

Equilibrium Sorption of Cd(II), Pd(II) and Zn(II) from Solution onto Cassava (*Manihot esculenta*) Leaf: Kinetics, Isotherms, and Thermodynamics.

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ABSTRACT

In this study, Cassava (*Manihot esculenta*) leaf biomass has been investigated for its potential in the uptake of Cd(II), Pd(II), and Zn(II) from solutions. The FTIR spectra characteristics of *Manihot esculenta* leaf revealed the presence of ionizable groups that could participate in the binding of metal ions in solution. The biosorption of each of the ions was found to be dependent on the physicochemical parameters such as solution pH, contact time, initial metal ion concentrations, biosorbent dose, and temperature. The biosorption kinetics follows a pseudo-second-order kinetic model with biosorption rate of the order Pb(II)>Cd(II)>Zn(II). The biosorption capacity was found to be of the order Pb(II)>Zn(II)>Cd(II). Equilibrium isotherm studies showed that the biosorption followed the Freundlich isotherm model, which implies a heterogeneous sorption phenomenon. Thermodynamic parameters such as changes in free energy, enthalpy, and entropy have been calculated. The negative values of ΔG° show the spontaneity of the sorption process in the order Cd(II)>Pb(II)>Zn(II). The negative values of ΔH° implies exothermic nature of the sorption process in the order Pb(II) >Cd(II)>Zn(II) while the negative values of ΔS° shows decreased randomness at the solid-liquid interface during the sorption in the order Zn(II) >Cd(II)> Pb(II).

(Keywords: cassava, Cd(II), Pb(II), Zn(II), isotherm, biosorption)

INTRODUCTION

Rapid industrialization has led to an increased disposal of heavy metals into the environment. Process industries such as battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron, and steel manufacturing units generate large quantities of waste water contaminated with toxic metal ions. The presence of these heavy metals in the environment is of great concern due to their toxicity and health effects on humans and other living creatures (El-Said, 2010).

Of the several conventional methods available for their removal, biosorption technology is a user-friendly technique for the removal of heavy metal. This process seems to be most versatile and effective method for removal of heavy metal if combined with appropriate regeneration steps. This solves the problem of sludge disposal and renders the system more viable, especially if low cost adsorbents are used. The use of agricultural wastes in the treatment of industrial effluents has been on the increase in the last two decades (Babarinde *et al.*, 2009; 2012a-c; Babarinde and Babalola, 2010). Cassava is a perennial woody shrub with an edible root, which grows in tropical and subtropical areas of the world. Today, it is a dietary staple in much of tropical Africa. Cassava peeling wastes have been employed for the removal of Cu(II) and Zn(II) ions from wastewater (Horsfall *et al.*, 2003; Agiri and Akaranta, 2009; Kurniawan *et al.*, 2011; Abia *et al.*, 2003). The feasibility of cassava leaf biomass as a waste for biosorption is evaluated in this work.

Manihot esculenta leaf has been found to contain ionizable functional groups which are able to interact with cations. It is on this basis that this readily available leaf was investigated for its potential in treating industrial waste containing Cd(II), Pb(II), and Zn(II) in this present research.

METHODOLOGY

Biomass Preparation

Cassava (*Manihot esculenta*) leaves were harvested from the mini campus of Olabisi Onabanjo University, Ago-Iwoye, Ogun State, Nigeria. The leaves were carefully collected inside a sack, properly rinsed with distilled 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 of Cd(II), Pb(II), and Zn(II) used for the study were prepared from $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively. 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. 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 $400\text{-}4000\text{ cm}^{-1}$ using a Shimadzu FT-IR model 8400S spectrophotometer.

Batch Biosorption Study

The biosorption study was determined batch wise by contacting 0.5g of the Cassava (*Manihot esculenta*) leaf with 25ml of each metal ion solution under different conditions for a period of time in a boiling tube. The biosorption studies

were conducted at 25°C using thermostated water bath to determine the effect of pH, contact time and initial metal ion concentration on the biosorption. The residual metal ion of the supernatant 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 pH 1-6 to prevent precipitation of metal ions. This was done by contacting 0.5g of *Manihot esculenta* 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 boiling tubes containing the mixture were left in a water bath for 5 hours. The biomass was removed from the solution by decantation. The residual metal ion concentration in the supernatant 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 Cassava (*Manihot esculenta*) leaf was studied at various time intervals and at the concentration of 100 mg L^{-1} . This was done by contacting 0.5g of Cassava 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 different periods of time. At predetermined time, the boiling tubes were withdrawn from the water bath, and the residual metal ions concentration in the solution was determined using Atomic Absorption Spectrophotometer. The amount of metal ions biosorbed was calculated for each sample.

Effect of Initial Concentration on Biosorption

Batch biosorption study of metal ion was carried out using a concentration range of $10\text{-}100\text{ mgL}^{-1}$. This was done by introducing 0.5 g of the Cassava (*Manihot esculenta*) leaf with 25ml of each solution at optimal pH. The tubes were left in a thermostated water bath maintained at 25°C for the predetermined optimum time. The Cassava leaf was removed from the solution by

decantation, 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 within the range 20 - 50°C in order to investigate the effect of temperature on the biosorption process. This was done by contacting 0.5 g of Cassava (*Manihot esculenta*) leaf with 25ml of 100 mgL⁻¹ of metal ion solution at the optimal pH.

