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Biosorption of Lead Ions on Biosorbent Prepared from Plumb Shells (*Spondias mombin*): Kinetics and Equilibrium Studies

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Abstract. Plumb shell was used to prepare an adsorbent for biosorption of lead ions in aqueous solution at 25 °C. The adsorption capacity of the adsorbent at equilibrium was found to increase from 2.8 to 49.0 mg/g with an increase in the initial lead ion concentration from 50 to 200 mg/L. Using the equilibrium and kinetics studies, isotherm of the lead ions on the biosorbent was determined and correlated with common isotherm equations. The equilibrium data for lead ion adsorption fitted well into the Freundlich equation, with a value of 0.76 ($R^2 = 0.9$), with distribution coefficient of 4.90. The biosorption of lead ions on the adsorbent from plumb shells could best be described by the pseudo-second-order equation. The kinetic parameters of this best-fit model were calculated and discussed.

Keywords: plumb shell, biosorption, lead ions, isotherm, kinetics

Introduction

The presence of heavy metal ions in the environment has been a matter of major concern due to their toxicity to human life. Unlike organic pollutants, heavy metal ions do not degrade into harmless end products (El-Nady and Atta, 1996). Toxic metal compounds not only contaminate seas, lakes, ponds and reservoirs but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow (Igwe and Abia, 2006). Although some heavy metals are necessary for the growth of plants, but above the permissible levels, bioaccumulation of heavy metals is poisonous to both plants and animals as well as to man through their consumption (Igwe and Abia, 2006). Therefore, the treatment of effluent containing such metal ions is important due to their impact on human health through the receiving waters.

The conventional methods used for the removal of heavy metals from aqueous solutions include chemical precipitation, ion exchange, electrodialysis, membrane separation, reverse osmosis, adsorption on activated carbon, oxidation and reduction, solvent extraction, fixation or cementation. These methods are economically unfavourable or technically complicated and are used only in special cases of wastewater treatment (Kratochvil and Volesky, 1998). The search for new and effective technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption based on metal binding capacities of various biological materials at little or no cost (Babrinde *et al*., 2006). Biosorption of heavy metals from aqueous solutions is a relatively new technology for the treatment of industrial wastewater. The major advantages of biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials (Volesky, 2001). A wide range of commercial sorbents including chelating resins and activated carbon are available for metal sorption, but they are relatively expensive. In recent years, numerous low cost natural materials have been proposed as potential biosorbents. Biosorption is a process that utilizes biological materials as adsorbents, and has been studied by several researchers as an alternative technique to conventional methods for heavy metal removal from wastewater (Jeon *et al*., 2001; Volesky, 2001; Yu and Kaewsam, 1999).

Diffusion of metals from the bulk solution to active sites of biosorbent occurs predominantly by passive transport mechanisms (Veglio and Beolchini, 1997). Various functional groups such as carboxyl, hydroxyl, amino and phosphate existing on the cell wall of biosorbents can bind the heavy metals (Avery and Tobin, 1992). Living or dead biomass can be used to remove metals, but maintaining a living biomass during metal biosorption is difficult because it requires continuous supply of nutrients and toxicity of microorganism might take place. On the other hand, the use of dead biomass can avoid these problems and the used cells can be easily regenerated (Bai and Abraham, 2001). A variety of biomaterials such as bacteria, yeast, algae and fungi have been successfully used as biosorbent for the removal of heavy metals (Volesky, 2001). These raw materials are renewable and potentially less expensive as well. Their utilization in the removal of metal ions

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will not only help in reducing exposure of man to such heavy metal ions, but also solve littering problems which these shells invariably constitute in some areas. The present study was undertaken to evaluate the efficiency of a biosorption process using plumb shell as biosorbent in the removal of lead ions from aqueous solutions.

Materials and Methods

Lead ions. Aqueous solutions of lead ions of different concentrations were prepared from lead nitrate (KNO_3) obtained from British Drug House, London (BDH). These were used as adsorbate and were not purified prior to use. Distilled water was employed twice for preparing all the solutions and reagents.

