Kinetic, Equilibrium, and Thermodynamic Studies of the Biosorption of Cd(II), Pb(II), and Zn(II) from Aqueous Solutions using Coconut (*Cocos nucifera*) Leaf.

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ABSTRACT

The biosorption characteristics of Cd(II), Pb(II), and Zn(II) from solution using coconut (*Cocos nucifera*) leaf were investigated. Optimum biosorption conditions were determined as a function of solution pH, contact time, initial metal ion concentration, dosage, and temperature. Optimum pH for each metal ion was obtained as the biosorption of each of the metal ions was found to be pH-dependent. Kinetic study showed that the pseudo-second-order kinetic model best represents the biosorption of the metal ions. The biosorption capacity of coconut leaf for Cd(II), Pb(II), and Zn(II) are 97.28, 69.54 and 50.18 mg g^{-1}, respectively. The sorption of each metal ion was analyzed with Freundlich and Langmuir isotherm models, in each case, the Freundlich model appears to have better regression coefficients than the Langmuir model. The study on the effect of dosage showed that the dosage of the biomass significantly affected the uptake of the metal ions from solution. The calculated thermodynamic parameters (ΔG°, ΔH°, and ΔS°) showed that the biosorption of each of the metal ions onto coconut leaf was feasible, spontaneous, and endothermic. The order of spontaneity of the biosorption process being Cd(II)>Pb(II)>Zn(II). Similarly, positive change in entropy was observed for each and the order of disorder is Cd(II) >Zn(II)>Pb(II).

(Keywords: biosorption, coconut, Cocos nucifera, cadmium, lead, zinc)

INTRODUCTION

Increase in industrial operations world wide has led to increase in heavy metal pollution. Heavy metal ions are contained in untreated effluents of different industrial operations such as mining, sludge disposal, metal plating and manufacture of ellectrical appliances.They turn to pollutants on release into the environment. The heavy metals are known to be hazardous to living organisms. They are non-biodegradable and hence the need for their removal before they enter the food chain.

The nature of these pollutants has caused increased concern for their removal from industrial effluents. The conventional approach to their removal from effluents are rather expensive with associated demerits. Biosorption has been found to be an efficient and effective alternative technology at little or no cost [Babarinde et al., 2008a,b; Babarinde et al., 2009a,b; Babarinde et al., 2010; Chakravarty et al., 2010; Liu et al., 2010; Uluozlu et al., 2010; Zhang and Wang, 2010; Vijayaraghavan and Balasubramanian, 2010; Fiorentin et al., 2010; Qu et al., 2010; Basu et al., 2010; Babarinde et al., 2011].

Coconut (*Cocos nucifera*) is a plant that is grown across the world for its fruit. However, the leaf is unutilized thereby becoming environmental nuisance. It is found to contain aboundant functional groups such as hydroxyl, amino and carbonyl groups which contain lone pairs of electrons needed for biosorption of cationic pollutants in solution. It was on this basis that this readily available agricultural waste was investigated for its potential in treating industrial effluents containing Cd(II), Pb(II), and Zn(II).

METHODOLOGY

Biomass Preparation

Coconut (*Cocos nucifera*) leaves were harvested from a farm near the mini campus of Olabisi

Onabanjo University, Ago-Iwoye, Ogun State, Nigeria. The leaves were properly rinsed with water, sun dried immediately, and later cut into pieces of approximately 0.5cm.The leaf sample was kept dry till time of usage.

Preparation of Solution

All chemicals used in this study were of analytical reagent grade and were used without further purification. Standard solutions used for the study were prepared from $3CdSO_4.8H_2O$, $Pb(NO_3)_2$, and $Zn(NO_3)_2.6H_2O$. The working solutions with different concentrations of the metal ions were prepared by appropriate dilutions of the stock solution immediately prior to their use with distilled water. The initial pH of the solution was adjusted accordingly with a pH meter. A thermostated water bath (Haake Wia Model) was used as the medium for the process. The concentration before and after biosorption of each metal ion was determined using a Perkin-Elmer Analyst 700 flame atomic absorption spectrophotometer with deuterium background corrector. Fourier transform infrared (FT-IR) spectra of dried unloaded biomass and metal loaded biomass were recorded at 400-4000 cm^{-1} using a Shimadzu FT-IR model 8400S spectrophotometer.

Batch Biosorption Study

The biosorption study was carried out by contacting 0.5g of the coconut leaf with 25ml of the metal ion solution under different conditions for a period of time in a boiling tube. The biosorption studies were conducted at 27^{o}C using thermostated water bath to determine the effect of pH, contact time, initial metal ion concentration and dosage on the biosorption. The residual metal ion was analyzed using Atomic Absorption Spectrophotometer. The amount of metal ion biosorbed from solution was determined by difference and the mean value calculated.

Effect of pH on Biosorption

The effect of pH on the biosorption of the metal ion was carried out within the range that would not be influenced by the metal precipitated. This was done by contacting 0.5g of coconut leaf with 25ml of 100 mgL^{-1} metal ion solution in a boiling tube. The pH of each solution was adjusted to the desired value by drop wise addition of 0.1M HNO_3 and/or 0.1M NaOH. The studies were conducted within the range pH 1-7. The boiling tubes containing the mixture were left in a water bath for 6 hours. The biomass was removed from the solution by decantation. The residual metal ion concentration in the solution was analyzed. The optimum pH was determined as the pH with the highest biosorption of each metal ion.