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

RESULTS AND DISCUSSION

Physical Characterization of *Manihot esculenta* Leaf

The biosorption capacity of *Manihot esculenta* leaf biomass depends upon the chemical reactivity of functional groups at the surface. *Manihot esculenta* leaf shows the presence of several ionisable groups that could participate in the biosorption of the metal ions from solution. The FT-IR spectral analysis of dried unloaded Cassava leaf (*Manihot esculenta*) and metal loaded biomass were taken to obtain information on the nature of the possible interactions between the functional groups of *Manihot esculenta* leaf biomass and the metal ions as presented in Figure 1.

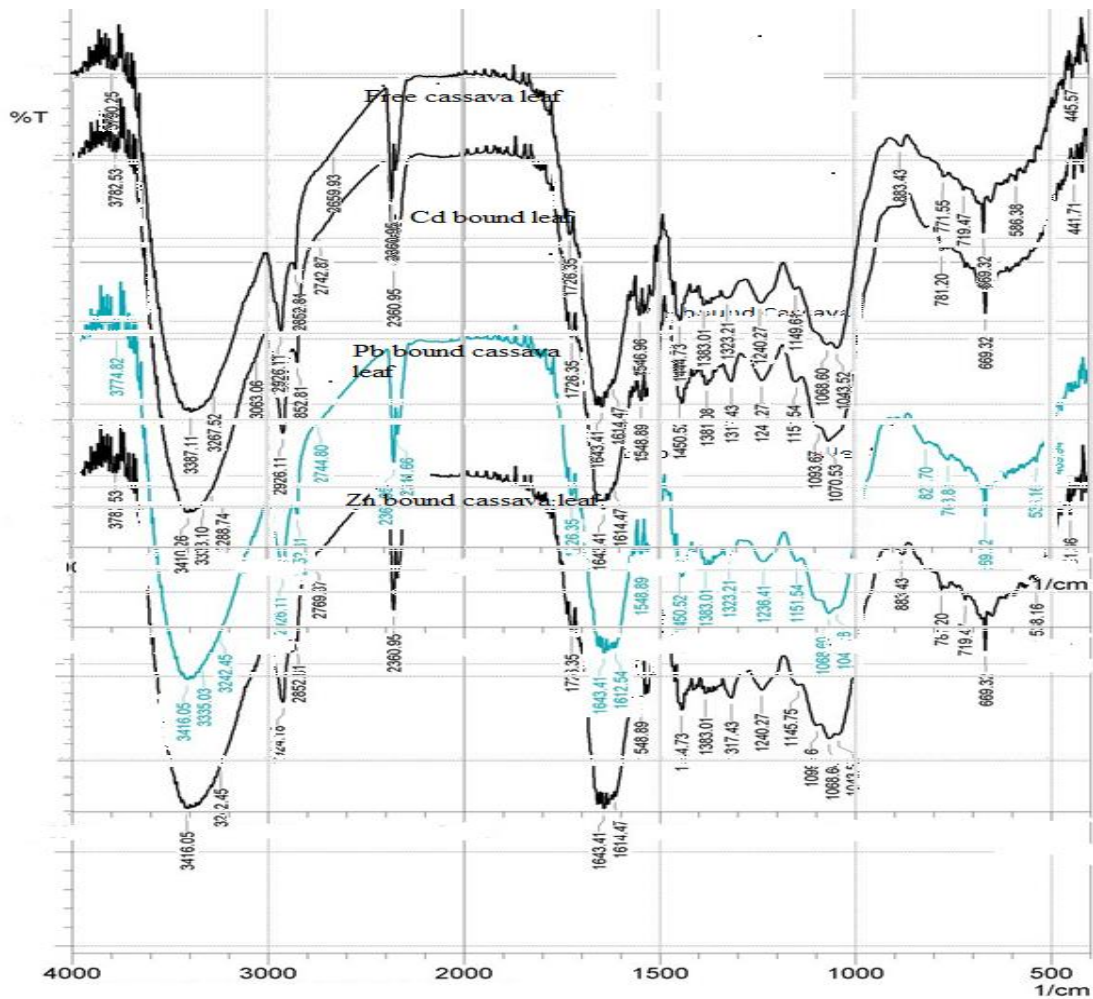


Figure 1: FT-IR Spectra of the Free and Metal-Bound Cassava (*Manihot esculenta*) Leaf.

Table 1: FT-IR Spectra Characteristics of Cassava (*Manihot esculenta*) Leaf before and after Biosorption of Cd(II), Pb(II), and Zn(II).

