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Comparative study on the biosorption of Pb(II), Cd(II) and Zn(II) using Lemon grass (*Cymbopogon citratus*): Kinetics, isotherms and thermodynamics

Adesola Babarinde*, Kemi Ogundipe, Kikelomo Tobi Sangosanya, Babatunde Damilare Akintola and Aanu-Oluwa Elizabeth Hassan

Department of Chemical Sciences, Olabisi Onabanjo University, Ago- Iwoye, Ogun State, Nigeria
*Corresponding author's E. mail: adesola.babarinde@oouagoiwoye.edu.ng, solababarinde@yahoo.com

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ABSTRACT

A comparative study for the biosorption of Pb(II), Cd(II) and Zn(II) using Lemon grass (*Cymbopogon citratus*) was investigated under various physicochemical parameters. Optimisation studies were carried out using batch biosorption studies. The biosorption of each of the metal ions was found to be pH-dependent. Kinetic study showed that each biosorption process followed the pseudo-second-order kinetic model. The sorption of each metal ion was analysed with Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherm models, in each case, the equilibrium data were best represented by Freundlich isotherm model. Thermodynamic parameters such as standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°), standard entropy (ΔS°) and the activation energy (A) were calculated. The biosorption of each metal ion was spontaneous and the order of spontaneity of the biosorption process being Zn(II) > Cd(II) > Pb(II). Similarly, the change in entropy shows that the order of disorder is Cd(II) > Zn(II) > Pb(II). In each case, the value of activation energy obtained shows that each process is a diffusion-controlled adsorption process.

Capsule Summary: A comparative study for the sorption of Pb(II), Cd(II) and Zn(II) from solution using Lemon grass was carried out, process variables were optimized, sorption data were subjected to kinetic and isotherm models and thermodynamic studies were also performed. Results showed that Lemon grass has high potential for the sorption of the metal ions and could possibly be used for treating wastewater containing metal ions.

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INTRODUCTION

The release of toxic metals into the water bodies causes serious problem because of their persistence in the ecosystem, thereby leading to a high risk to both wildlife and humans. Pb(II), Cd(II) and Zn(II) are heavy metals that have been implicated in causing health challenges such as accumulative poisoning, cancer, brain damage, lung damage, renal damage and even death. Therefore, it is necessary to propose alternative method for the treatment of metal-containing effluents (Manzoor et al., 2013; Ullah et al., 2013). The conventional metal removal technologies are chemical precipitation and filtration, chemical oxidation or reduction, electrochemical treatment, reverse osmosis, ion exchange, adsorption and evaporation (Sari et al., 2008; Uluozlu et al., 2008). Among these, adsorption is by far the most versatile and widely used because of its low cost, simplicity of design, facile operation, and insensitivity to toxic substances (Volesky, 2001). All these methods are, in this case, either economically unfavourable or technically complicated and thus used only in special cases. Each of these methods has some limitations in practice. The problems with the aforementioned methods make it necessary to develop easily available, inexpensive, eco-friendly, and equally effective alternatives for water and wastewater treatment (Iqbal et al., 2013).

Considering the vast wastewater quantities, the current metal removal technologies are either not effective enough or are prohibitively expensive and inadequate. Therefore, there is a need for a cost effective treatment method that is capable of removing heavy metals from solution even at low metal concentrations. Biosorption seems to be the answer to this important industrial demand based on the following advantages: regeneration of biosorbent, possibility of metal recovery, minimization of chemical and biological sludge (Prasad et al., 2013). Biosorption technology based on the utilization of dead biomass offers several major advantages, such as lack of toxicity, constraints, non-requirement of nutrient supply, high availability and low cost of biomass (Gupta and Rastogi, 2008).

