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Comparative study on batch equilibrium biosorption of Cd(II), Pb(II) and Zn(II) using plantain (*Musa paradisiaca*) flower: kinetics, isotherm, and thermodynamics

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ABSTRACT

The potential of plantain (*Musa paradisiaca*) flower to remove Cd(II), Pb(II) and Zn(II) from aqueous solutions has been investigated under different process parameters like pH, contact time, biomass dose and initial metal ion concentration. The optimum pH for the biosorption of each of the metal ions is pH 6. The kinetic data obtained were subjected to four kinetic models, among which the pseudo-second order kinetic model was found to be the best model that describes the biosorption of each of the metal ions. The equilibrium sorption data were fitted into Langmuir, Freundlich, Temkin and D-R isotherms. In each case, the Freundlich isotherm model gave the best fit giving the sorption intensity (n) values of 1.17, 0.91 and 0.90 which indicate favourable sorption of Cd(II), Pb(II) and Zn(II), respectively. The heat of the sorption process was estimated from Temkin Isotherm model and the mean free energy was estimated from D-R isotherm model to be 312.81Jmol^{-1} , 223.61Jmol^{-1} and 316.55Jmol^{-1} for Cd(II), Pb(II) and Zn(II), respectively. Thermodynamically, the biosorption of each of the metal ions is endothermic and the order of spontaneity of the biosorption process being $\text{Cd(II)} > \text{Zn(II)} > \text{Pb(II)}$. Similarly, positive change in entropy was observed for each, the order of disorderliness is $\text{Cd(II)} > \text{Zn(II)} = \text{Pb(II)}$.

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Capsule Summary: Plantain flower was investigated for the sorption of Cd(II), Pb(II), and Zn(II), process variables were optimized, sorption data was subjected to kinetic and isotherm models, and thermodynamic studies were also performed. Results showed that plantain has high potential for the sorption of Cd(II), Pb(II), and Zn(II) and could possibly be used for treating wastewater containing these metal ions.

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INTRODUCTION

The contamination of the environment by heavy metals has received much attention worldwide recently. Waste water from industries represents the major source of heavy metals

pollution of the environment. This is one of the most serious challenges facing the world today. This is because heavy metals are highly toxic, non-biodegradable, and tend to accumulate causing different health problems in living organisms (Jafarinejad, 2016a; Jafarinejad, 2016b; Jamal et al., 2015; Majolagbe et al., 2016; Pandey et al., 2016a, b; Peter

and Chinedu, 2016; Qureshi et al., 2015; Sayed, 2015; Shindy, 2016; Ukpaka, 2016a; Ukpaka et al., 2015; Ukpaka, 2016b, c; Ukpaka, 2016d; Ukpaka, 2016e). The extent of the wide spread of heavy metal has become a major threat to plant, animal and human life due to their bioaccumulation tendency and toxicity. Therefore, heavy metal should be removed from industrial waste waters before they are discharged into the ambient environment. Heavy metals can damage liver and nerves and block functional groups of vital enzymes and. Lead and cadmium are considered the most toxic and hazardous to the environment (Abbas et al., 2015; Awwad et al., 2013; Bilal et al., 2016a; Bilal et al., 2016b; Bilal et al., 2014; Iqbal, 2016; Iqbal et al., 2015; Iqbal and Bhatti, 2014, 2015; Iqbal et al., 2014; Iqbal and Nisar, 2015)

Zinc is a common metal ions found in effluents of a large number of industries. This metal is an essential element for life and is a micronutrient in trace amounts (Bhattacharya et al., 2006). However, a chronic exposure to Zn ion is detrimental for human health. At elevated level, zinc can cause damage to the pancreas, upset protein metabolism and cause arteriosclerosis. Consequently, there is a need to reduce zinc concentrations in waste water to acceptable levels. The toxicological profile of this pollutant has been well documented in literature and its presence in water and wastewaters is a potential risk for the environment and public health (Bhattacharya et al., 2006; Mishra and Patel, 2009).

A wide range of conventional treatment techniques such as chemical precipitation, coagulation, solvent extraction, electrolytic processes, membrane separation, ion-exchange, reverse osmosis, and ultra-filtration have been reported to be used for removal of heavy metal ions from industrial effluents. However, these processes are not economical due to huge capital investment. The disadvantages of these conventional methods like incomplete metal removal, expensive cost, time consumption, ineffectiveness, high reagent and energy requirements, generation of toxic sludge and so on, have made it imperative to search for alternative methods that have low cost, simple and sludge free, and environmentally friendly. However, adsorption has been universally accepted as one of the most effective pollutant removal processes, with low cost, ease in handling, low consumption of reagents, as well as scope for recovery of value added components through desorption and regeneration of adsorbent (Gode and Petilivan, 2005; Igwe and Abia, 2006; Abdel-Ghani et al., 2007; Subramanyam and Das, 2009, Babarinde and Babalola, 2008, 2009, 2013).

Another advantage of this sorption technique is the use of waste to clean up another waste hence resulting to environmental sustainability (Abasi, 2011). A notable and growing trend is to evaluate the feasibility and suitability of natural, viable, renewable and low-cost materials which will be used as adsorbent to combat the menace of heavy metal pollution. Plantain peel has been reported to effective in the sorption of Pb(II) and Cd(II) (Adesola et al., 2016; Asiagwu, 2012; Babarinde and Onyiaocha, 2016; Bhatti et al., 2016; Iqbal and Khera, 2015; Islam et al., 2015; Manzoor et al.,

2013; Mushtaq et al., 2016; Nadeem et al., 2016; Rashid et al., 2016; Tahir et al., 2016; Ullah et al., 2013; Younas et al., 2015).

The main objectives of the present study were to determine the capacity of plantain flower (PF) for sorption of Cd(II), Pd(II) and Zn(II) from solution and to determine the optimum values of the physicochemical parameters which influence the sorption process. The sorption of these metal ions by different biosorbents has been reported but none utilized PF, which is an agricultural waste found in different tropical regions of the world.