Effect of Contact Time on Biosorption

The biosorption of the metal ions by coconut (*Cocos nucifera*) leaf was studied at various time intervals (0-360 min) and at the concentration of 100 mg L^{-1}. This was done by weighing 0.5g of coconut leaf into each boiling tube and 25ml of 100 mg L^{-1} of metal ion solution at optimal pH was introduced into it. The leaf was left in solution for varying periods of time. The solution in the boiling tube was decanted at different time intervals from the first to the last tube. The aliquot was then taken for analysis using an Atomic Absorption Spectrophotometer. The amount of metal ions biosorbed was calculated for each sample.

Effect of Initial Metal Ion Concentration on Biosorption

Batch biosorption study of metal ion was carried out using a concentration range of 10 -300 mgL^{-1}. This was done by introducing 0.5 g of the coconut leaf into each of the boiling tubes employed and 25 ml of 100 mgL^{-1} of metal ion solution at optimal pH was added to the tube. Two boiling tubes were used for each concentration. The tubes were left in a thermostated water bath maintained at 27˚C. The coconut leaf was removed from the solution and the concentration of residual metal ion in each solution was determined.

Effect of Temperature on Biosorption

The batch biosorption process was studied at different temperatures of 20 - 50^{o}C in order to investigate the effect of temperature on the biosorption process. This was done by contacting 0.5 g of coconut leaf with 25ml of 100 mgL^{-1} of metal ion solution at the optimal pH. The biosorption of metal ion may involve chemical bond formation and ion exchange since the temperature is a main parameter affecting them.

Statistical Analyses

The curve fittings of the data obtained were performed using Microcal Origin 6.0 software.

RESULTS AND DISCUSSION

FT-IR Studies of the Free and Metal-Bound Coconut Leaf

\The FT-IR spectra of dried unloaded, Cd-loaded, Pb-loaded and Zn-loaded coconut (*Cocos nucifera*) leaf were taken to obtain information on the nature of possible interactions between the functional groups of coconut leaf biomass and the metal ions as presented in Figure 1. The IR spectra pattern of the biomass showed distinct and sharp absorptions indicative of the existence of the -NH, S-O, -C-O- and -C-N- groups as shown in Figure 1. These bands are due to the functional groups of coconut leaf that participate in the biosorption of Cd(II), Pb(II) and Zn(II). On comparison, there are clear band shifts and decrease in intensity of bands as reported in Table1.

The FT-IR spectra of the coconut leaf biomass indicated slight changes in the absorption peak frequencies due to the fact that the binding of the metal ions causes reduction in absorption frequencies. These shifts in absorbance observed implies that there were metal binding processes taking place on the active sites of the biomass. Analysis of the FT-IR spectra showed the presence of ionizable functional groups (C=O, O-H, NH_2) which are able to interact with cations [Pradhan et al., 2007; Bueno et al., 2008; Sun et al., 2008; Ertugay and Bayhan, 2008; Uluozlu et al., 2008]. This implies that these functional groups were mainly involved in the removal of positively charged ions from solution.

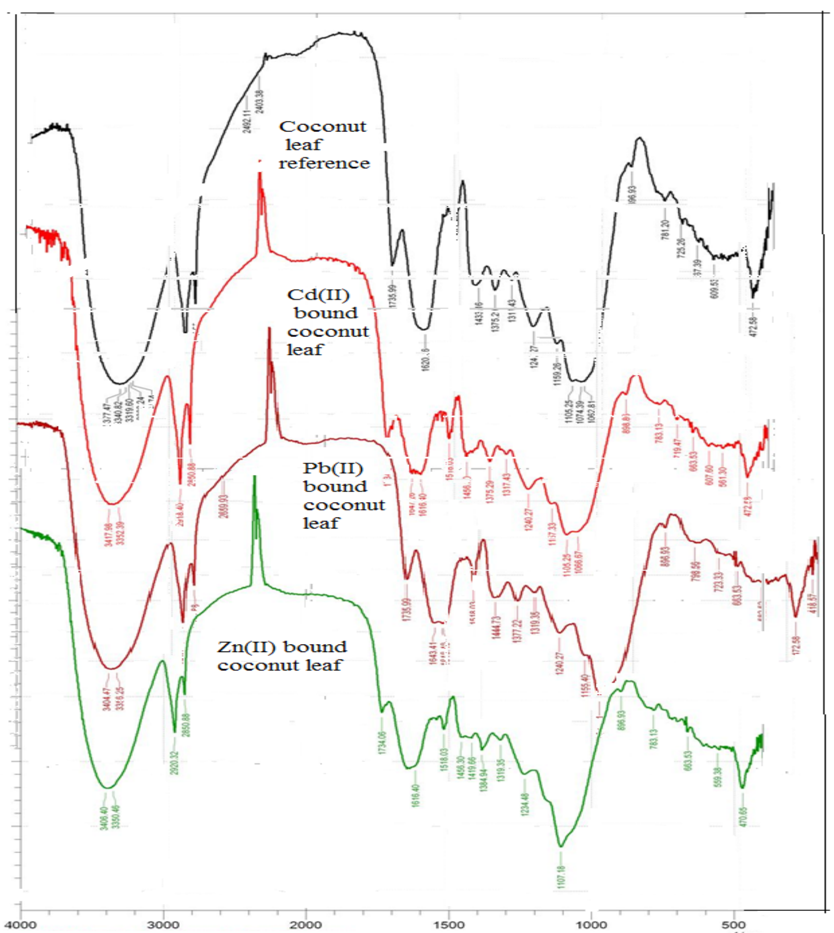

Figure 1: FT-IR Spectra of the Free and Metal-Bound Coconut (*Cocos nucifera*) Leaf.

