of Pb^{2+} suggests its higher rate of biosorption onto cocoa pod husk biomass compared to Cu^{2+} , while the negative ΔG° values indicate that the biosorption process was spontaneous.

Table 4: Thermodynamic parameters for the biosorption of Pb(II) and Cu(II) ions onto cocoa pod husk at 30 °C.

Metal ion	K'_c	ΔG° (kJ mol^{-1})
Pb^{2+}	3.348	-3.0439
Cu^{2+}	1.851	-1.5512

The biosorption mean free energy (E) represents the mean free energy of sorption per molecule of the sorbate when it is transferred to the surface of the sorbent from infinity and it is calculated from the following equation (Khan *et al.*, 1995):

$$E = (-2K_E)^{-1/2} \quad (12)$$

where K_E is a constant related to the biosorption energy ($\text{mol}^2 \text{ kJ}^{-2}$) and calculated using the Dubinin-Radushkevich (D-R) equation:

$$\ln q_e = \ln q_m - K_E \varepsilon^2 \quad (13)$$

where q_m is the monolayer capacity (mg g^{-1}) and ε is the Polanyi potential, given by the expression:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (14)$$

K_E and q_m can be calculated from the slope and intercept respectively of the plot of $\ln q_e$ versus ε^2 as shown in Fig. 6. Table 5 shows the values of K_E , q_m and E obtained. The value of E is very useful in predicting the type of biosorption. If the value is less than 8 kJ mol^{-1} , then the sorption is physical in nature, if it is between 8 and 16 kJ mol^{-1} , then the sorption is of the ion exchange type and if it is higher than 16 kJ mol^{-1} , the sorption is due to ion exchange as well as other chemical processes (Onyango *et al.*, 2004). The value of E in this study was found to be greater than 16 kJ mol^{-1} and this suggests that the biosorption of Pb^{2+} and Cu^{2+} occurs via ion exchange mechanism as well as other chemical processes.

Effect of NaCl and CaCl₂ Concentrations on Biosorption:

Industrial effluents and wastewaters contain a variety of metal ions as well as suspended and dissolved compounds which can be considered as impurities. Cations such as Na^+ , K^+ , Cu^{2+} , Ca^{2+} and Cr^{3+} are the most common metal ions present in wastewater (Correia *et al.*, 1994). The presence of these ions leads to high ionic strength, which may significantly affect the performance of the biosorption process for specific target ions (Greene *et al.*, 2000). Accordingly, the effect of salt concentration (ionic strength) on the percent sorption or amount of metal ion sorbed by cocoa pod husk was analyzed by incorporation of NaCl or CaCl_2 . The concentration of these ions was varied in the range 0 to 0.20 mol dm^{-3} with other experimental conditions maintained at optimum level. The results presented in Fig. 7 and 8 show that for both salts studied, sorption potential decreased with increase in ionic strength.

Table 5: Dubinin-Radushkevich parameters for the biosorption of Pb(II) and Cu(II) onto cocoa pod husk.

Metal ion	K_F ($\text{mol}^2 \text{kJ}^{-2}$)	q_m (mg g^{-1})	E (kJ mol^{-1})	R^2
Pb(II)	-0.0003	20.10	24.50	0.9591
Cu(II)	-0.0003	16.56	24.50	0.9647

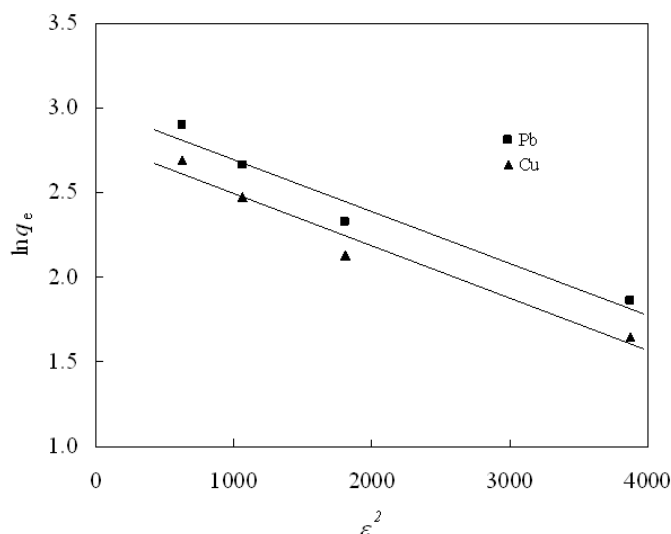


Fig. 6: Dubinin-Radushkevich plots for Pb(II) and Cu(II) sorption onto cocoa pod husk at 30 °C.