MATERIAL AND METHODS

Instrumentation

The analysis of the metal ions was carried out using a flame atomic absorption spectrophotometer (FAAS) equipped with a flame burner. The concentration before and after biosorption of each metal ion was determined using a Perkin-Elmer analyst 700 (FAAS) with deuterium background corrector. Operational parameters for the metals under study were those recommended by the manufacturer. All the metals were measured under optimised operating conditions by FAAS with an air-acetylene flame. Fourier Transform Infrared (FTIR) spectra of dried unloaded biomass and metal loaded biomass were recorded at 400-4000 cm^{-1} , using a Shimadzu FTIR model 8400 S spectrophotometer.

Preparation of biosorbent

PF used in the present study was collected from a farm at Olabisi Onabanjo University, Ago-Iwoye, Nigeria. The sample was thoroughly rinsed with distilled water to remove dust and other impurities. The PF was dried in a hot oven and kept dried till time of usage.

Standard solution and reagents

All chemical used in this study were of analytical grade. Standard solutions of Cd(II), Pb(II) and Zn(II) used for this study were prepared from $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, respectively. The working standard solutions were prepared daily by stepwise dilution of stock solutions. Adjustment of the solution pH was done using 0.1M HNO_3 and 0.1M NaOH . Synthetic samples of different concentrations of Cd(II), Pb(II), and Zn(II) were prepared from this stock solution by appropriate dilutions. 100 mgL^{-1} of each metal ion was prepared by diluting 100 ml of 1000 mgL^{-1} of stock solution with distilled water. 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.

FT-IR analysis

The functional groups present on the surface of PF would give insight to the biosorption capacity of the biomass.

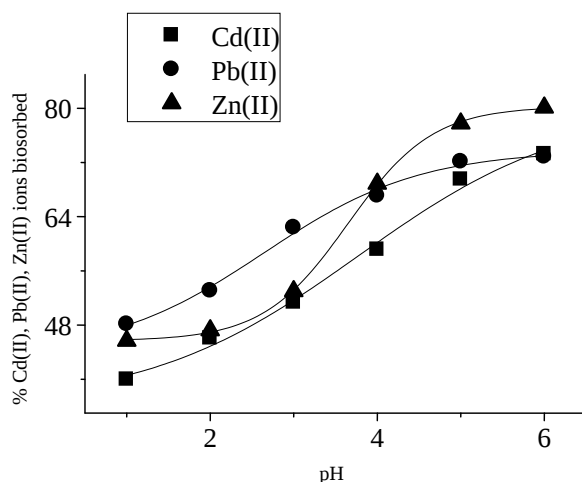


Fig 1: pH dependence profile for the biosorption of Cd(II), Pb(II), and Zn(II) onto PF (dosage of PF: 0.5 g; concentration of metal ions: 100 mgL⁻¹; pH: 6.0).

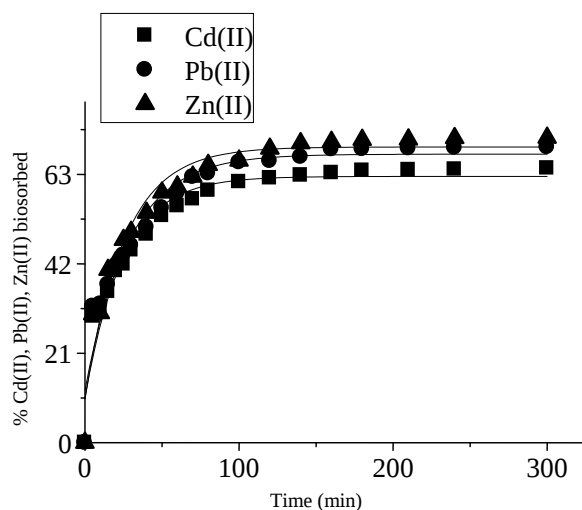


Fig. 2 Time course of the biosorption of Cd(II), Pb(II), and Zn(II) using PF (dosage of PF: 0.5 g; concentration of metal ions: 100 mgL⁻¹; contact time: 5 h; pH 6.0).

These groups would form active sites for sorption on the biomass. Therefore, the FT-IR spectra of dried unloaded, Cd-loaded, Pb-loaded and Zn-loaded PF were taken to obtain information on the nature of possible interactions between the functional groups of plantain flower and the metal ions.

Batch biosorption studies

The biosorption study was carried out batchwise by contacting 0.5g of the PF with 25 ml of each metal ion solution under different conditions for a predetermined time in a glass tube. The biosorption studies were conducted at 25°C using thermostated water bath to determine the effect of pH, contact time, biosorbent dosage, initial metal ion concentration and temperature on the biosorption of each of the metal ions. The residual metal ions were analyzed using FAAS. The amount of metal ion biosorbed from solution was determined by difference.

Statistical analyses

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

RESULTS AND DISCUSSION

FT-IR studies of unloaded and metal-loaded PF

FT-IR spectra of the biosorbent before and after biosorption of the metal ions were recorded in the range 4000 - 400 cm⁻¹. The FT-IR spectra of dried unloaded and metal-loaded plantain flower were taken to obtain information on the nature of possible interactions between the functional groups of PF biomass and the metal ions. The FT-IR spectra pattern of the biomass showed distinct and sharp absorptions indicative of the existence of the functional groups. These bands are due to the functional groups of PF 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 Table 1. The FT-IR spectra of the PF 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 imply 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 such as C=O, O-H, and C≡N which interacted with cations (Bueno et al., 2008; Ertugay and Bayhan, 2008; Pradhan et al., 2007; Sun et al., 2008; Uluozlu et al., 2010). This implies that these functional groups would serve in the removal of positively charged ions from solution.