Preparation and characterization of biosorbent. The plumb fruit shells (*Spondias mombin*), used as the adsorbent, were obtained from the fruit tree growing in the premises of the University of Agriculture Abeokuta, Ogun State, Nigeria. The shells were removed from the fruits, rinsed with distilled water, sun-dried and crushed and pulverized to powder form. The powder was washed thoroughly with distilled water and dried in the oven for 2 h at 100 °C (Popuri *et al*., 2007).

Batch equilibrium studies. Adsorption isotherms were performed in a set of 43 Erlenmeyer flasks (100 mL) wherein the solutions of lead ions (50 mL) with different initial concentrations (50-200 mg/dm^3) were placed. Equal mass of 0.2 g of the biosorbent (particle size 150 µm) prepared from plumb shell was added to lead ion solutions and kept on an isothermal shaker (orbital shaker) at 25 ± 1 °C for 48 h to reach equilibrium of the solid-solution mixture. Similar procedure was followed for another set of Erlenmeyer flask containing the same lead ion concentration without adsorbate to be used as a control. The pH was adjusted to 7.0 by adding few drops of diluted hydrochloric acid or sodium hydroxide (0.1 mol/dm^3). The flasks were then removed from the shaker and the final concentrations of lead ions in the solutions were determined. The concentration of lead ions in the supernatant solution after and before adsorption was determined using an atomic absorption spectrophotometer model 200 VGP, from Buck Scientific with the range 200-710 nm. The samples were filtered prior to analysis in order to minimize interference of the adsorbent particles with the analysis. Each experiment was duplicated under identical conditions. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{1}$$

where:

C_o and C_e (mg/dm^3) are the liquid-phase concentrations of lead ion at initial and equilibrium stage, respectively,
V is the volume of the solution (L) and
W is the mass of dry adsorbent used (g).

Batch kinetic studies. The procedures of kinetic experiments were basically identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals, and the concentrations of lead ion were similarly measured. The amount of adsorption q_t (mg/g), at time t, was calculated by:

$$q_t = \frac{(C_o - C_t)V}{W} \tag{2}$$

where:

C_o and C_t (mg/dm^3) are the liquid-phase concentrations of lead ion at initial and any time t, respectively,
V is the volume of the solution (L) and
W is the mass of dry adsorbent used (g).

Results and Discussion

Effect of agitation time and concentration of lead ions on biosorption. Ten contact time experiments for lead ion have been carried out at different initial concentrations (50-200 mg/dm^3) and at temperature of 25 °C. Figure 1 shows that the contact time necessary for lead ions with initial concentrations of 50-200 mg/dm^3 to reach equilibrium is about 1 h. As can be seen from Fig. 1, the amount of the lead ion biosorbed onto plumb shell increases with time and, at some point in time, reaches a constant value beyond which no more ions are

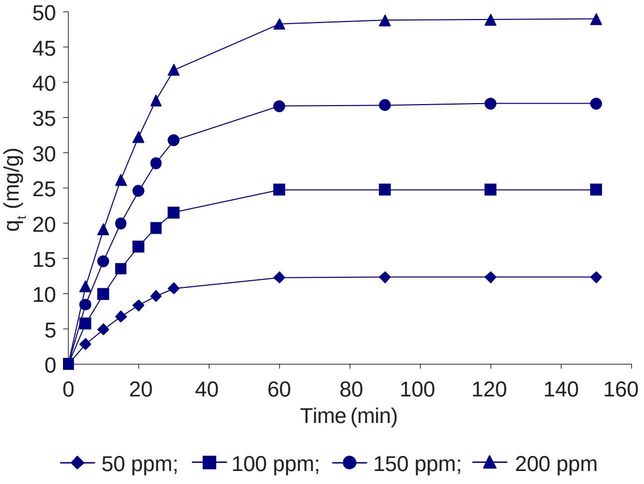

Fig. 1. The variation of adsorption capacity with biosorption time at various concentrations of lead ions at 25 °C (pH 7, W = 0.2 g).

removed from the solution. At this point, the amount of the lead ions desorbing from the adsorbent is in a state of dynamic equilibrium with the amount of the lead ions being biosorbed onto the plumb shell. The time required to attain this state of equilibrium is termed the equilibrium time, and the amount of lead ions adsorbed at the equilibrium time reflects the maximum adsorption capacity of the adsorbent under those operating conditions.