Lemon grass (*Cymbopogon citratus*) is a perennial herb, with slightly branched partly aerial rhizome that belongs to the section of Andropogoneae called cymbopogam of the family Poaceae (Vaqar et al., 2007). It contains a variety of compounds like terpenes, flavonoids and alkaloids depending on the habitat. *Cymbopogon citratus*'s oil is used to cure various ailments like cough, cold, rheumatism, digestive problems, bladder problems and as mouth wash for toothache and swollen gums (Perry, 1980; Vinitketumnuen et al., 1994; Costa et al., 2011; Shah, 2011; Franscisco et al., 2013; Balakrishnan et al., 2014; Campos et al., 2014; Ahmad and Viljoen, 2015). The biomass of Lemon grass has been used for the biosorption of Cu(II), Ni(II) and Pb(II) (Zuo et al., 2012; Lee et al., 2014; Sobh et al., 2014). In the present study, a comparative study on the removal of Pb(II), Cd(II) and Zn(II) using *Cymbopogon citratus* to has been investigated in different experimental conditions.

MATERIAL AND METHODS

Chemical, reagents and sample collection

Lemon grass (*Cymbopogon citratus*) was harvested from the Campus of Olabisi Onabanjo University, Ago-Iwoye, Ogun State, Nigeria. It was rinsed with tap water several times and then with distilled water thrice to remove dirt and other particulate matter that might interact with sorbed metal ions. It was then air dried immediately and kept dry till time of usage. All chemicals (BDH, England) used in this study were of analytical reagent grade and were used without further purification. Standard solutions of Pb(II), Cd(II) and Zn(II) used for the study were prepared from $Pb(NO_3)_2$, $3CdSO_4.8H_2O$ and $Zn(NO_3)_2.6H_2O$, respectively. The working solutions with different concentrations of the metal ions were prepared by appropriate dilutions of the stock solution prior to their use with distilled water.

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, except for the experiment on the effect of pH where the study was carried out at different pH values. The concentration before and after biosorption of each metal ion was determined using a Perkin-Elmer Analyst 700 flame atomic absorption spectrophotometer (AAS). Fourier Transform Infrared (FTIR) spectra of dried unloaded biomass and metal loaded biomass are recorded at 400-4000 cm^{-1}, using a Shimadzu FTIR model 8400 S spectrophotometer.

Biosorption studies

The biosorption study was carried out by batch experiments by contacting 0.5g of the lemon grass with 25ml of each metal ions solution under different conditions for a period of time in a glass tube. The biosorption studies were conducted at 25^{o}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 metal ion. The residual Pb(II), Cd(II) and Zn(II) were 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

The effect of pH on the biosorption of the metal ion was carried out within pH 1-6 to prevent the precipitation of metal ions (Pavasant et al., 2006). This was done by contacting 0.5g of lemon grass with 25ml of 100 mgL^{-1} metal ion solution in glass tubes. The glass tubes containing the mixture were suspended in a water bath for three hours. The biomass was removed from the solution by decantation. The residual metal ion concentration in the solution was analyzed. The procedure used is similar to those earlier reported (Babarinde et al., 2006; Vasuderan et al., 2003; Xu et al., 2006). The optimum pH was determined as the pH with the highest biosorption of each metal ion.

Effect of contact time

The biosorption of the metal ions by lemon grass was studied at various time intervals (5-300 min) and at the concentration of 100 mgL^{-1}. This was done by contacting 0.5g of lemon grass with 25 ml of 100 mgL^{-1} of metal ion solution at optimal pH. The lemon grass was left in solution for different periods of time. At predetermined time, the glass tubes were withdrawn from the bath, and the residual metal ion concentration in solution was determined using AAS. The amount of metal ions biosorbed was calculated for each sample.