Effect of solution pH on biosorption

The effect of pH on the biosorption of each metal ion onto PF was investigated by varying the pH of the metal solution from 1.0 to 6.0. The initial pH values of the metal solutions were adjusted before mixing with the biosorbent. This was done by contacting 0.5g of PF with 25ml of 100 mgL⁻¹ of each of the solutions in glass tubes suspended in a water bath. The pH of each solution was adjusted to the desired value using a pH meter by drop wise addition of 0.1M HNO₃ and/or 0.1M NaOH. The biomass was removed from the solution by decantation at the specified time and the residual metal ion concentration in the solution was analyzed. Fig. 1 shows the pH dependence profile for the biosorption of the metal ions. In each case, as pH increases, the amount of metal ions uptake increases. The effect of pH on the biosorption of

Table 1: FT-IR Spectra characteristics of PF before and after biosorption of Cd(II), Pb(II) and Zn(II) for 4 hours.

Metal ions	Absorption bands (cm ⁻¹)			Assignment
	Before	After	Difference	
Cd(II)	3759.10	3759.10	0	O-H Stretching
Pb(II)		3759.10	0	O-H Stretching
Zn(II)		3759.10	0	O-H Stretching
Cd(II)	2360.00	2360.08	-0.08	C≡N stretching
Pb(II)		2364.14	-4.14	C≡N stretching
Zn(II)		2364.14	-4.14	C≡N stretching
Cd(II)	1630.60	1629.45	1.15	C=O stretching
Pb(II)		1631.00	-0.4	C=O stretching
Zn(II)		1629.74	0.86	C=O stretching
Cd(II)	3432.26	3435.00	-2.74	O-H Stretching
Pb(II)		3435.73	-3.47	O-H Stretching
Zn(II)		3431.21	1.05	O-H Stretching

Table 2: Kinetic parameters for the biosorption of Cd(II), Pb(II) and Zn(II) onto plantain flower at 100 mgL⁻¹

Kinetic model	Parameters	Cd(II)	Pb(II)	Zn(II)
Pseudo-first-order	q _e (mgg ⁻¹)	39.90	43.16	48.81
	k ₁ (min ⁻¹)	2.5 x 10 ⁻²	2.3 x 10 ⁻²	2.5 x 10 ⁻²
	R ²	0.997	0.984	0.988
Pseudo-second-order	q _e , cal(mgg ⁻¹)	67.16	72.73	74.96
	k ₂ (g mg ⁻¹ min ⁻¹)	1.35 x 10 ⁻³	1.11 x 10 ⁻³	1.11 x 10 ⁻³
	R ²	0.999	0.998	0.998
Elovich	A	11.05	9.60	8.97
	B	10.22	11.40	12.00
	R ²	0.956	0.953	0.959
Intraparticle diffusion	K _d (mgg ⁻¹ min ^{-1/2})	22.20	22.67	23.18
	B	0.21	0.22	0.22
	R ²	0.937	0.942	0.943

Cd(II), Pb(II) and Zn(II) ion was carried out within pH 1- 6 in order to avoid the formation of metal hydroxides, which could occur at pH > 6.5 (Pavasant et al., 2006).

The optimum pH was determined as the pH with the highest biosorption of each metal ion. The pH of the solutions has been identified as the most important variable governing metal adsorption. This is partly due to the fact that hydrogen ions (H⁺) themselves are strong competing ions and partly that the solution pH influences the chemical speciation of the functional groups on to the biosorbent surface. Biosorption process occurs by means of adsorption, ion exchange, and covalent binding with the biosorptive sites of the biomass cell wall. The cell wall has hydroxyl, carboxyl, and cyano functional groups. The solution pH can change the solubility

of metal ions and the ionization state of the functional groups on the biomass cell wall (Bayramoğlu et al., 2003). The main cell wall constituents of PF used in this study have carbonyl, hydroxyl and amino functional groups. The negative charges of functional groups, carboxylate and phosphate provide the biosorption of metal ions (Say et al., 2001).

The maximum uptake was observed at pH of 6.0 for the three metal ions. The hydrogen ions compete with metal ions for the exchange sites in the system at low pH value. In each case, the low biosorption capacity at lower pH is attributed to hydrogen ions. On the other hand, at low pH values, biosorbent cell wall ligands are saturated with the hydronium ions, and repulsive forces prevent the effective

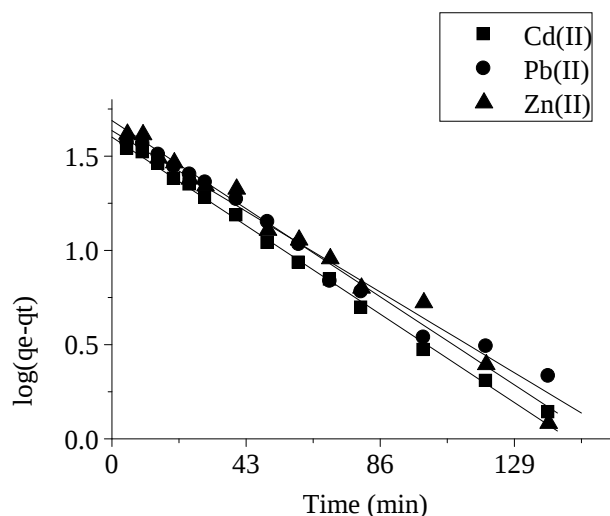


Fig 3: Pseudo-first-order plot for the biosorption of Cd(II), Pb(II), and Zn(II) onto PF.

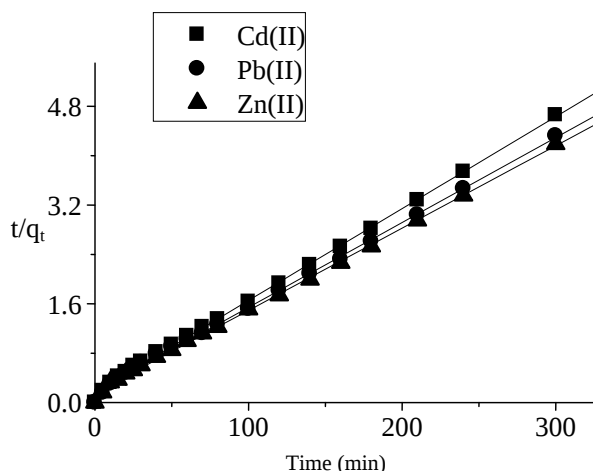


Fig. 4: Pseudo-second-order plot for the biosorption of Cd(II), Pb(II), and Zn(II) using PF.

biosorption of metal ions on the cell wall (Kalyani et al., 2004).