It was observed that the adsorption capacity at equilibrium increased from 2.8 to 49.0 mg/g with an increase in the initial lead ion concentration from 50 to 200 mg/L. It is evident from the figure, that the biosorbent prepared from plumb shell is efficient to adsorb lead ions from aqueous solution; this is because, the process attains the equilibrium gradually.

Adsorption kinetics. The rate constant of adsorption was determined from the pseudo first-order equation given by Lagergren (1898):

$$1n(q_e - q_t) = 1n\ q_e - k_1 t \tag{3}$$

where:

q_e and q_t are the amounts of lead ion biosorbed (mg/g) at equilibrium and at time t (min), respectively, and
k_1 the rate constant of adsorption (per hour).

Values of k_1 were calculated from the plots of $\ln(q_e - q_t)$ *vs* t for different concentrations of lead ions. If the correlation coefficient values are higher than 0.90, the experimental q_e values also agree slightly (difference of about 4.7%) with the calculated ones, obtained from the linear plots (Table 1). This shows that the biosorption of lead ions onto plumb shell is first-order kinetics.

On the other hand, a pseudo second-order equation based on equilibrium adsorption (Malik, 2004) is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_t}\right)t \tag{4}$$

where:

k_2 (g/mg/s) is the rate constant of the second-order adsorption.

If second-order kinetics is applicable, the plot of t/q *vs* t should show a linear relationship. There is no need to know any parameter beforehand and q_e and k_2 can be determined from the slope and intercept of the plot. Also, this procedure is more likely to predict the behaviour over the whole range of adsorption. The linear plots of t/q *vs* t (Fig. 2) show a good agreement between experimental and calculated q_e values (Table 1).

The correlation coefficients for the second-order kinetic model are about 0.99 indicating the applicability of this kinetic equation and the second-order nature of the biosorption process of lead ion on the adsorbent.

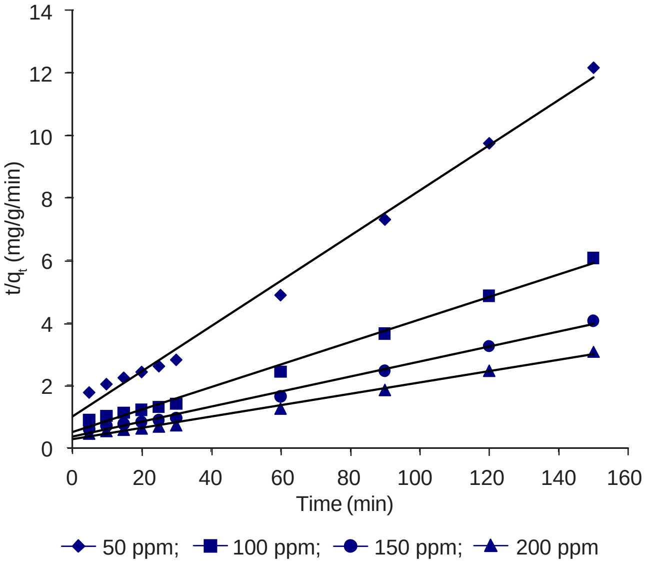

Fig. 2. Pseudo-second order kinetics for the biosorption of lead ions on plumb shell at 25 °C.