Metal ion	Absorption bands (cm ⁻¹)			Assignment
	Before	After	Difference	
Cd(II)	1043.52	1070.53	27.01	C-O C-N
Pb(II)		1068.60	25.08	
Zn(II)		1068.60	25.08	
Cd(II)	1643.41	1651.12	-7.71	C=O
Pb(II)		1612.54	-30.87	
Zn(II)		1643.41	0	
Cd(II)	3387.11	4310.26	23.15	OH NH stretch
Pb(II)		3416.05	28.94	
Zn(II)		3416.05	28.94	

Several peaks were observed from the spectra indicating that *Manihot esculenta* leaf is composed of various functional groups which are responsible for binding of the cations. The FT-IR spectra pattern of the biomass showed distinct and sharp absorptions indicating the presence of the -OH, -NH, -C=O, -C-O, and -C-N groups as shown in Table 1. These bands are as a result of the functional groups that participate in the biosorption of Cd(II), Pd(II), and Zn(II). On comparison, there are clear band shift and decrease in intensity between the bands of the unloaded biomass and the metal bound biomass as shown in Table 1.

The FT-IR spectra of the *Manihot esculenta* leaf biomass indicated slight changes in the absorption peak frequencies. These observed shifts in absorbance imply that there were metal binding processes taking place on the active sites of the biomass. Analysis of FT-IR spectra showed the presence of ionizable functional groups (O-H, NH, C-O, C=O and C-N) which are able to interact with cations (Bueno *et al.*, 2008; Uluzlu *et al.*, 2010; Pradhan *et al.*, 2007; Sun *et al.*, 2008; Ertugay and Bayhan, 2008). This implies that these functional groups would serve in the removal of positively charged ions from solution.

Effect of Solution pH on Metal Ion Biosorption

The pH of the solution usually plays an important role in the biosorption process of the metal ions (Vijayaraghavan *et al.*, 2006; Sun *et al.*, 2008; Babarinde *et al.*, 2012a-c). It is an important parameter governing the uptake of heavy metals by biosorption process as it does not only affect metal species in solution, but also influences the

surface properties of biosorbents in terms of dissociation of binding sites and surface charge (Akar *et al.*, 2007).

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 biomass. Consequently, the biosorption of the metal ions increases.

Figure 2 shows the variation of the metal ion biosorbed on Cassava (*Manihot esculenta*) leaf at various solution pH values. In each case, the biosorption increased steadily as the pH increased from pH 1 to pH 6. 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+}) from the liquid phase to the solid phase, the biosorbent with lone pair of electrons (represented as \ddot{A}), 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:



The reversibility of the biosorption process is observed when the metal-bound biomass is treated with dilute HNO₃ which is a desorption process.

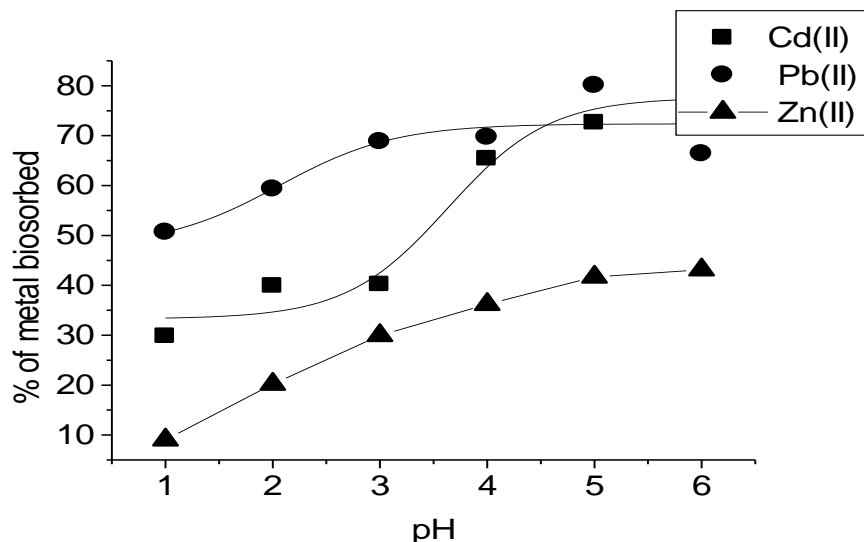


Figure 2: pH-Dependence Profile of the Biosorption of Cd(II), Pb(II), and Zn(II) by Cassava (*Manihot esculenta*) Leaf at 25°C and 100 mgL⁻¹.

Biosorption Kinetics.

Figure 3 illustrates the dynamic biosorption process of the three metal ions on Cassava (*Manihot esculenta*) leaf. It is observed that the biosorptive quantities of the three metal ions on Cassava (*Manihot esculenta*) leaf increased with increasing contact time. In each case, biphasic 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 although their rates of uptake and times of reaching equilibrium are different. This might be due to the differences in hydrated ionic sizes of the metal ions (Kielland, 1937).

Four kinetic models were applied to the kinetic data obtained in order to establish the mechanism of the biosorption of Cd(II), Pb(II), and Zn(II) on *Manihot esculenta* leaf. These are the pseudo-first-order, the pseudo-second-order, the Elovich kinetic model, and the Intraparticle diffusion model 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).