Table 1: The FT-IR Spectral Characteristics of Coconut (*Cocos nucifera*) Leaf Before and After Biosorption of Cd(II), Pb(II), and Zn(II).

Metal ion	Absorption bands (cm^{-1})			Functional groups
	Before	After	Difference	
Cd(II)	3340.82	3346.61	5.79	N-H stretch (amines),bonded hydroxyl group
Pd(II)	3340.82	3356.25	15.43	N-H stretch (amines),bonded hydroxyl group
Zn(II)	3340.82	3350.46	9.64	N-H stretch (amines),bonded hydroxyl group
Cd(II)	1735.99	1734.06	1.93	C=O stretch (esters)
Pd(II)	1735.99	1735.99	0	C=O stretch (esters)
Zn(II)	1735.99	1734.06	1.93	C=O stretch (esters)
Cd(II)	1620.26	1616.40	3.86	N-H bend (amides)
Pb(II)	1620.26	1616.40	3.86	N-H bend (amides)
Zn(II)	1620.26	1616.40	3.86	N-H bend (amides)
Cd(II)	1240.27	1246.06	5.79	C-O stretch (alcohols)
Pb(II)	1240.27	1240.27	0	C-O stretch (alcohols)
Zn(II)	1240.27	1234.48	5.79	C-O stretch (alcohols)
Cd(II)	896.93	895.00	1.93	S-O stretch sulfonates
Pb(II)	896.93	896.93	0	S-O stretch sulfonates
Zn(II)	896.93	896.93	0	S-O stretch sulfonates

Effect of Solution pH on Metal Ion Biosorption

Figure 2 shows the variation of the metal ion biosorbed on coconut leaf at various solution pH values. The biosorption increased sharply as the pH increased from pH 1 to pH 2. The maximum biosorption was found to be 91% for Cd(II), 72% for Pb(II) and 99% for Zn(II) at pH 2-6, pH4 and pH 4-6, respectively. The increase observed in the biosorption with increase in pH implies that ion-exchange process is involved. The reaction involved the biosorption of metal ion (represented as M^{x+} for a metal ion) from the liquid phase to the solid phase, the biosorbent with lone pair of electron (represented as Ä), and can be considered as a reversible reaction with an equilibrium being made between the two phases as schematically shown below for a divalent metal ion in solution:

$$\ddot{A} + M^{2+} \rightleftharpoons A\text{-}M \qquad \textbf{(1)}$$

The pH of solution has been established to be a vital parameter in biosorption process (Sari et al., 2007; Babarinde, 2011). The net charge of the sorbate and that of the sorbent are dependent on the pH of the solution. At low pH, the metal ion uptake is inhibited by net positive charge on the sorbent and the competition between the metal ions and the hydrogen ions in solution. As the pH increases, the negative charge density on biomass increases as a result of deprotonation of the metal binding sites on the leaf, consequently, the biosorption of the metal ions increases. The reversibility of the biosorption process is observed when the metal-bound biomass is treated with dilute HNO_3 which is a desorption process

Biosorption Kinetics

Figure 3 illustrates the dynamic biosorption process of the three metal ions on coconut leaf. It is observed that the biosorptive quantities of the three metal ions on coconut leaf increase with increasing contact time. In each case, bipahsic kinetics is observed: an initial rapid stage (fast phase) where biosorption is fast and contributes to equilibrium uptake and a second stage (slow phase) whose contribution to the metal ion biosorption is relatively smaller.

The fast phase is the instantaneous biosorption stage, it is assumed to be caused by external biosorption of metal ion to the leaf surface. The second phase is a gradual biosorption stage, which is diffusion rate controlled. Finally, the biosorption sites are used up, the uptake of the metal ion reached equilibrium. This phase mechanism has been suggested to involve two diffusion processes, external and internal, respectively (Wu et al., 2009). The biosorption of each of the three metal ions achieves equilibrium within 3 hrs. although their rates of uptake are different. This might be due to the differences in hydrated ionic sizes of the metal ions [Kielland, 1937].