Increased ionic strength led to a decrease in the sorption potential of the biosorbent for the target metal ions. The adverse effect of ionic strength on metal ion sorption supports the earlier proposed ion exchange mechanisms, in which case the impurity ions (Na^+ and Ca^{2+}) compete for binding sites with the target metal ions. It is also possible that as the ionic strength increases, the activity (effective concentration) of metal ions and the active sites decrease, so the adsorption capacity of metal ions onto the biosorbent decreases. Some authors have reported similar results for the sorption of heavy metals onto different biosorbents (Dahiya *et al.*, 2008; Donmez and Aksu, 2002).

From Fig. 7 and 8, it could also be observed that the effect of Ca^{2+} on the biosorption of the target ions is more deleterious than that of Na^+ . This could be attributed to the fact that Ca^{2+} has more contribution to ionic strength. In addition, the divalent Ca^{2+} ion has a greater affinity and binding ability to the active sites and as such can compete more vigorously for such binding sites than the monovalent Na^+ ions. But even at 0.20 mol dm^{-3} of both salts, cocoa pod husk still exhibited a high percent sorption for the target metal ions hence could be used to effectively remove metal ions from aqueous solutions with high impurity ion concentration.

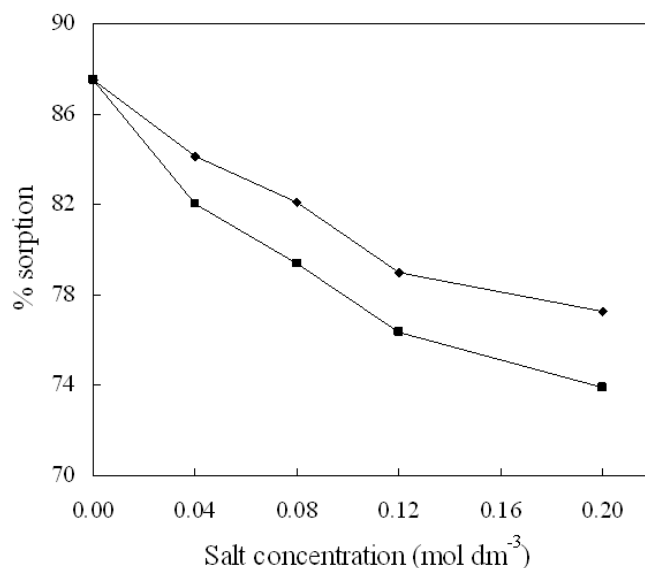


Fig. 7: Effect of NaCl (◆) and CaCl_2 (■) on percent sorption of Pb(II) onto cocoa pod husk.

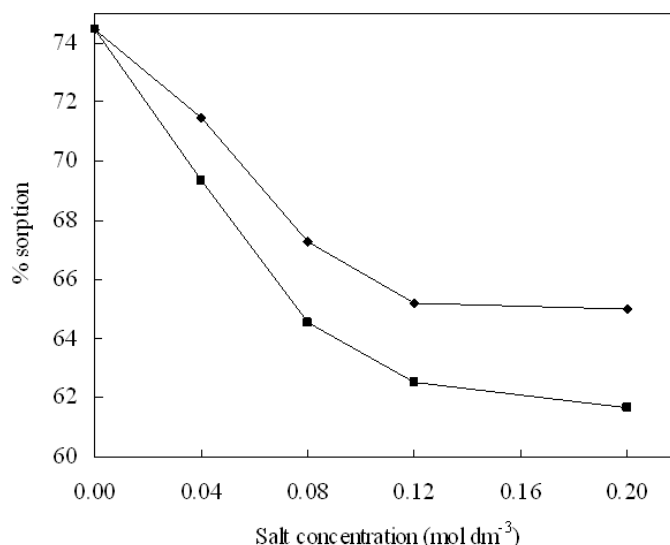


Fig. 8: Effect of NaCl (♦) and CaCl₂ (■) on percent sorption of Cu(II) onto cocoa pod husk.