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

Which can also be written as;

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

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

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

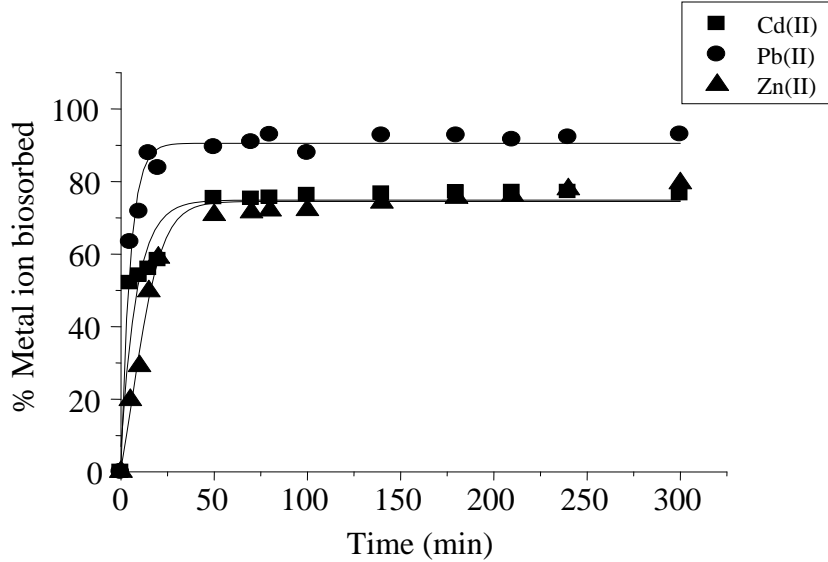


Figure 3: Time Course of the Biosorption of Cd(II), Pb(II), and Zn(II) by Cassava (*Manihot esculenta*) Leaf at 25°C and 100mgL⁻¹.

This can be rearranged to obtain a linear form:

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

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 mgL^{-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:

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

On integrating between boundary conditions, we have:

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

On rearrangement, we have:

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

Where k_2 is the equilibrium rate constant of pseudo-second-order biosorption process ($\text{g mg}^{-1} \text{ min}^{-1}$). In the three metal ions under study the pseudo-first-order kinetics did not fit the data obtained. However, the straight line plots of t versus t/q_t showed good fitness of experimental data with the second-order kinetic model for different initial concentrations of the three metal ions as presented in Figure 4.

The data were equally subjected to the Elovich kinetic model given by:

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

The intra-particle diffusion equation given as:

$$R = K_s t^b \quad (10)$$

has been used to indicate the behaviour of intra-particle diffusion as the rate limiting step in the

biosorption process. R is the percent metal ion biosorbed, K_s is the intra-particle diffusion constant, t , is the contact time, while b is the gradient of the linear plot. In the linear form, Equation (10) turns to:

$$\log R = b \log t + \log K_s \quad (11)$$

Out of the four kinetic models tested, the correlation coefficient was found to be highest for the pseudo-second-order kinetic equation and in each case it is in excess of 0.99 as presented in Table 2.

On comparing 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 Cassava (*Manihot esculentum*) leaf. The result shows that the rate of biosorption of the metal ions is of the order Pb(II) > Cd(II) > Zn(II). Biosorption capacity is in the order Pb(II) > Zn(II) > Cd(II). The differences observed in the rate of biosorption as well as in the biosorption capacity may be due to the differences in ionic charges and hydrated ionic sizes of the ions in solution (Kielland, 1937).

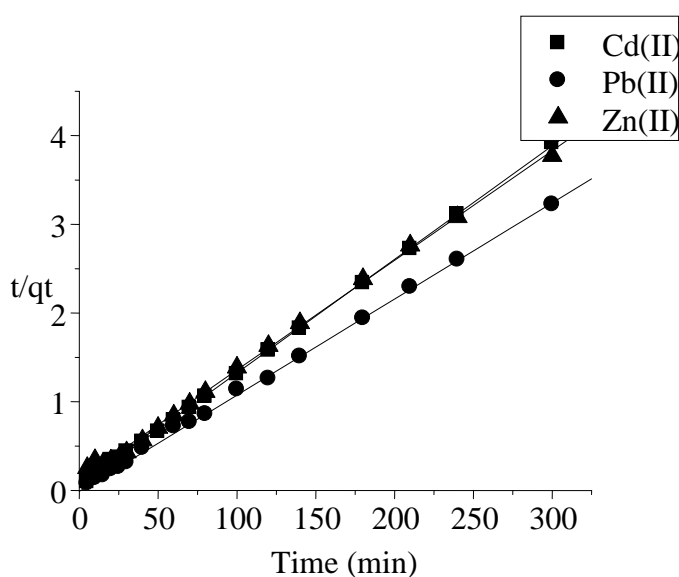


Figure 4: The Pseudo-Second-Order Kinetic Plot for the Biosorption of Cd(II), Pb(II), and Zn(II) by Cassava (*Manihot esculenta*) Leaf at 25°C, 100 mgL⁻¹.