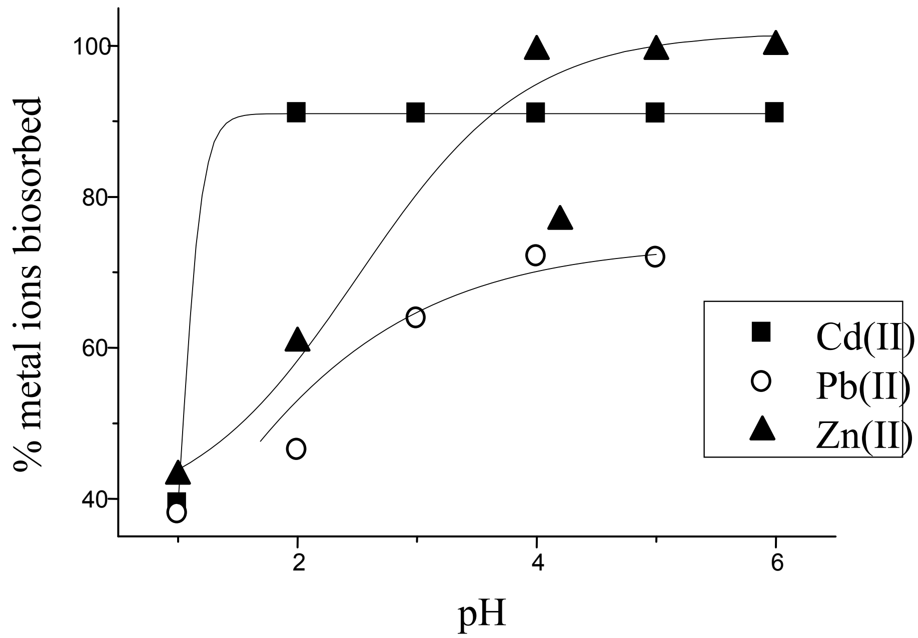

Figure 2: pH-Dependent Profile for the Biosorption of Cd(II), Pb(II), and Zn(II) by coconut (*Cocos nucifera*) Leaf at 27 °C.

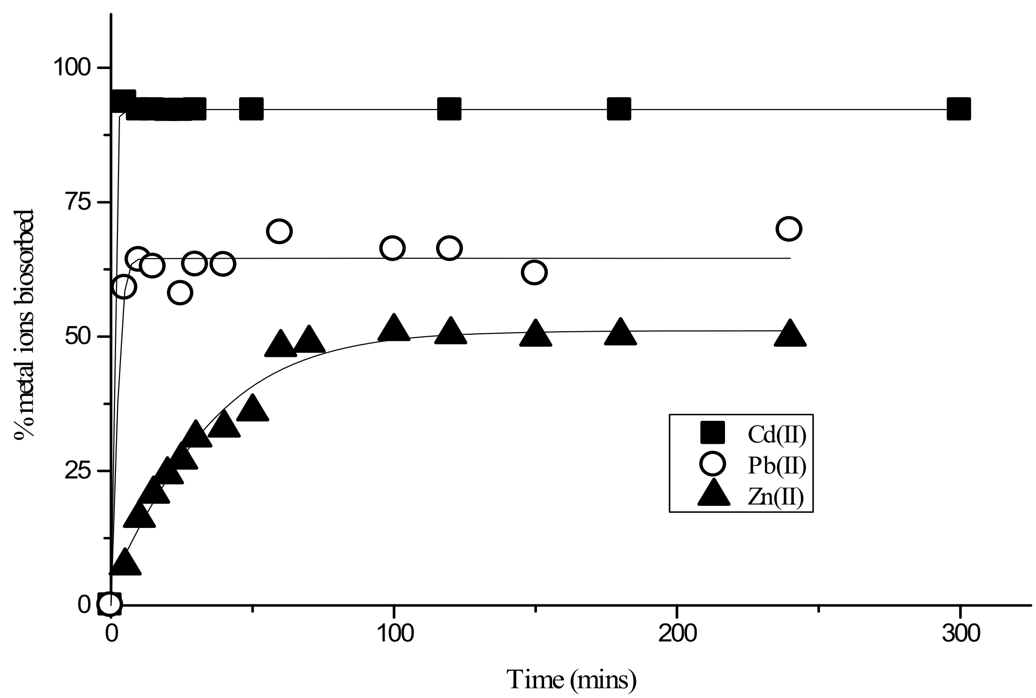

Figure 3: Time Course of the Biosorption of Cd(II), Pb(II), and Zn(II) by Coconut (*Cocos nucifera*) Leaf at 27°C.

Several kinetic models are needed to establish the mechanism of a biosorption process. In order to investigate the kinetics of the biosorption of these metal ions on coconut leaf, three kinetic models were employed. These are the pseudo-first-order, the pseudo-second-order, and the Elovich equations. One of such models is the Lagergren pseudo-first-order model which considers that the rate of occupation of the biosorption sites is proportional to the number of the unoccupied sites [Ertugay and Bayhan, 2008]:

$$rate = -\frac{d[A]}{dt} = k\ [A]^n \quad \textbf{(2)}$$

which can also be written as:

$$\frac{d}{d_t} q_t = k_1 (q_e - q_t) \quad \textbf{(3)}$$

Integrating between the limits q_t = 0 at t =0 and q_t = q_t at t =t, we obtain:

$$\log\left[\frac{q_e}{(q_e - q_t)}\right] = \frac{k_1}{2.303} t \quad \textbf{(4)}$$

This can be rearranged to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \textbf{(5)}$$

where k_1 is the Lagergren rate constant of the biosorption (min^{-1}); q_e and q_t are the amounts of metal ions sorbed (mg g^{-1}) at equilibrium and at time t, respectively. The plot of $\log(q_e - q_t)$ versus t for the biosorption of metal ions on the biomass at initial concentration of 100 mg L^{-1} should give a straight line for a process that follows first-order kinetic model. The data was equally subjected to the pseudo-second-order kinetic model. The pseudo-second-order kinetic model is represented as:

$$\frac{d}{d_t} q_t = k_2 (q_e - q_t)^2 \quad \textbf{(6)}$$

On integrating between boundary conditions, we have:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad \textbf{(7)}$$

On rearrangement, we have:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad \textbf{(8)}$$

where k_2 is the equilibrium rate constant of pseudo-second-order biosorption process (g mg^{-1} min^{-1}). In the three metal ions under study, the straight line plots of t versus t/qt showed good fitness of experimental data with the second-order kinetic model for different initial concentration of the three metal ions as presented in Figure 4. The data were equally subjected to the Elovish kinetic model given by:

$$q_t = A + B \ln t \quad \textbf{(9)}$$

The correlation coefficients for the pseudo-second-order kinetic model obtained were found to be highest for the pseudo-second-order kinetic equation and also each is in excess of 0.99 as presented in Table 2.