Biosorption kinetics

Biosorption kinetics was investigated in order to have a good understanding of the dynamics of the biosorption process. The biosorption of the metal ions onto PF was studied at various time intervals (0-300 min) and at the concentration of 100 mgL⁻¹. The kinetics of sorption is an important factor in predicting the rate at which sorption takes place for a given system and also very essential in understanding the

mechanism of the process. However, sorption kinetics shows a large dependence on the physical and/or chemical characteristics of the sorbent material, which also influences the sorption process and the mechanism.

The equilibrium time required for biosorption of Cd(II), Pb(II) and Zn(II) on PF obtained by studying biosorption of each metal ion at various contact times. The study of biosorption kinetics describes the solute uptake rate and evidently these rate controls the residence time of biosorbate uptake at the solid/solution interface. The kinetic study for the biosorption of Cd(II), Pb(II) and Zn(II) were conducted at optimum pH 6.0 for the three metal ions, where maximum biosorption took place. Fig. 2 shows the effect of contact time of Cd(II), Pb(II) and Zn(II) on PF. The data obtained from the biosorption of the three metal ions onto PF showed that the biosorption increased with increasing contact time. It can be seen that the biosorption process occurred very rapidly within the first 5 min before equilibrium was reached at 240 min. The fast initial uptake occurred in the early stage of the biosorption was due to the fact that most of the binding sites on PF were free which allowed quick binding of the metal ions on the biomass (Gupta *et al.*, 2008). No further increase in the level of bound metal ions after 120 min, hence it was taken as the equilibrium time for biosorption process.

The biosorption data were evaluated with four different kinetic models: pseudo-first order, pseudo-second order, Elovich and intra-particle diffusion kinetic models.

The pseudo first order was studied with Lagergren equation which considers that the rate of occupation of the biosorption site is proportional to the number of the unoccupied sites (Ertugay and Bayhan, 2008). The pseudo first-order equation is derived from the rate law as shown in equations (1) to (5) below.

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

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

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

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 (min⁻¹) is the rate constant of pseudo first-order biosorption rate constant, q_e and q_t are amounts of metal ion biosorbed (mgg⁻¹) on biosorbent at equilibrium, and at

time t (s), respectively. The rate constants, k_1 , was calculated from the plots of $\log (q_e - q_t)$ versus t for each metal ion as shown in Fig. 3. The kinetic parameters are presented in Table 2.

The pseudo-second order kinetic model based on adsorption equilibrium capacity can be expressed as (Ho *et al.*, 2000):

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

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 pseudo-second order rate constant ($\text{mgg}^{-1}\text{min}^{-1}$). The experimental and calculated values of q_e showed a good agreement. The correlation coefficients for the pseudo-second order kinetic model were higher than 0.99, and there was good agreement between experimental and calculated values of equilibrium biosorption capacity (q_e) indicating the applicability of this kinetic model for the biosorption process of Cd(II), Pb(II) and Zn(II) onto PF.

However, plots of t versus t/q_t showed good fitness of experimental data with the pseudo-second-order kinetic model as presented in Fig. 4. The kinetic parameters are presented in Table 2.

The data were equally analysed with the Elovich kinetic model given by

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

Where, q_t is the amount (mgL^{-1}) of metal ion biosorbed after a given time t .

Where A and B are the Elovich constants corresponding to the extent of surface coverage and rate of sorption at zero coverage, respectively. These constants were determined from the linear plot of q_t versus $\ln t$ as shown in Fig. 5 and the kinetic parameters are presented in Table 2.

The intra-particle diffusion kinetic model was also employed by using the intra-particle diffusion from the following equation:

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

Apart from outer surface adsorption, there is also the possibility of intraparticle diffusion from the outer surface into the pores of the materials. The adsorption mechanism of a sorbate onto the adsorbent follows three steps viz: film diffusion, pore diffusion and intraparticle transport (Pant and Sing, 2004). In a rapidly stirred batch adsorption, the

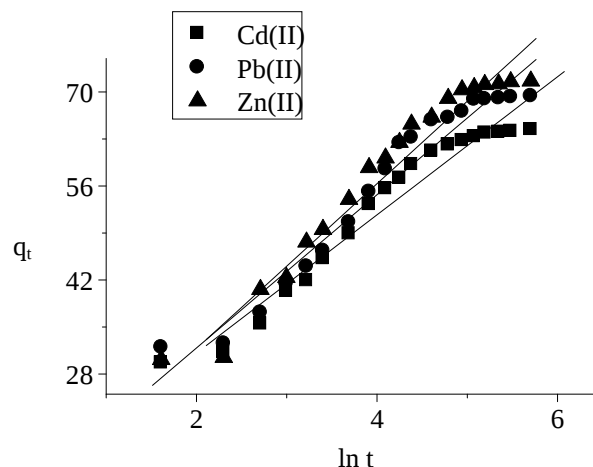


Fig. 5: Elovich-graph for the biosorption of Cd(II), Pb(II), and Zn(II) onto PF.