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

Metal ion	$k_2(\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1})$	$q_e(\text{mg} \cdot \text{g}^{-1})$	R^2	S.D
Cd(II)	3.69×10^{-3}	78.13	0.9997	0.0199
Pb(II)	4.86×10^{-3}	93.37	0.9992	0.0273
Zn(II)	1.23×10^{-3}	80.97	0.9982	0.0490

Biosorption Isotherm

Figure 5 illustrates the biosorption isotherm of Cd(II), Pb(II), and Zn(II) on Cassava (*Manihot esculenta*) leaf. 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:

$$\log \Gamma = \frac{1}{n} \log C_e + \log K_f \quad (12)$$

Where K_f 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:

$$\frac{1}{\Gamma} = \frac{1}{b_m} \frac{1}{C_e} + \frac{1}{\Gamma_m} \quad (13)$$

Where Γ , Γ_m and b_m are the Langmuir parameters. The results show that the regression coefficients obtained for the Freundlich isotherm are higher than for Langmuir isotherm. This connotes that the biosorption energetic distribution of active sites is accompanied by interactions between biosorbed molecules. The parameters are presented in Table 3.

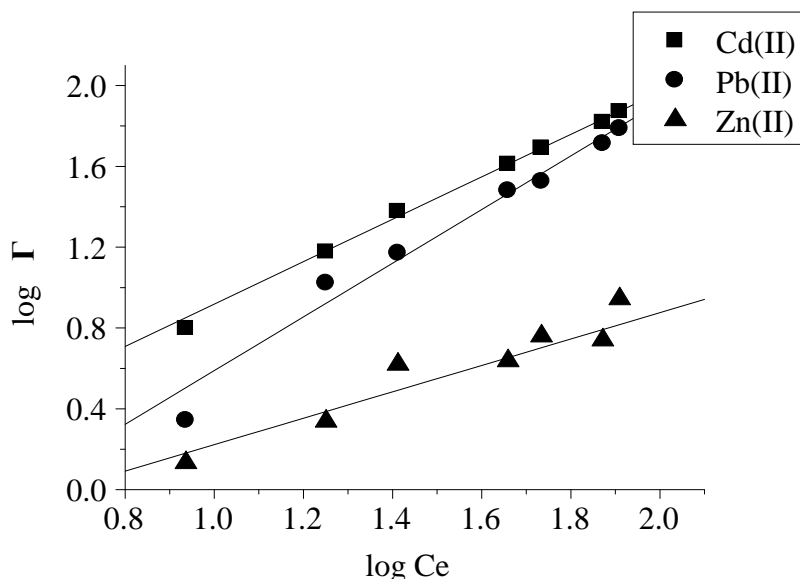


Figure 5: Freundlich Isotherm for the Biosorption of Cd(II), Pb(II), and Zn(II) using Cassava (*Manihot esculenta*) Leaf.

Table 3: Freundlich Isothermal Parameters for the Biosorption of Cd(II), Pb(II), and Zn(II) using Cassava (*Manihot esculenta*) Leaf.

Metal ion	1/n	K_f	R	S.D.
Cd(II)	1.0495	0.7396	0.9932	0.0435
Pb(II)	1.3278	0.1826	0.9781	0.0998
Zn(II)	0.6538	0.3705	0.9266	0.1045

Effect of Initial Concentration on 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 increased with increase in the initial metal ion concentration for all the metal ions which might be due to increase in effective collision between the metal ions and the active sites. The biosorption efficiency (E) for each metal ion was calculated as:

$$E = 100 \left(\frac{C_i - C_e}{C_i} \right) \quad (14)$$

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 biosorption efficiency is reported in Figure 7. 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. It was found out that biosorption capacity increases with increase in dosage of the biosorbent. This is as a result of the fact that increase in dosage leads to increase in the number of active sites available for biosorption. The difference in the biosorption capacity q (mg g^{-1}) at the same initial metal ion concentration and contact time may also be attributed to the difference in their chemical affinities and ion exchange capacity, with respect to the chemical functional group on the surface of the biosorbent. However, this trend has been reported for other biosorbent (Miranda *et al.*, 2010).

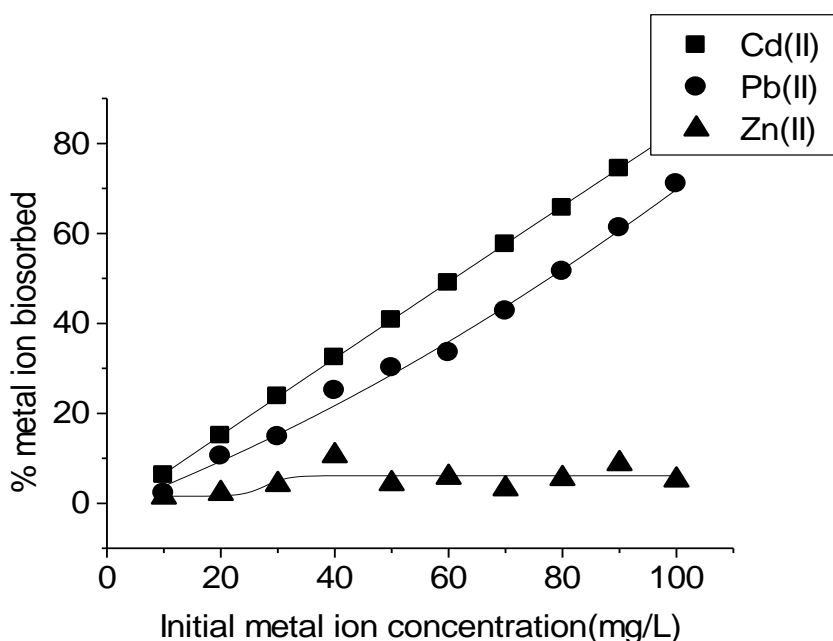


Figure 6: Effect of Initial Metal Ion Concentration on the Biosorption of Cd(II), Pb(II), and Zn(II) by Cassava (*Manihot esculenta*) leaf at 25°C.