On comparison of the values of R^2 for the experimental points, the pseudo-second-order kinetic model is the best kinetic model to predict the dynamic biosorption of Cd(II), Pb(II), and Zn(II) on coconut leaf. The result shows that the rate of biosorption of the metal ions is of the order Cd(II) >Zn(II)>Pb(II) which may be due to the differences in hydrated ionic sizes of the ions in solution [Kielland, 1937]. The biosorption capacity is in the order Cd(II)>Pb(II) >Zn(II).

Biosorption isotherm

Figure 5 illustrates the biosorption isotherm of Cd(II), Pb(II), and Zn(II) on coconut (*Cocos nucifera*) leaf. The equilibrium biosorption q_e increases with increase in metal ion concentration.

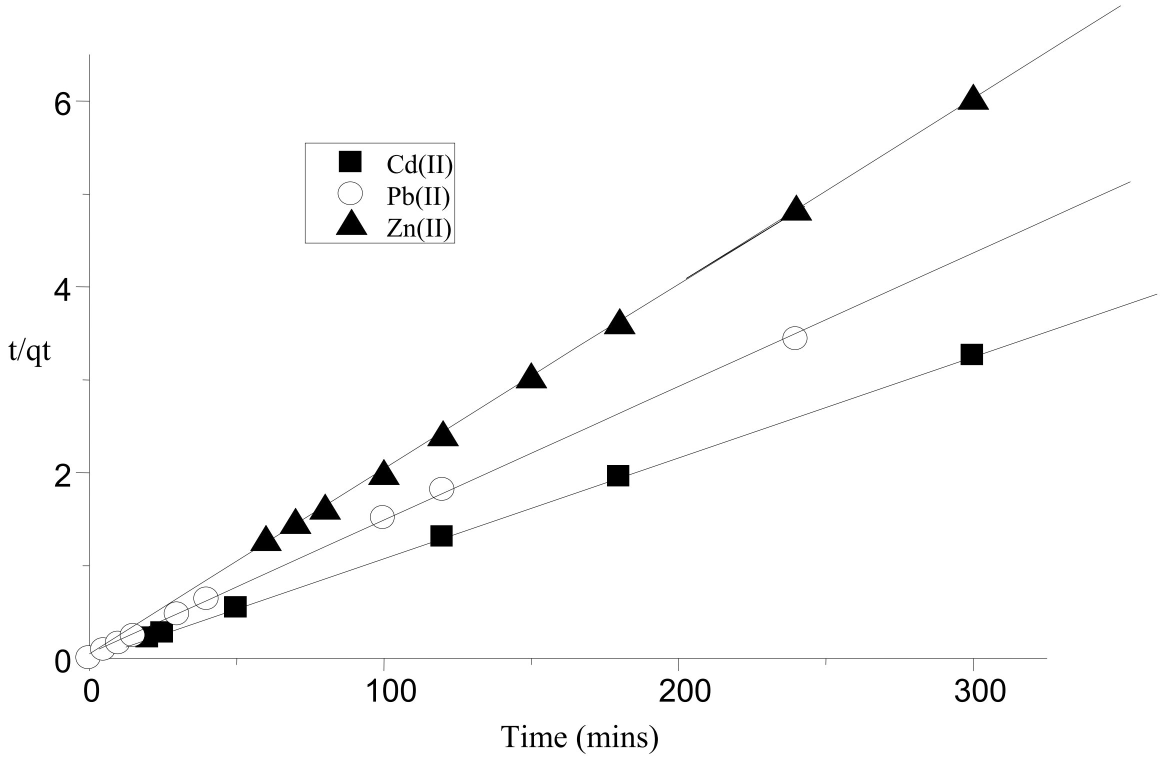

Figure 4: Pseudo-Second-Order Kinetic Plot for Biosorption of Cd(II), Pb(II), and Zn(II) Coconut (*Cocos nucifera*) Leaf at 27°C.

Table 2: Parameters of the Pseudo-Second-Order Kinetic Model for the Biosorption of Cd(II), Pb(II), and Zn(II) by Coconut (*Cocos nucifera*) Leaf.

Metal ion	k_2 (g.mg^{-1}.min^{-1})	q_e (mg g.$^{-1}$)	R^2	S.D.
Cd(II)	7.867×10^{-1}	97.08	1.0000	0.0003
Pb(II)	2.0678×10^{-4}	69.54	0.9991	0.0365
Zn(II)	3.972×10^{-4}	50.18	0.9997	0.0285

The Freundlich and Langmuir isotherms, were employed to calculate the biosorption capacity. The Freundlich isotherm is an empirical equation describing adsorption onto a heterogenous surface. The Freundlich isotherm is expressed as

$$\log \Gamma = \frac{1}{n} \log C_e + \log K_f \qquad \textbf{(10)}$$

where K and $\frac{1}{n}$ are the Freundlich constants related to the biosorption capacity and biosorption intensity of the biosorbent, respectively.

The linear form of the Langmuir equation is expressed as:

$$\frac{1}{\Gamma} = \frac{1}{b_m} \frac{1}{C_e} + \frac{1}{\Gamma_m} \qquad \textbf{(11)}$$

where Γ, Γ_m and b_m are the Langmuir parameters. The parameters of the isotherms are presented in Table 3.