Conclusion:

Cocoa pod husk was found to be a low cost biosorbent for Pb²⁺ and Cu²⁺ ions from aqueous solutions. The percent sorption increased with contact time and the pseudo-second-order expression better predicted the sorption kinetics of the metal ions onto cocoa pod husk. The percent sorption increased with pH and decreased with increasing ionic strength suggesting the involvement of ion exchange mechanism. However, the effect of Ca²⁺ on the biosorption of Pb²⁺ and Cu²⁺ was more pronounced than that of Na⁺. Cocoa pod husk exhibited high percent sorption of metal ions even at high impurity ion concentrations.

ACKNOWLEDGMENT

The first author wishes to acknowledge the award of USM-TWAS postdoctoral fellowship (2009) in aid for research.

REFERENCES

Adomako, D., 1972. Cocoa pod husk pectin. *Phytochemistry*, 11: 1145-1148.

Benhammou, A., A. Yaacoubi, L. Nibou and B. Tanouti, 2005. Adsorption of metal ions onto Moroccan stevensite: kinetic and isotherm studies. *J. Colloid Interface Sci.*, 282: 320-326.

Chojnacka, K., 2005. Biosorption of Cr(III) ions by eggshells. *J. Hazard. Mater.*, 121: 167-173.

Cimino, G., A. Passerini and G. Toscano, 2000. Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. *Water Res.*, 34: 2955-2962.

Correia, V.M., T. Stephenson and S.J. Judd, 1994. Characterisation of textile wastewaters – a review. *Environ. Technol.*, 15: 917-927.

Dahiya, S., R.M. Tripathi and A.G. Hedge, 2008. Biosorption of lead and copper from aqueous solutions by pre-treated crab and arca shell biomass. *Bioresour. Technol.*, 99: 179-187.

Davis, T.A., B. Volesky and R.H.S.F. Vieira, 2000. Sargassum seaweed as biosorbent for heavy metals. *Water Res.*, 34: 4270-4278.

Donmez, G., Z. Aksu, 2002. Removal of chromium (VI) from saline wastewaters by *Dunaliella* species. *Process Biochem.*, 38: 751-762.

Goel, J., K. Kadirvelu, C. Rajagopal and K. Garg, 2005. Investigation of adsorption of lead, mercury and nickel from aqueous solutions onto carbon aerogel. *J. Chem. Technol. Biotechnol.*, 80: 469-476.

Greene, B., R. McPherson and D. Darvall, 2000. Algal sorbents for selective metal ions recovery. In metal speciation, separation and recovery, Eds., Patterson, J.W. and R. Pasino, Chelsea, MI, USA: Lewis Publishers, pp: 315-338.

Gupta, S. and B.V. Babu, 2009. Utilization of waste product (tamarind seeds) for the removal of Cr(VI) from aqueous solutions: Equilibrium, kinetics, and regeneration studies. *J. Environ. Manage.*, 90: 3013-3022.