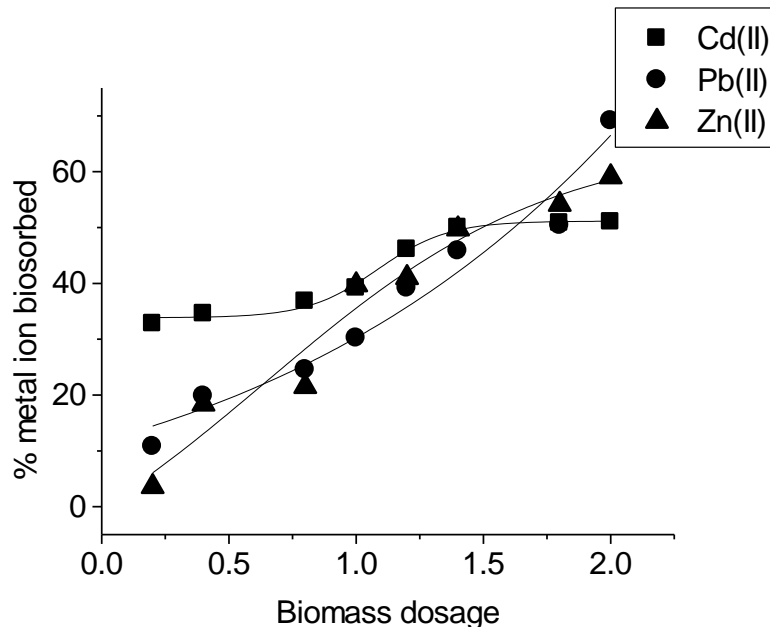


Figure 7: Effect of Biomass Dosage on the Biosorption of Cd(II), Pb(II), and Zn(II) by Cassava (*Manihot esculenta*) Leaf at 25°C, and 100 mgL⁻¹.

Biosorption of Thermodynamics

The temperature of the system 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 (Sun *et al.*, 2008 and de la Rosa *et al.*, 2008).

$$\Delta G^\circ = -RT \ln K_c \quad (15)$$

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

$$K_c = \frac{C_{ad}}{C_e} \quad (16)$$

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 Cassava (*Manihot esculenta*) leaf was evaluated through the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The thermodynamic parameters were calculated using Van't Hoff equation (Uluozlu *et al.*, 2010 and Qu *et al.*, 2010). The change in free energy is related to other thermodynamic properties as:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (17)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (18)$$

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 T⁻¹. 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.

Table 4: Thermodynamic Parameters for Biosorption of Cd(II), Pb(II), and Zn(II) by Cassava (*Manihot esculenta*) Leaf.

Metal ion	ΔH° (kJ mol ⁻¹)	ΔS° (J mol ⁻¹ K ⁻¹)	A (kJ mol ⁻¹) @308K	A (kJ mol ⁻¹) @313K
Cd(II)	-11.24	- 22.31	-8.68	-8.64
Pb(II)	-18.17	- 51.24	-15.61	-15.57
Zn(II)	-4.45	- 9.48	-1.89	-8.85

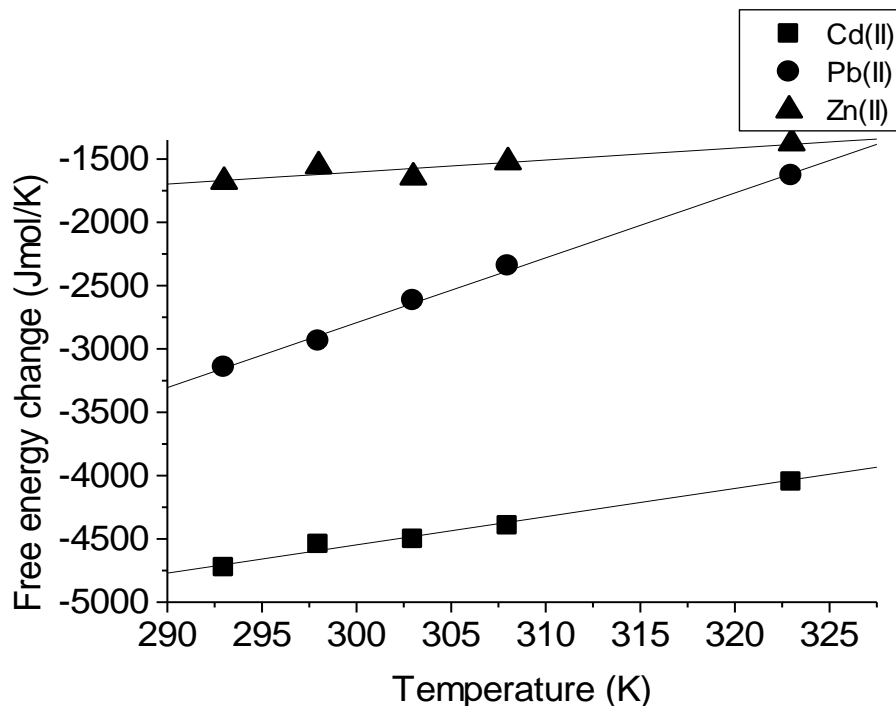


Figure 8: Thermodynamic Plots for Biosorption of Cd(II), Pb(II), and Zn(II) by Cassava (*Manihot esculenta*) Leaf.