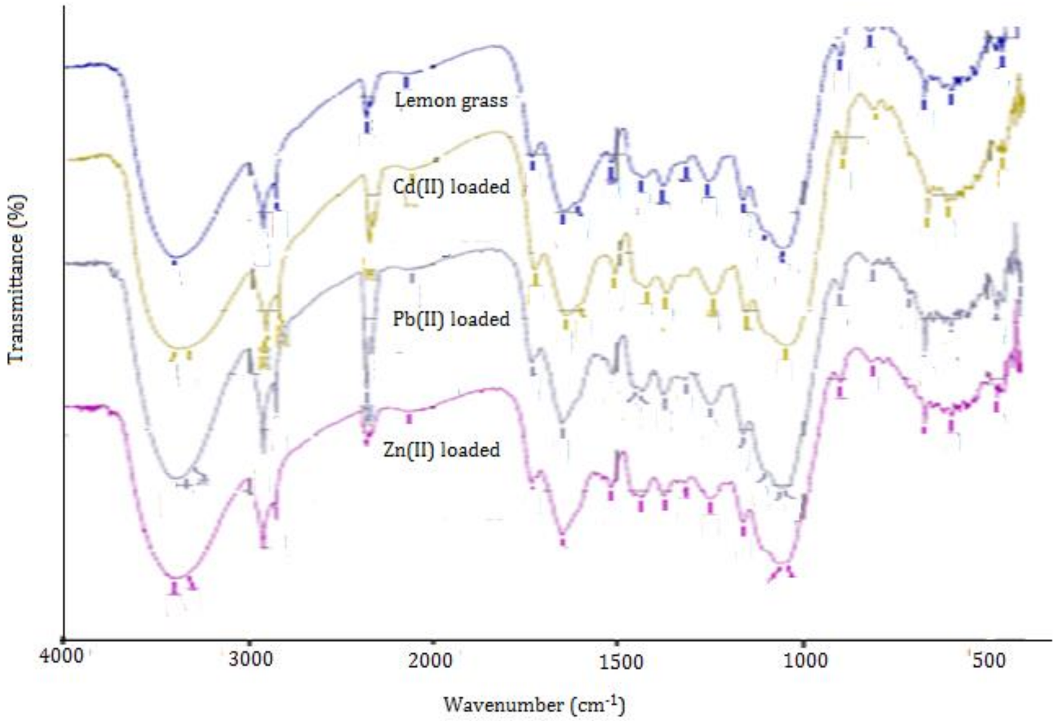

Fig. 1: FTIR spectra of the free and metal bound Lemon grass (*Cymbopogon citratus*)

Effect of concentration

Batch biosorption study of metal ion was carried out using a concentration range of 10-100 mgL^{-1}. This was done by contacting 0.5g of lemon grass with 25ml of 100 mgL^{-1} of metal ion solution at optimal pH. Two glass tubes were used for each concentration. The tubes were left in a thermostated water bath maintained at 25°C for the predetermined optimum time. The grass was removed from the solution, and the concentration of residual metal ion in each solution was determined.

RESULTS AND DISCUSSION

Physical characterization of Lemon Grass

The FTIR spectra of dried unloaded and metal-loaded lemon grass (*Cymbopogon citratus*) taken are presented in Figure 1. The FTIR spectrum was measured within the range of 500-4000cm^{-1} wave number. As shown in Figure 1, the FTIR spectrum displays a number ofabsorption peaks, indicating the complex nature of the bosorbent. The presence of the carboxylic, hydroxyl and amines groups on the biosorbent makes biosorption possible.These bands are due to the functional groups of lemon grass that participate in the biosorption of Cd(II), Pb(II), and Zn(II). The spectra shows that there are clear band shifts and decrease in intensity of bands as reported in Table1. The FTIR spectra of the lemon grass biomass indicated slight changes in the absorption peak frequencies due to the fact that the binding of the metal ions causes change 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 FTIR spectra showed the presence of ionizable functional groups (O-H , C-O, C=O and C≡N) which are able to interact 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.