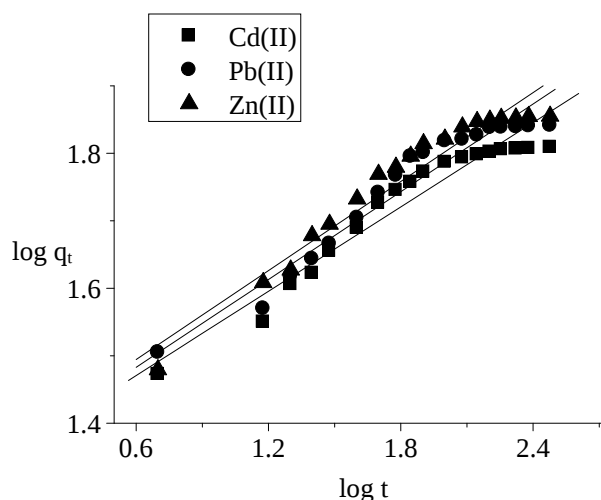


Fig. 6: Intraparticle kinetic plot for the biosorption of Cd(II), Pb(II), and Zn(II) onto PF.

diffusive mass transfer can be related by an apparent diffusion coefficient which will fit the experimental sorption rate data. Generally, a process is diffusion controlled if it is dependent upon the role at which components diffuse towards one another. The possibility of intra particle diffusion was explored by using the intra particle diffusion model. The intraparticle diffusion equation has been used to indicate the behaviour of intraparticle diffusion as the rate limiting step in the biosorption process. R is the percent metal ions biosorbed, K_d ($\text{mgg}^{-1}\text{min}^{-1/2}$) is the intraparticle diffusion rate constant, t is the contact time, while b is the

gradient of the linear plot. In the linear form, equation (10) turns to Eq. 11.

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

The Intraparticle kinetic plot is presented in Fig. 6 while the kinetic parameters are presented in Table 2.

The results presented in Table 2 show that the value of R^2 was highest for the pseudo-second-order kinetics, hence the best kinetic model for the biosorption process in the sorption of these metal ions by plantain flower.

Effect of biomass dosage on biosorption

The biomass dose is an important parameter in biosorption studies because it determines the capacity of adsorbent for a given initial concentration of metal ion solution. The effect of biomass dosage on biosorption efficiency is reported in Fig. 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. This is due to the facts that increase in biomass dosage tends to increase the number of active sites available for biosorption. As expected, at initial concentration of metal ions, increasing the sample dose provides a greater surface area and larger number of sorption sites and hence enhancement of metal ion uptake. Hence, the amount of metal ions available for biosorption per gram of biosorbent will be less when the amount of biosorbent is increased. The difference in 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.

Biosorption isotherms

Equilibrium studies were also carried out as another way to simulate the metal uptake by the biomass, just as the kinetic studies. The purpose of the equilibrium studies is to relate the adsorbate concentration in the bulk solution and the amount adsorbed at the interface. The analysis of the isotherm data is important to develop an equation which accurately represents the results and which could be used for the design purpose. The modelling of the biosorption process on PF was obtained by using different biosorption isotherms. In order to clarify the biosorption isotherms, Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich equations were employed.

The Freundlich Isotherm model is an empirical equation describing adsorption onto a heterogeneous surface. The Freundlich model was chosen to estimate the adsorption intensity of the sorbate on the sorbent surface. The Freundlich isotherm is expressed as

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

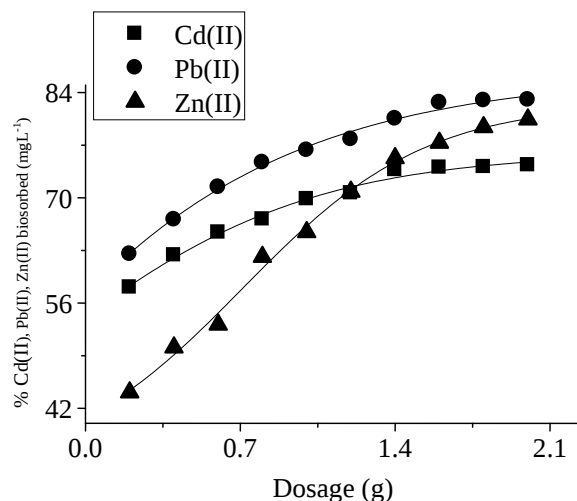


Fig 7: Effect of biomass dosage on the biosorption of Cd(II), Pb(II) and Zn(II) using PF (pH6.0; T= 25°C; t= 4 h).

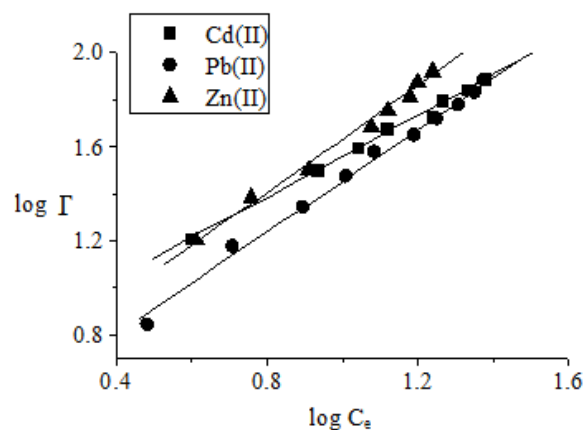


Fig. 8: Freundlich isotherm for the biosorption of Cd(II), Pb(II) and Zn(II) onto PF.

Where, K_f and n are empirical Freundlich constants, and indicative of adsorption capacity and adsorption intensity, respectively. C_e is equilibrium concentration of metal ion in solution (mol L^{-1}). Fig. 8 illustrates the biosorption isotherm of Cd(II), Pb(II) and Zn(II) ions onto PF. The equilibrium biosorption capacity, q_e , increases with increase in initial metal ions concentration. The higher K_f value of Cd(II) above that of Pb(II) and Zn(II) suggests that Cd(II) had a greater affinity towards the PF than either of Pb(II) and Zn(II). The isotherm parameters are presented in Table 3.