The negative values of ΔG° indicate spontaneity of each biosorption process, with the order of spontaneity being Cd(II)>Pd(II)>Zn(II). The negative value of ΔH° for the biosorption of each of the metal ions suggests exothermic nature of the biosorption processes. This is also supported by the increase in the value of biosorption capacity of the biosorbent with rise in temperature. The negative values of ΔS° observed for the biosorption of these metal ions indicate a decrease in randomness at the solid/solution interface during their biosorption. The order of decreasing disorder being Zn(II)>Cd(II)>Pb(II).

Generally, the change of standard free energy for physisorption is in the range of -20 to 0 kJ mol⁻¹ and for chemisorption varies between -80 and -400 kJmol⁻¹ (Vimonses *et al.*, 2009; Sen *et al.*, 2011). In the present study, the overall ΔG° has values ranging from -4.8 to -1.5 kJ mol⁻¹. These results correspond to a spontaneous physical adsorption of the metal ions, indicating that this system does not gain energy from external resource (Vimonses *et al.*, 2009; Arias and Sen 2009).

The decrease in ΔG° with increase in temperature indicates more efficient biosorption at higher temperature. This is also supported by the

increase in the value of biosorption capacity of the biosorbent with rise in temperature. Furthermore, the magnitude of activation energy (A) gives an idea about the type of adsorption which is mainly diffusion controlled process (not diffusivity of solute through micropore wall surface of a particle) or chemical reaction processes (Abd El-Latif *et al.*, 2010). Energies of activation, A, below 42 kJ/mol indicate diffusion-controlled processes, and higher values give chemical reaction-based processes. Therefore, energy of activation, A, has been calculated as per the following relation:

$$A = \Delta H^\circ + RT \quad (19)$$

The values of A at two different temperatures have been tabulated in Table 4. In this study, the activation energy (A) values were less than 42 kJmol⁻¹ indicating diffusion-controlled adsorption processes.

CONCLUSIONS

In this work we have studied the biosorption of Cd(II), Pb(II), and Zn(II) by Cassava (*Manihot esculenta*) leaf biomass under various conditions. The pH has much effect on the biosorption of these metal ions from aqueous solutions. The rate of the biosorption of these metal ions followed pseudo-second-order kinetics. 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. This study shows that Cassava leaf has high potential for treating industrial effluents containing Cd(II), Pb(II) and Zn(II).

REFERENCES

1. Abia, A.A., M. Horsfall, Jr., and O. Didi. 2003. "The Use of Chemically Modified and Unmodified Cassava Waste for the Removal of Cd, Cu, and Zn Ions from Aqueous Solution". *Bioresource Technology*. 90(3):345-8.
2. Abd El-Latif, M.M., A.M. Ibrahim, and M.F. El-Kady. 2010. "Adsorption Equilibrium, Kinetics and Thermodynamics of Methylene Blue from Aqueous Solutions using Biopolymer Oak Sawdust Composite". *Journal American Science*. 6(6):267–283.
3. Agiri, G.O. and O. Akaranta. 2009. "Adsorption of Metal Ions by Dye Treated Cassava Mesocarp". *Scientific Research and Essay*. 4(5):526-530.
4. Akar, T., S. Tunali, and A. Çabuk. 2006. "Study on the Characterization of Lead (II) Biosorption by Fungus *Aspergillus parasiticus*". *Applied Biochemistry and Biotechnology*. 136:389- 406.
5. Arias, F. and T.K. Sen. 2009. "Removal of Zinc Metal Ion (Zn²⁺) from its Aqueous Solution by Kaolin Clay Mineral: A Kinetic and Equilibrium Study". *Colloids and Surfaces. A*. 348:100–108.
6. Babarinde, N.A.A., J.O. Babalola, A.O. Ogunfowokan, and A.C. Onabanjo. 2009. "Kinetic, Equilibrium and Thermodynamic Studies of the Biosorption of Cadmium (II) from Solution by *Stereophyllum radiculosum*". *Toxicological and Environmental Chemistry*. 91(5):911-922.
7. Babarinde, N.A.A. and J.O. Babalola. 2010. "Kinetic, Equilibrium and Thermodynamic Studies of the Biosorption of Cd(II) and Pb(II) from solutions using Siam leaf (*Chromolaena odorata*)". *International Review of Chemical Engineering*. 2(1):18-24.
8. Babarinde, N.A.A., J.O. Babalola, J. Adegoke, U. Maraizu, T. Ogunbanwo, and F. Ogunjinrin. 2012a. "Kinetic, Equilibrium and Thermodynamic Studies of the Biosorption of Ni(II), Cr(III), and Co(II) from Aqueous Solutions using Banana (*Musa acuminata*) Leaf". *International Journal of Physical Science*. 7(9):1376 – 1385.
9. Babarinde, N.A.A., J.O. Babalola, J. Adegoke, A.O. Osundeko, B.O. Orhewere, O.E. Sanya, and C.O. Olayinka. 2012b. "Biosorption of Ni(II), Cr(III) and Co(II) from Solutions using *Acalypha wilkesiana* leaf: Equilibrium, Kinetics and Thermodynamics". *Pacific Journal of Science and Technology*. 13(2):261-271.
10. Babarinde, N.A.A., J.O. Babalola, J. Adegoke, A.O. Osundeko, T.J. Ibadapo, C. Nwabugwu, and V. Ogundimu. 2012c. "Biosorption of Ni(II), Cr(III) and Co(II) from Aqueous Solutions using Cocoyam (*Colocasia esculenta*) Leaf: Kinetic, Equilibrium and Thermodynamic Studies". *Pacific Journal of Science and Technology*. 13(2):272-282.
11. Bueno, B.Y.O., M.L. Torem, F. Molina, and L.M.S. de Mesquita. 2008. "Biosorption of Lead(II), Chromium (III), and Copper (II) by *R. opacus*: Equilibrium and Kinetic Studies". *Mineral Engineering*. 21:65-75.
12. El-Said, A.G. 2010. "Biosorption of Pb(II) Ions from Aqueous Solutions Onto Rice Husk and its Ash". *Journal of American Science*. 2010:6(10).