The effect of solution pH on biosorption

The pH of the solution is plays very significant role on the sorption process (Hamdaoui and Chiha, 2007; Volesky, 2007; Babarinde et al., 2008; Babarinde et al., 2012; Farghali et al., 2013). It affects the metal chemistry (species) in solution, the surface properties of biosorbents in terms of dissociation of binding sites and surface charge (Akar et al., 2007). There are three ways in which the pH can influence metal biosorption: first, it affects the configuration of the active ion-exchange sites; second, it affects the ionic state of the sorbate in the solution; and third, extreme pH values may damage the structure of the biosorbent material (Saxena et al., 2006).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

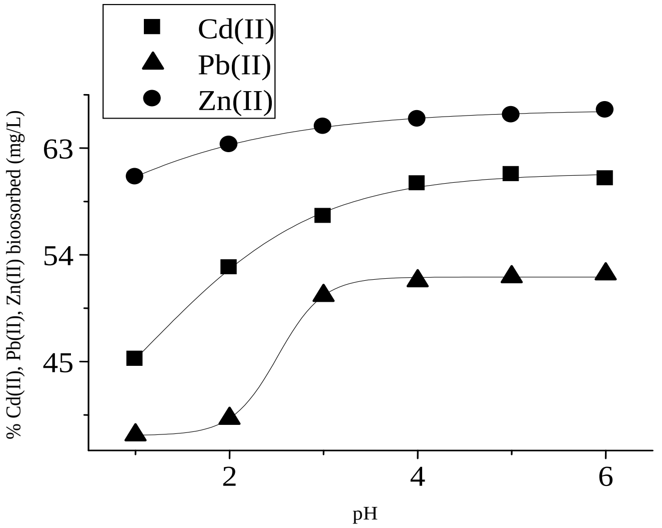

Fig. 2: pH dependence profile for the biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass

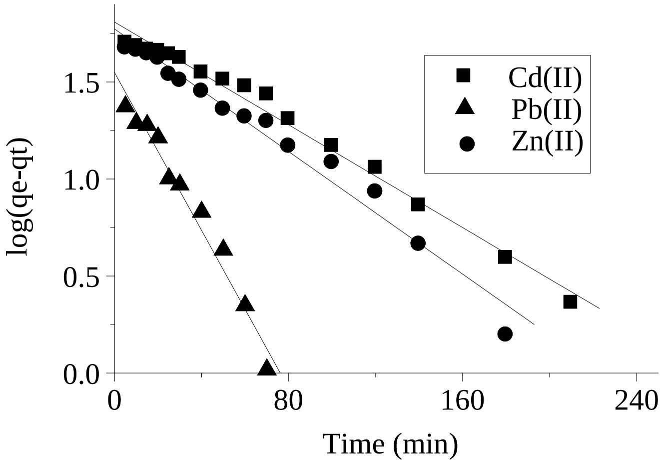

Fig. 4: Pseudo-first-order kinetic plot for the biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass

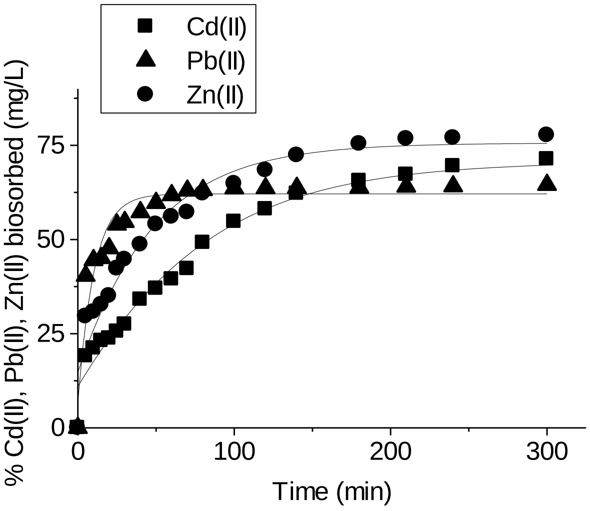

Fig. 3: Contact time dependent profile for the biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass

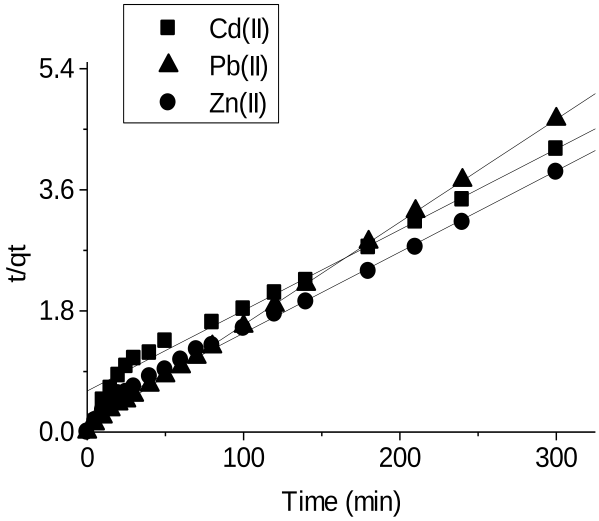

Fig. 5: Pseudo-second-order kinetic plot for the biosorption of Pb(II), Cd(II) and Zn(II) by lemon grass

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 ions biosorbed on lemon grass at various pH values. As the pH increases from pH 1-6 for the three metal ions, more ligands such as carboxyl, phosphate and imidazole groups carry negative charges with a subsequent attraction of metal ions and thus biosorption onto the cell surface increases (Vilar et al., 2005; Volesky, 2007). The increase observed in the biosorption with increase in pH implies that ion exchange process was involved. The pH study showed that maximum sorption occurred at pH 6 for the three metals as shown in Figure 2.

Kinetics of the biosorption process

The effect of contact time on the biosorption of Pb(II), Cd(II) and Zn(II) was studied over the time period of 5 – 300 min. Figure 3 shows the time-dependent profile for the biosorption of the three metals by lemon grass. It is observed that the biosorptive quantities of the three metal ions on the lemon grass increased with increasing contact time. In each case, biphasic kinetics are observed (Hamdaoui and Chiha, 2007): 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 biosorbed 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 biomass surface. The second phase is a gradual biosorption stage, whose diffusion rate is 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., 2010). The biosorption of each of the metal ions eventually achieves equilibrium, although their rates of uptake and times of reaching equilibrium are different.

In order to establish the mechanism of the biosorption of Pb(II), Cd(II) and Zn(II) unto lemon grass, four kinetic models were applied to the biosorption process. These are the pseudo-first-order, pseudo-second-order, Elovich, and Intraparticle model equations. One of such models is the Lagergren pseudo-first-order model which considers that the rate of occupation of the biosorption site is proportional to the number of the unoccupied sites (Ertugay and Bayhan, 2008) (Eq. 1).

$$rate = -\frac{d[A]}{dt} = k\,[A]^n \qquad (1)$$

Which can also be written as, Eq. 2.

$$\frac{d}{dt}q_t = k_1(q_e - q_t) \qquad (2)$$

Integrating between the limits $q_t = 0$ at t =0 and $q_t = q_t$ at t =t, we obtain Eq. 3.

$$\log\left[\frac{q_e}{(q_e - q_t)}\right] = \frac{k_1}{2.303}t \qquad (3)$$

This can be rearranged to obtain a linear form (Eq. 4)

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \qquad (4)$$

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 (mgg^{-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 lemon grass at initial concentration of 100 mg L^{-1} should give a straight line for a process that follows first-order kinetic model as represented in Figure 4. The kinetic parameters are presented in Table 2.