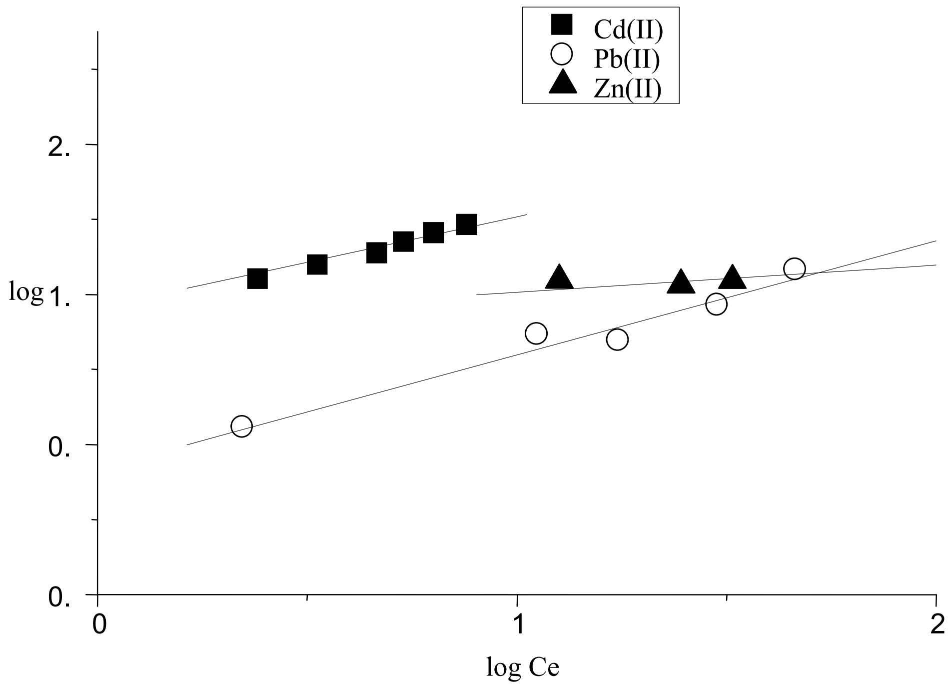

Figure 5: Freundlich Isotherm for the Biosorption of Cd(II), Pb(II), and Zn(II) by Coconut (*Cocos nucifera*) Leaf.

Table 3: Freundlich Isothermal Parameters for the Biosorption of Cd(II), Pb(II), and Zn(II) by Coconut (*Cocos nucifera*) Leaf.

Freundlich Isotherm Model	K_f	N	R^2	S.D.
Cd(II)	27.8824	1.7134	0.9902	0.0120
Pb(II)	4.8477	1.6645	0.9632	0.0691
Zn(II)	30.6704	7.4521	0.9927	0.0351

The regression coefficients obtained for Freundlich isotherm are higher than the values obtained for Langmuir isotherm. This implies that the biosorption is assumed to be a multilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between biosorbed molecules [Bueno et al., 2008]

Biosorption Efficiency

The result of the study on the effect of initial metal ion concentration on biosorption efficiency is shown in Figure 6. The plots show that the biosorption efficiency of the biomass reduced with increase in the initial metal ion concentration of Cd(II) and Zn(II) which might be due to the fixed number of binding sites in the biosorbent having more ions than at lower concentration. On the other hand the biosorption efficiency increased with increase in initial metal ion concentration for Pb(II). The biosorption efficiency (E) for each metal ion was calculated as:

$$E = 100\left(\frac{C_i - C_e}{C_i}\right) \quad \textbf{(12)}$$

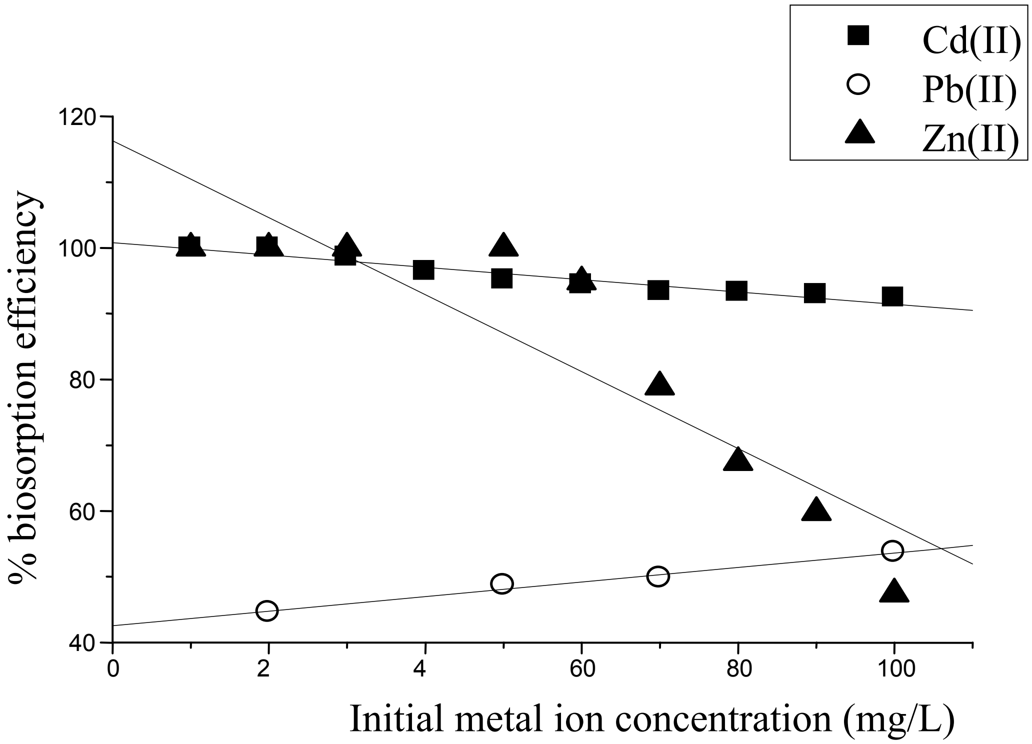

Figure 6: Effect of Initial Metal Ion Concentration on the Efficiency of the Biosorption of Cd(II), Pb(II), and Zn(II) by Coconut (*Cocos nucifera*) Leaf at 27°C.

where C_i and C_e are the initial and the equilibrium metal ion concentrations (mg L^{-1}), respectively.

Effect of Biomass Dosage on Biosorption

The effect of biomass dosage on the efficiency of biosorption of Cd(II), Pb(II), and Zn(II) was studied using biomass in the range 0.1- 1.0 g/25 ml as reported in Figure 7. The biosorption of each metal ion became constant at dosage higher than 0.8g/ml. This type of phenomenon has been reported to be the consequence of a partial aggregation which occurs at higher biomass dosage giving rise to a decrease in the number of active sites on the biomass [Sari et al., 2007]. The general trend of increase in metal ion biosorbed with increase in biomass dosage indicates an increase in uptake due to more binding sites on the biomass available for biosorption. This trend has been reported for other biosorbents [Babalola et al., 2009].

Biosorption Thermodynamics

The variation of temperature affects the biosorption of metal ions onto solid surfaces of biomass since the biosorption process is a reversible one. The nature of each side of the equilibrium determines the effect temperature has on the position of equilibrium. The side that is endothermic is favored by increase in temperature while the contrary holds for the exothermic side. The corresponding free energy change was calculated from the relation [de la Rosa et al., 2008; Sun et al., 2008]

$$\Delta G^{\circ} = -RT \ln K_c \qquad \textbf{(13)}$$

where T (K) is the absolute temperature. The equilibrium constant (K_c) was calculated from the following relationship:

$$K_c = \frac{C_{ad}}{C_e} \qquad \textbf{(14)}$$

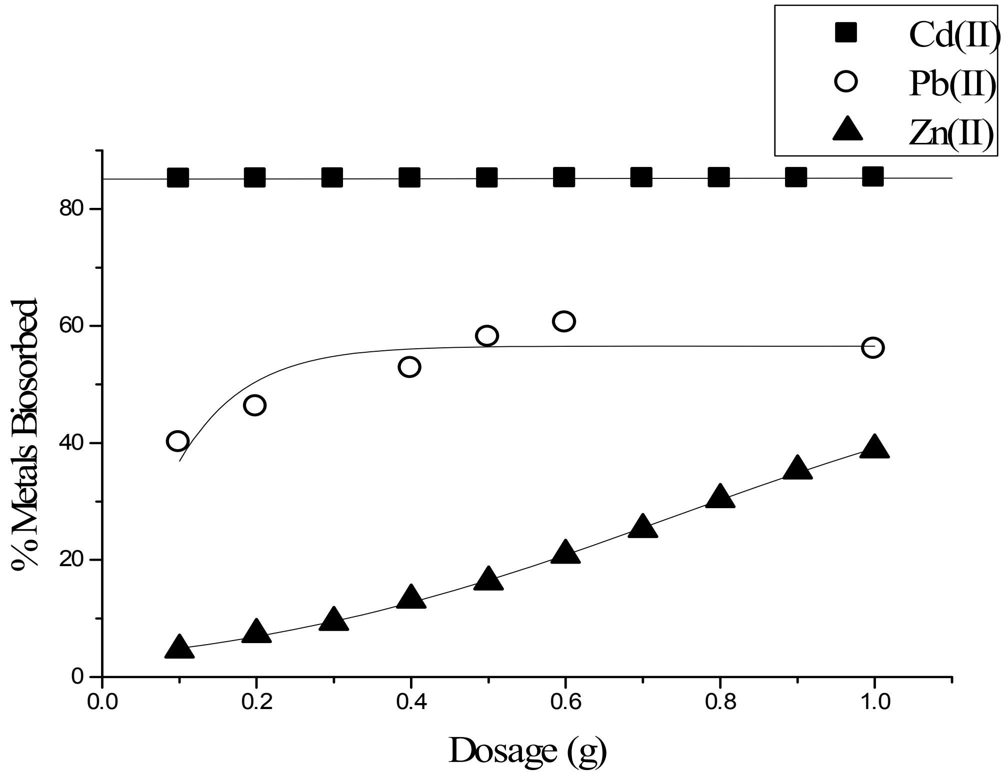

Figure 7: Effect of Biomass Dosage on the Biosorption of Cd(II), Pb(II), and Zn(II) by Coconut (*Cocos nucifera*) Leaf at 27° C.