13. Ertugay, N. and Y.K. Bayhan. 2008. "Biosorption of Cr(VI) from Aqueous Solutions by Biomass of *Agaricus bisporus*". *Journal of Hazardous Materials*. 154:432- 439.
14. Horsfall, M., Jr., A.A. Abia, and A.I. Spiff. 2003. "Removal of Cu (II) and Zn (II) Ions from Wastewater by Cassava (*Manihot esculenta* Cranz) Waste Biomass". *African Journal of Biotechnology*. 2(10):360-364.
15. Kielland, J.1937. "Effective Diameters of Un-hydrated and Hydrated Ions". *Journal of American Chemical Society*. 59:1675-1678.
16. Kurniawan, A., A.N. Kosasih, J. Febrianto, Y.H. Ju, J. Sunarso, N. Indraswati, and S. Ismadji. 2011. "Evaluation of Cassava Peel Waste as Low Cost Biosorbent for Ni-Sorption: Equilibrium, Kinetics, Thermodynamics, and Mechanism". *Chemical Engineering Journal*. 01/2011; 172:158-166.
17. Miranda, M.A, P. Dhandapani, M.H. Kalavathy, and L.R. Miranda. 2010. "Chemically Activated *Ipomoea carnea* as an Adsorbent for the Copper Sorption from Synthetic Solutions". *Adsorption*. 16:75–84.
18. Pradhan, S., S. Singh, and L.C. Rai. 2010. "Characterization of Various Functional Groups Present in the Capsule of *Microcystis* and study of their Role in Biosorption of Fe, Ni and Cr". *Bioresource Technology*. 98:595-601.
19. de la Rosa, G., H.E. Reynel-Avila, A. Bonilla-Petriciolet, I. Cano-Rodríguez, C. Velasco-Santos, R. Martínez-Elangovan, L. Pilip, and K. Chandraraj. 2008. "Biosorption of Chromium Species by Aquatic Weeds: Kinetics and Mechanism Studies". *Journal of Hazardous Materials*. 152:100-12.
20. Sun, X.F., S.G. Wang, X.W. Liu, W.X. Gong, N. Bao, B.Y. Gao, and H.Y. Zhang. 2008. "Biosorption of Malachite Green from Aqueous Solutions onto Aerobic Granules: Kinetic and Equilibrium Studies". *Bioresource Technology*. 99:3475 – 3483.
21. Uluozlu, O.D., A. Sari, and M. Tuzen. 2010. "Biosorption of Antimony from Aqueous Solution by Lichen (*Physcia tribacia*)". *Chemical Engineering Journal*. 163:382-388.
22. Vijayaraghavan, K., T.V.N. Padmesh, K. Palanivelu, and M. Velan. 2006. "Biosorption of Nickel (II) Ions onto *Sargassum wightii*: Application of Two-Parameter and Three-Parameter Isotherm Models". *Journal of Hazardous Materials B*. 133: 304-308.
23. Vimonses, V., S. Lei, B. Jin, C.W.K. Chow, and C. Saint. 2009. "Kinetic Study and Equilibrium Isotherm Analysis of Congo Red Adsorption by Clay Materials". *Chemical Engineering Journal*. 148:354–364.
24. Wu, Y., L. Zhang, C. Gao, X. Ma, and R. Han. 2009. "Adsorption of Copper Ions and Methylene Blue in a Single and Binary System on Wheat Straw". *Journal of Chemical Engineering Data*. 54:3229-3234.

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