- Han, R., J. Zhang, W. Zou, H. Xiao, J. Shi and H. Liu, 2006. Biosorption of copper(II) and lead(II) from aqueous solution by chaff in a fixed-bed column. *J. Hazard. Mater.*, 133: 262-268.
- Ho, Y.S., 2003. Removal of copper ions from aqueous solution by tree fern. *Water Res.*, 37: 2323-2330.
- Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. *Process Biochem.*, 76: 451-465.
- Ho, Y.S. and A.E. Ofomaja, 2006. Pseudo-second-order model for lead ion sorption from aqueous solutions onto palm kernel fiber. *J. Hazard. Mater.*, 129: 137-142.
- Jain, M., V.K. Garg and K. Kadirvelu, 2010. Adsorption of hexavalent chromium from aqueous medium onto carbonaceous adsorbents prepared from waste biomass. *J. Environ. Manage.*, 91: 949-957.
- Khan, S.A., Riaz-ur-Rehman and M.A. Khan, 1995. Adsorption of chromium (III), chromium (VI) and silver (I) on bentonite. *Waste Manage.*, 15: 271-282.
- Kumar, K.V. and K. Porkodi, 2007. Mass transfer, kinetics and equilibrium studies for the biosorption of methylene blue using *Paspalum notatum*. *J. Hazard. Mater.*, 146: 214-226.
- Low, K.S. and C.K. Lee, 1990. The removal of cationic dyes using coconut husk as an adsorbent. *Pertanika*, 13: 221-228.
- Ma, W. and J.M. Tobin, 2004. Determination and modelling of effects of pH on peat biosorption of chromium, copper and cadmium. *Biochem. Engineering J.*, 18: 33-40.
- Namasivayam, C. and K. Ranganathan, 1993. Waste Fe(III)/Cr(III) hydroxide as adsorbent for the removal of Cr(VI) from aqueous solution and chromium plating industry wastewater. *Environ. Pollut.*, 82: 255-261.
- Ngah, W.S.W. and S. Fatinathan, 2010. Adsorption characterization of Pb(II) and Cu(II) ions onto chitosan-tripolyphosphate beads: Kinetic, equilibrium and thermodynamic studies. *J. Environ. Manage.*, 91: 958-969.
- Njoku, V.O., E.E. Oguzie, C. Obi, O.S. Bello and A.A. Ayuk, 2011. Adsorption of Copper(II) and Lead(II) from Aqueous Solutions onto a Nigerian Natural Clay. *Aust. J. Basic Appl. Sci.*, 5: 346-353.
- Ofomaja, A.E., 2010. Equilibrium studies of copper ion adsorption onto palm kernel fibre. *J. Environ. Manage.*, 91: 1491-1499.
- Ofomaja, A.E., E.B. Naidoo and S.J. Modise, 2010. Biosorption of copper(II) and lead(II) onto potassium hydroxide treated pine cone powder. *J. Environ. Manage.*, 91: 1674-1685.
- Okieimen, F.E. and V.U. Onyenkpa, 1989. Removal of heavy metal ions from aqueous solutions with melon (*Citrullus vulgaris*) seed husks. *Biol. Waste*, 29: 11-16.
- Onyango, M.S., Y. Kojima, O. Aoyi, E.C. Bernardo, H. Matsuda, 2004. Adsorption equilibrium modeling and solution chemistry dependence of fluoride removal from water by trivalent-cation-exchanged zeolite F-9. *J. Colloid Interface Sci.*, 279: 341-350.
- Oo, C.W., M.J. Kassim and A. Pizzi, 2009. Characterization and performance of *Rhizophora apiculata* mangrove polyflavonoid tannins in the adsorption of copper(II) and lead(II). *Ind. Crops Prod.*, 30: 152-161.
- Saeed, A. and M. Iqbal, 2003. Bioremoval of cadmium from aqueous solution by blackgram husk (*Cicer arietinum*). *Water Res.*, 37: 3472-3480.
- Salim, R., M. Al-Subu and E. Dawod, 2008. Efficiency of removal of cadmium from aqueous solutions by plant leaves and the effects of interaction of combinations of leaves on their removal efficiency. *J. Environ. Manage.*, 87: 521-532.
- Sawalha, M.F., J.R. Peralta-Videa, B. Sanchez-Salcido and J.L. Gardea-Torresdey, 2009. Sorption of hazardous metals from single and multi-element solutions by saltbush biomass in batch and continuous mode: Interference of calcium and magnesium in batch mode. *J. Environ. Manage.*, 90: 1213-1218.
- Sivaraj, R., C. Namasivayam and K. Kadirvelu, 2001. Orange peel as an adsorbent in the removal of Acid violet 17 (acid dye) from aqueous solutions. *Waste Manage.*, 21: 105-110.
- Sousa, F.W., A.G. Oliveira, J.P. Ribeiro, M.F. Rosa, D. Keukeleire and R.F. Nascimento, 2010. Green coconut shells applied as adsorbent for removal of toxic metal ions using fixed-bed column technology. *J. Environ. Manage.*, 91: 1634-1640.
- Tondi, G., C.W. Oo, A. Pizzi, A. Trosa and M.F. Thevenon, 2009. Metal adsorption of tannin based rigid foams. *Ind. Crops Prod.*, 29: 336-340.
- Vadivelan, V. and K.V. Kumar, 2005. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *J. Colloid Interface Sci.*, 286: 90-100.
- Vilar, V.J.P., C.M.S. Botelho and R.A.R. Boaventura, 2006. Equilibrium and kinetic modeling of Cd(II) biosorption by algae *Gelidium* and agar extraction algal waste. *Water Res.*, 40: 291-302.
- Wang, X.S. and Y. Qin, 2005. Equilibrium sorption isotherms for of Cu²⁺ on rice bran. *Process Biochem.*, 40: 677-680.