where C_e and C_{ad} are the equilibrium concentrations of metal ions (mg L^{-1}) in solution and on biosorbent , respectively. Consequently, the thermodynamic behavior of the biosorption of Cd(II), Pb(II), and Zn(II) onto coconut leaf was evaluated through the change in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°). The thermodynamic parameters like enthalpy and entropy are obtained using van't Hoff equation [Qu et al., 2010; Uluozlu et al., 2010]. The change in free energy is related to other thermodynamic properties as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \textbf{(15)}$$

$$\ln K_c = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad \textbf{(16)}$$

where T is the absolute temperature (K); R is the gas constant (8.314 $Jmol^{-1}.K^{-1}$). ΔH° ($J.mol^{-1}$) and ΔS° ($J.mol^{-1}.K^{-1}$) were calculated from the slope and intercept of the linear plot of ln K_c vs 1/T. The thermodynamic parameters obtained for this study are presented in Table 4. The plots shown in Figure 8 are linear over the entire range of temperature investigated.

The positive values of ΔH° for the biosorption of the three metal ions suggest an endothermic nature of each biosorption process. This is also supported by the increase in the value of biosorption capacity of the biosorbent with rise in temperature. The positive value of ΔH° indicates the presence of an energy barrier in the biosorption process. Similarly, the ΔS° values are positive indicating increase in randomness during the biosorption process for these three metal ions. These positive values of ΔS° observed for the biosorption of these metal ions showed an increase in randomness at the solid/solution interface during their biosorption.

CONCLUSIONS

This study focused on the biosorption of Cd(II), Pb(II), and Zn(II) by coconut (*Cocos nucifera*) leaf under various conditions.

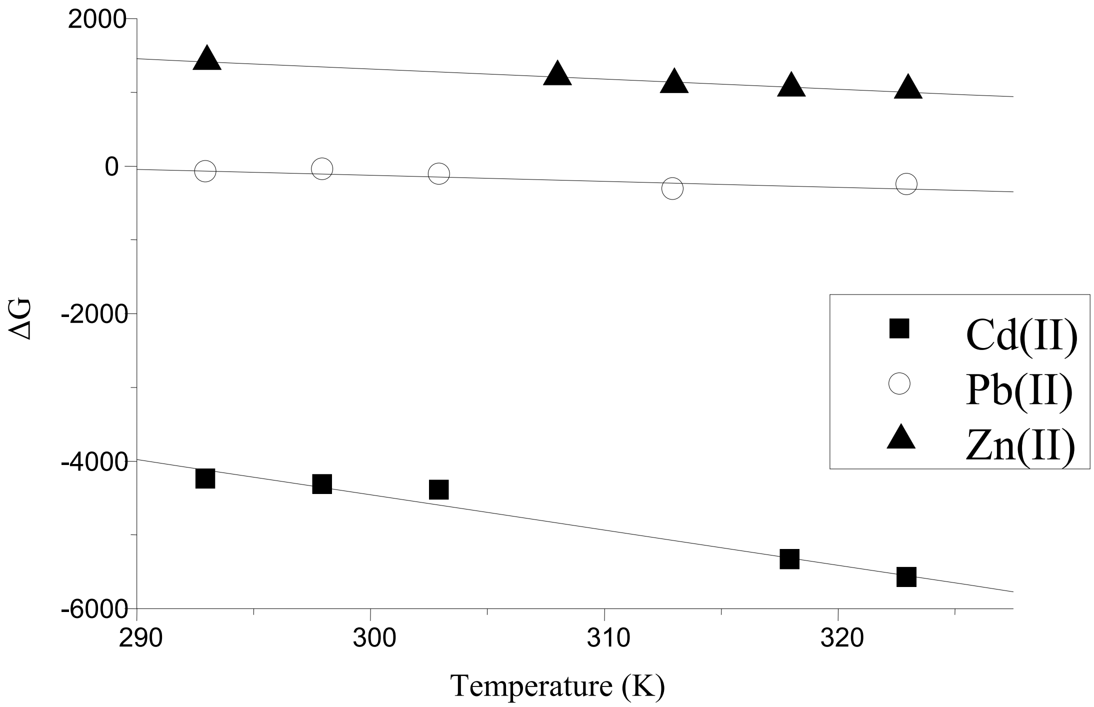

Figure 8: Thermodynamic Plots for the Biosorption of Cd(II), Pb(II), and Zn(II) onto Coconut (*Cocos nucifera*) Leaf at 27˚C.

Table 4: Thermodynamic Parameters for the Biosorption of Cd(II), Pb(II), and Zn(II) by Coconut (*Cocos nucifera*) Leaf.

Metal ion	ΔH˚ (kJ mol^{-1})	ΔS˚(J $mol^{-1}K^{-1}$)	R^2	S.D.
Cd(II)	9.878	47.7854	0.9640	137.9644
Pb(II)	2.308	8.1153	0.7261	69.3095
Zn(II)	5.421	13.6855	0.9794	26.3791

The pH has much effect on the biosorption of these metal ions from aqueous solutions. The kinetics of the biosorption of these metal ions followed pseudo-second-order kinetic model. The sorption isotherms of these metal ions onto the biosorbent are well described by the Freundlich isotherm model. The thermodynamic study shows that the biosorption of each of Cd(II), Pb(II) and Zn(II) was spontaneous, endothermic and chaotic in the order Cd(II)> Zn(II)>Pb(II).It can be concluded that the coconut leaf has high potentials for the removal of these metal ions from solution and could therefore serve as effective and efficient biomass for treating wastewaters in terms of high biosorption capacity and natural abundance.

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