Table 1. Comparison of the pseudo first- and second-order adsorption rate constants and calculated and experimental q_e values for different initial concentrations of lead ions

Initial		First order kinetic model				Second order kinetic model			
concentration (mg/L)	$Q_{e\ exp}$ (mg/g)	k_1 (min^{-1})	$q_{e\ cal}$ (mg/g)	R^2	SSE (%)	k_2 (g/mg/min)	$q_{e\ cal}$ (mg/g)	R^2	SSE (%)
50	12.34	0.077	14.25	0.98	0.60	0.0053	13.83	0.99	0.48
100	24.77	0.082	26.60	0.90	0.57	0.0026	27.78	0.99	0.95
150	37.00	0.061	37.12	0.98	0.037	0.0017	41.49	0.99	1.42
200	49.00	0.058	46.82	0.98	0.69	0.0012	55.25	0.99	1.98

SSE = sum of square error.

Test of kinetic models. Besides the value of R^2, the applicability of both kinetic models were verified through the sum of error squares (SSE, %). The biosorption kinetics of lead ion on adsorbent prepared from plumb shell was tested at different initial concentrations. The validity of each model was determined by the sum of error squares (SSE, %) given by:

$$\text{SSE}\,(\%) = \sqrt{\frac{\Sigma\,(q_{e,exp} - q_{e,cal})^2}{N}} \tag{5}$$

where:

N is the number of data points.

The higher is the value of R^2 and the lower is the value of SSE; the better will be the goodness of fit.

Table 1 lists the calculated results. It was found that the biosorption kinetics of lead ion on adsorbent prepared from plumb shell can be best described by the secon-order kinetic model.

Adsorption isotherms. The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of equilibrium adsorption data, by fitting them to different isotherm models, is an important step to find the suitable model that can be used for design purpose (Haghseresht and Lu, 1998). Adsorption isotherm study was carried out on two well-known isotherms, Langmuir and Freundlich. Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface (Fytianos *et al*., 2003), while, Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in Langmuir equation varies as a function of the surface coverage (Fytianos *et al*., 2003). The applicability of the isotherm equation was compared by judging the correlation coefficients, R^2.

Langmuir isotherm. The linear form of Langmuir's isotherm model is given by the following equation:

$$C_e/Q_e = 1/Q_o b + (1/Q_o)C_e \tag{6}$$

where:

C_e is the equilibrium concentration of the adsorbate (lead ion) (mg/L),

q_e, the amount of adsorbate adsorbed per unit mass of adsorbate (mg/g) and

Q_o and b are Langmuir constants related to monolayer adsorption capacity and affinity of adsorbent towards adsorbate, respectively.

When c_e/q_e was plotted against c_e, straight line with slope $1/q_o$ was obtained (Fig. 3), indicating that the biosorption of the lead ions onto plumb shell follows the Langmuir isotherm. The Langmuir constants 'b' and 'q_o' were calculated from this isotherm and their values are given in Table 2.

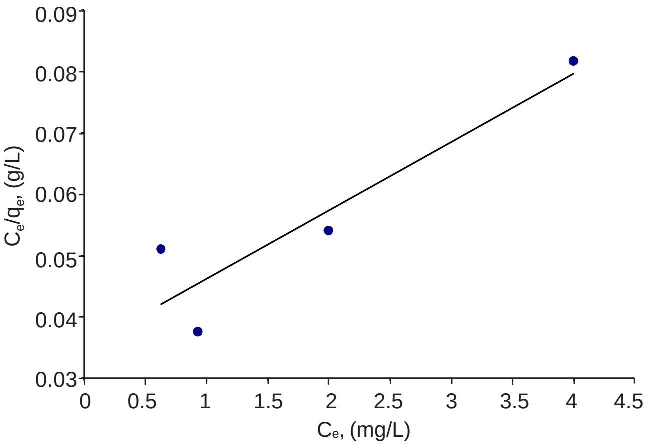

Fig. 3. Langmuir adsorption isotherm for the biosorption of lead ions on plumb shell at 25 °C.