The Langmuir Isotherm model was employed for the estimation of maximum adsorption capacity corresponding to complete monolayer coverage on the biomass surface. It was used to describe observed sorption phenomena and suggests that uptake occurs on a homogenous surface by

monolayer sorption without interaction between adsorbed molecules. The linear form of the Langmuir equation is expressed as

$$\frac{1}{q_e} = \frac{1}{q_{\max}} \frac{1}{K_L C_e} + \frac{1}{q_{\max}} \quad (13)$$

Where, C_e is the equilibrium concentration of metal ion (mgL^{-1}), q_e is the amount of metal ion biosorbed per specific amount of biosorbent (mgg^{-1}), $q_{\max}$ is the maximum biosorption capacity (mgg^{-1}), and K_L is an equilibrium constant (Lmg^{-1}) related to energy of biosorption which quantitatively reflects the affinity between the biosorbent and the biosorbate. Where $q_{\max}$ and K_L can be determined from the linear plot of $1/q_e$ versus $1/C_e$. The shape of the Langmuir isotherm can be used to predict whether a sorption is favourable or unfavourable in a batch biosorption process. The essential features of the isotherm can be expressed in terms of a dimensionless constant separation factor, R_L , which is defined (Anirudhan and Radhakrishnan, 2008) as shown in Eq. 14.

$$R_L = \frac{1}{1 + K_L C_i} \quad (14)$$

Where, C_i is the initial concentration (mgL^{-1}) and K_L is the Langmuir equilibrium constant (Lmg^{-1}). The value of the separation factor, R_L , provides vital information about the nature of biosorption. The value of R_L implies the type of Langmuir isotherm to be reversible ($R_L=0$), favourable ($0 < R_L < 1$), linear ($R_L=1$), or unfavourable ($R_L > 1$) (Das and Mondal, 2011). The Langmuir isotherm is presented in Fig. 9 while the evaluated constants are given in Table 3.

The value of K_L for the three metal ions are in the order $\text{Cd(II)} > \text{Zn(II)} > \text{Pb(II)}$ as presented in Table 3.

The Temkin Isotherm model was also used to fit the experimental data. Unlike the Langmuir and Freundlich, the Temkin isotherm takes into account the interactions between biosorbents and metal ions to be biosorbed and it is based on the assumption that the free energy of sorption is a function of the surface coverage (Chen *et al.*, 2008). The linear form of the Temkin isotherm is represented in Eq. 15.

$$q = B \ln A + B \ln C_e \quad (15)$$

Where, C_e is concentration of the biosorbate at equilibrium (mgL^{-1}), q_e is the amount of adsorbate adsorbed at equilibrium (mgg^{-1}). $B = RT/b_T$, where T is the temperature (K) and R is the ideal gas constant ($8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$), A and b_T are constants. A plot of q_e versus $\ln C_e$ enables the determination of constants A and b_T . The constant B is related to the heat of adsorption and A is the equilibrium binding constant (Lmin^{-1}) corresponding to the maximum binding energy.

The Temkin isotherm is presented in Fig. 10 while the evaluated constants are given in Table 3.

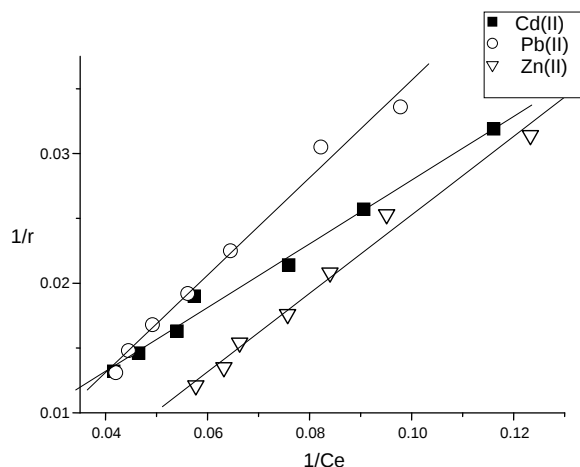


Fig. 9: Langmuir isotherm for biosorption of Cd(II), Pb(II) and Zn(II) onto PF.

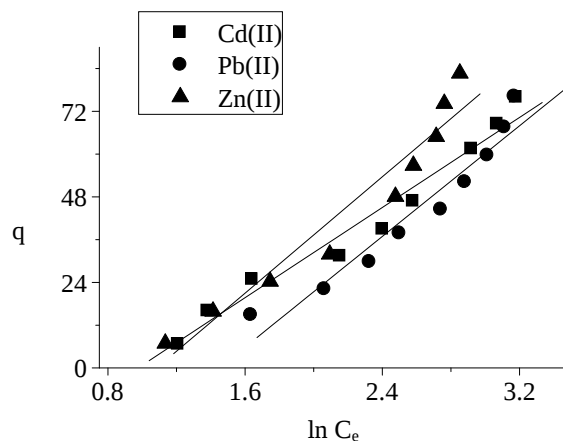


Fig. 10: Temkin isotherm for the biosorption of Cd(II), Pb(II) and Zn(II) by PF.

The Dubinin-Radushkevich (D-R) isotherm model was used to estimate the heterogeneity of the surface energies. The Dubinin-Radushkevich (D-R) isotherm approach assumes that there is a surface area where the adsorption energy is homogeneous. The D-R isotherm equation is linearly represented as;

$$\ln q = \ln q_m - \beta \varepsilon^2 \quad (16)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (17)$$

Where, q_m is the theoretical saturation capacity (molg^{-1}), β is a constant related to the mean free energy of adsorption per mole of the adsorbate ($\text{mol}^2 \text{ J}^{-2}$), and ε is the polanyi potential,

C_e is the equilibrium concentration of adsorbate in solution (mol/L), R ($\text{Jmol}^{-1}\text{K}^{-1}$) is the gas constant and T (K) is the absolute temperature. The D-R constants q_m and β were calculated from the linear plots of $\ln q_e$ versus ε^2 of Fig. 11 are presented in Table 3. The constant β gives an idea about the mean free energy E (Jmol^{-1}) of biosorption per molecule of the biosorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated from the relationship shown in Eq. 18 (Kundu and Gupta, 2006)

were found to be highest for the Freundlich isotherm and were found to be in excess of 0.995, 0.994 and 0.992 for Cd(II), Pb(II) and Zn(II) respectively. The Freundlich isotherm is therefore, the best isotherm to predict the dynamic biosorption of Cd(II), Pb(II) and Zn(II) ions onto PF. The value of E is less than 1 kJmol^{-1} for each metal ion implying that each metal biosorption process proceeded via physisorption.

Table 3: Isothermal parameters for the biosorption of Cd(II), Pb(II) and Zn(II) onto plantain flower at 100 mgL^{-1}

Isotherm	Parameters	Cd(II)	Pb(II)	Zn(II)
Freundlich	n	1.17	0.91	0.90
	$K_f (\text{mgg}^{-1})(\text{Lmg}^{-1})^{1/n}$	4.98	3.30	3.30
	R^2	0.995	0.994	0.992
Langmuir	$q_{\text{max}}(\text{mgg}^{-1})$	192.31	-144.72	-847.46
	$K_L(\text{L mg}^{-1})$	4.68	2.28	3.96
	R^2	0.970	0.985	0.979
Temkin	A	-31.91	-55.63	-44.83
	$B(\text{mgg}^{-1})$	32.04	38.64	40.92
	R^2	0.966	0.933	0.937
D-R	$q_m (\text{mgg}^{-1})$			
	$\beta(\text{mol}^2\text{J}^{-2})$	5.11×10^{-6}	1.0×10^{-5}	4.99×10^{-6}
	$E(\text{Jmol}^{-1})$	312.81	223.61	316.55
	R^2	0.957	0.918	0.944

Table 4: Thermodynamic parameters for the biosorption of Cd(II), Pb(II) and Zn(II) onto PF

Metal ion	ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1}\text{K}^{-1}$)	R^2	A (kJmol^{-1}) @ (303K)	A (kJmol^{-1}) @ (318K)
Cd(II)	20.82	+79.99	0.994	2.54	2.66
Pb(II)	12.88	+52.28	0.991	2.53	2.66
Zn(II)	12.90	+52.84	0.990	2.53	2.66

$$E = \frac{1}{\sqrt{2\beta}} \quad (18)$$

If the magnitude of E is between 8 and 16 kJmol^{-1} , the sorption process is supposed to proceed via chemisorption but if E is less than 8 kJmol^{-1} , the sorption process is of physical nature (Kundu and Gupta, 2006).

The isotherm constants were determined from linear isotherm plot for each of the equations tested. The values of the isotherm constants with the correlation coefficients are given in Table 3. On comparison of the values of R^2 for the experimental points, the correlation coefficients obtained

Biosorption efficiency

The biosorption efficiency (E) for each metal ion was calculated as shown in Eq. 19.

$$E = 100 \left(\frac{C_i - C_e}{C_i} \right) \quad (19)$$

Where, C_i and C_e are the initial and the equilibrium metal ion concentrations (mgL^{-1}), respectively. The result of the study

on the effect of initial metal ions concentration on biosorption efficiency is shown in Fig. 12. The plots show that the biosorption efficiency of the PF varies with increase in the initial metal ion concentration which might be due to increase in effective collision between the metal ions and the active sites in the biosorbent having more ions than at lower concentration.

Biosorption thermodynamics

The biosorption of metal ions may involve chemical bond formation and ion exchange since temperature is a major parameter affecting them. The variation of temperature affects the biosorption of Cd(II), Pb(II) and Zn(II) ions onto solid surfaces of PF 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 favoured by increase in temperature while the contrary holds for the exothermic side. The corresponding free energy change was calculated from the relation shown in Eq. 20 (de la Rosa *et al.*, 2008; Sun *et al.*, 2008).

$$\Delta G^\circ = -RT \ln K_c \quad (20)$$

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

$$K_c = \frac{C_{ad}}{C_e} \quad (21)$$

Where C_e and C_{ad} are the equilibrium concentrations of metal ions (mgL^{-1}) in solution and on biosorbent, respectively. Consequently, the thermodynamic behaviour of the biosorption of the metal ions onto PF was evaluated through the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°). The thermodynamic parameters like enthalpy and entropy were obtained using van't Hoff equation (Uluozlu *et al.*, 2010). The change in free energy is related to other thermodynamic properties as shown in Eqs. 22-23.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (22)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (23)$$

Where, T is the absolute temperature (K); R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$). The change in enthalpy and entropy were calculated from the intercept and slope of the plot of T versus ΔG° as presented in Fig. 13 while the thermodynamic parameters are presented in Table 4.

The negative values of ΔG° indicate spontaneity of each biosorption process. The positive value of ΔH° for the biosorption of Cd(II), Pb(II) and Zn(II) suggests endothermic 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 positive values of ΔS° observed for the biosorption of this metal ion indicate an

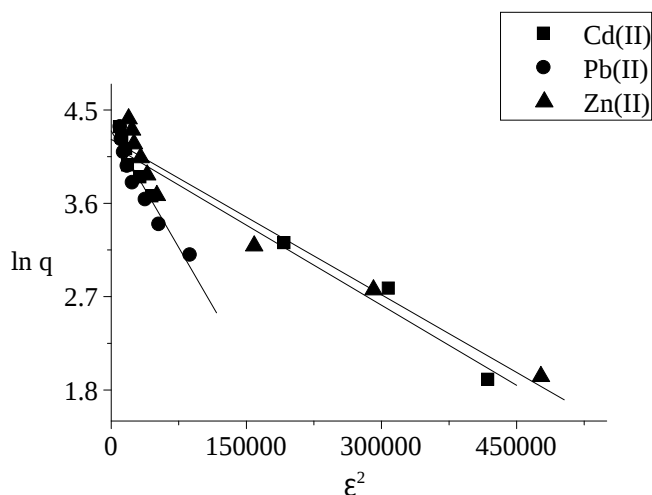


Fig. 11: D-R isotherm for the biosorption of Cd(II), Pb(II) and Zn(II) onto PF.