Table 2. Langmuir and Freundlich isotherm constants for lead ions at 25 °C

Langmuir isotherm	
Qo (mg/g)	28.57
b (L/mg)	0.31
R^2	0.85
R_L	0.016
Freundlich isotherm	
$1/n$	0.76
K_F [(mg/g) (1/mg)$^{1/n}$]	4.90
R^2	0.90

Conformation of the experimental data to Langmuir isotherm model indicates the homogeneous nature of plumb shell surface, i.e., each lead ion molecule/plumb shell biosorption has equal adsorption activation energy. The results also demonstrate the formation of monolayer coverage of lead ion at the surface of plumb shell. Similar observations were reported on the biosorption of chromium ion on tamarind (*Tamarindus indica*) fruit shell (Popuri *at al*., 2007).

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless equilibrium parameter

(R_L) (Webi and Chakarvort, 1974), which is defined by:

$$R_L = {}^{1}/_{(1 + bC_o)} \tag{7}$$

where:

b is the Langmuir constant and
C_o the highest dye concentration (mg/L).

The value of R_L indicates the type of the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$). Value of R_L was found to be 0.016 which confirmed that the biosorbent prepared from the plumb shell is favourable for biosorption of lead ion under conditions used in this study.

Freundlich isotherm. The well-known logarithmic form of Freundlich model is given by the following equation:

$$\log q_e = \log K_F + ({}^{1}/_{n})\log C_e \tag{8}$$

where:

q_e is the amount adsorbed at equilibrium (mg/g),
C_e the equilibrium concentration of the adsorbate (lead ion) and
K_F and n are Freundlich constants, n giving an indication of how favourable is the adsorption process and K_F [(mg/g) $(1/\mathrm{mg})^n$] is the adsorption capacity of the adsorbent.

K_F can be defined as the adsorption or distribution coefficient and represents the quantity of lead ion adsorbed onto biosorbent (plumb shell) for a unit equilibrium concentration.

The slope $1/n$ ranging between 0 and 1 is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero (Haghseresht and Lu, 1998). Value of $1/n$ below one indicates a normal Langmuir isotherm while above one is indicative of cooperative adsorption (Fytianos *et al.*, 2003). The plot of log q_e *versus* log C_e gives straight lines with slope '$1/n$' (Fig. 4), which shows that the biosorption of lead ions also follows the Freundlich isotherm. Accordingly, Freundlich constants (K_F and n) were calculated and recorded in Table 2.

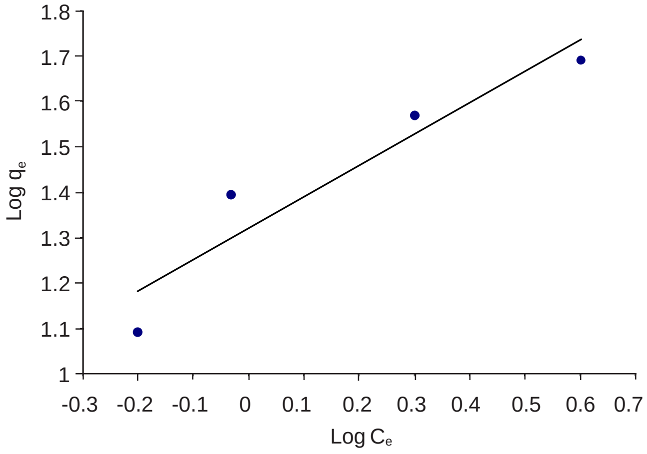

Fig. 4. Freundlich adsorption isotherm for the biosorption of lead ions on plumb shell at 25 °C.

Table 2 shows the values of the parameters of the two isotherms and the related correlation coefficients. As seen in Table 2, the Freundlich model yields a somewhat better fit ($R^2 = 0.90$) than the Langmuir model ($R^2 = 0.85$). The value of $1/n$ is 0.76 (Table 2) which indicates favourable adsorption (Adamson, 2001).

Conclusion

The present investigation showed that plumb shell can be effectively used as raw material for the preparation of biosorbent for the removal of lead ions from aqueous solutions over a wide range of concentrations. Biosorption behaviour is described by Freundlich type isotherm. Kinetic data follow pseudo second-order kinetic model. The value of the maximum adsorption capacity, Q_o (28.57 mg/g) is comparable with the values observed for other biosorbents reported in the earlier studies.

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