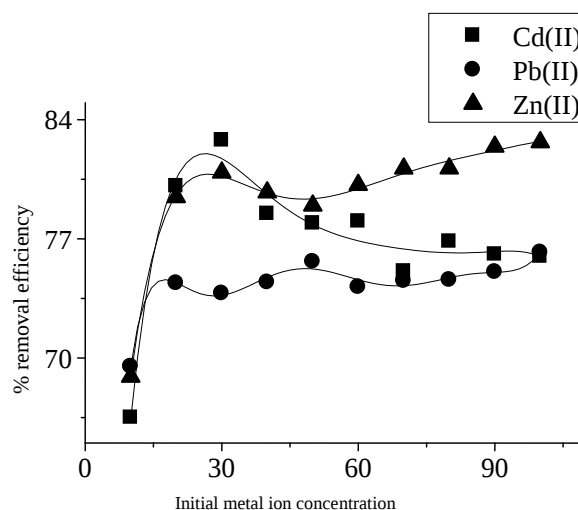


Fig. 12: Percentage efficiency plot for biosorption of Cd(II), Pb(II) and Zn(II) onto PF.

increase in randomness at the solid/solution interface during their biosorption.

Generally, the change of standard free energy for physiosorption is in the range of -20 to 0 kJ mol^{-1} and for chemisorption varies between -80 and -400 kJmol^{-1} (Sen *et al.*, 2011; Vimoses *et al.*, 2009). In the present study, the overall ΔG° has values ranging from -5.5 to -2.4 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 (Arias and Sen 2009; Vimoses *et al.*, 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 (Eq. 24).

$$A = \Delta H^\circ + RT \quad (24)$$

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

Free energy profile

The Gibbs free energy can change with the change of temperature and pressure of the thermodynamic system. The Van's Hoff isotherm can be used to determine the Gibbs free energy for non-standard state reaction at a constant temperature (Eq. 25).

$$\left(\frac{dG}{d}\right)_{T,P} = \Delta_r G + RT \ln Q_r \quad (25)$$

Where, $\Delta_r G$ is the Gibbs free energy for the reaction and Q_r is the reaction quotient. When a reaction is at equilibrium, $Q_r = K_c$. The Van't Hoff isotherm can help estimate the equilibrium reaction shift. When $\Delta_r G < 0$, the reaction moves in the forward reaction. When $\Delta_r G > 0$, the reaction moves in the backward reaction. Free energy profile for biosorption of the three metal ions is presented in Fig. 14.

The results show that the free energy change is dependent on the initial concentration of the metal ions. Thermodynamically, this implies that each biosorption process would be most spontaneous or favoured at concentration with the minimum free energy (Babarinde et al., 2008). So far, results revealed that the heavy metal ions can be removed using biosorption and these findings are in line with previous studies (Bozbaş and Boz, 2016; Bulgariu and Bulgariu, 2016; Masoumi et al., 2016; Mishra et al., 2016; Pepi et al., 2016; Ramrakhiani et al., 2016; Ronda et al., 2016; Venkatesh et al., 2016; Wei et al., 2016; Zhang et al., 2016).

CONCLUSIONS

In this study, batch biosorption studies for the removal of Cd(II), Pb(II) and Zn(II) from aqueous solutions have been carried out using plantain flower as a low cost, readily available biosorbent. The biosorption characteristics have been examined at different pH values, initial metal ion concentrations, contact time and biosorbent dosage. The optimum pH for the biosorption each metal ion was found to be pH 6. Increase in biosorbent dosage leads to increase in

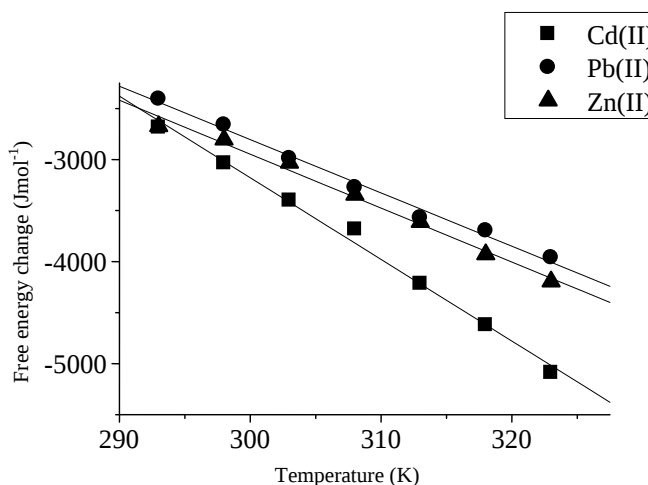


Fig. 13: Free energy change for the biosorption of Cd(II), Pb(II) and Zn(II) onto PF.

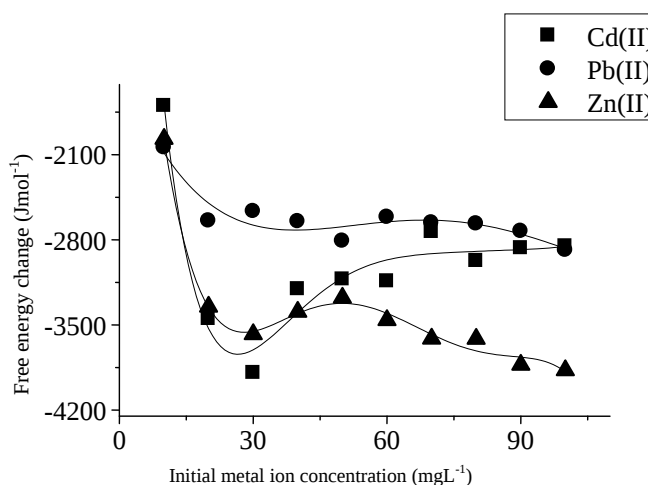


Fig. 14: Free energy profile for biosorption of Cd(II), Pb(II) and Zn(II) onto PF.

metal ion uptake to increased number of biosorption sites. Maximum uptake of the three metal ions was obtained at adsorbent dosage 2.0g. The kinetic studies show that the pseudo-second-order kinetics best describes the biosorption process. Equilibrium studies showed that Freundlich isotherm model were found to provide the best fit of the experimental data.

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