The kinetic data were also analyzed with the pseudo-second-order kinetic model. The pseudo-second-order kinetic model is represented in Eq. 5.

$$\frac{d}{d_t}q_t = k_2(q_e - q_t)^2 \qquad (5)$$

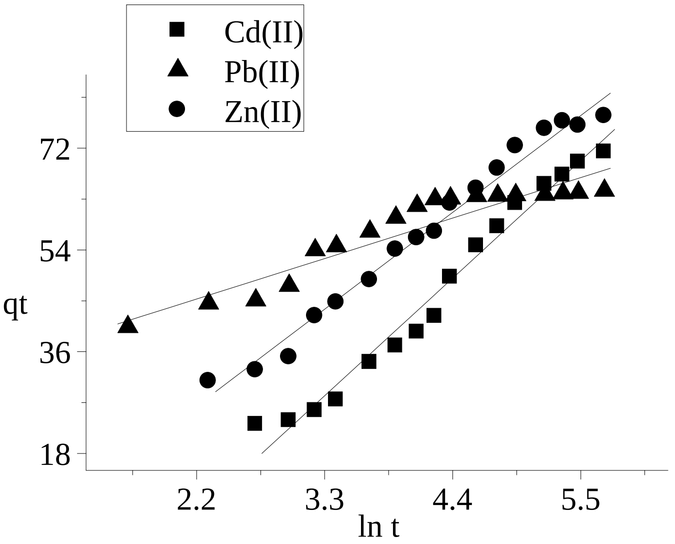

Fig. 6: Elovich kinetic plot for the biosorption of Pb(II), Cd(II) and Zn(II) by lemon grass

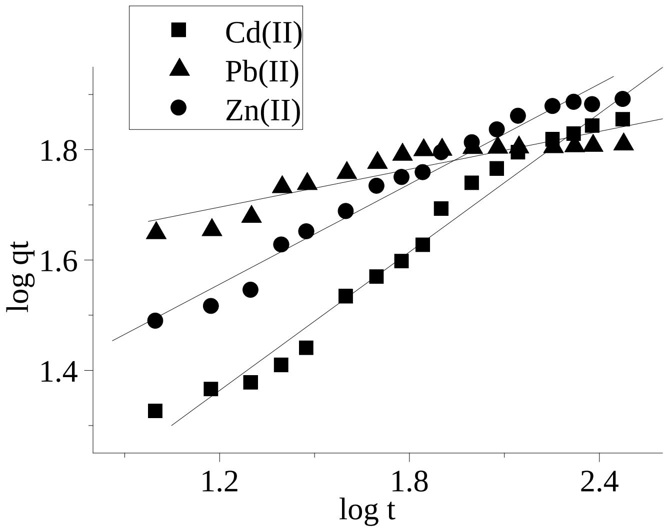

Fig. 7: Intraparticle diffusion kinetic plot for the biosorption of Cd(II), Pb(II), and Zn(II) by lemon grass

On integrating between boundary conditions, we have Eq. 6.

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \qquad (6)$$

On rearrangement, we have Eq. 7

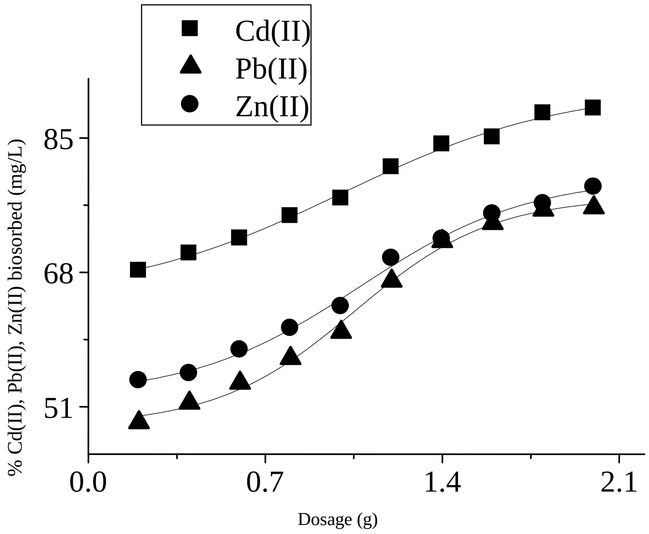

Fig. 8: Dosage plot for the biosorption of Pb(II), Cd(II) and Zn(II) by lemon grass

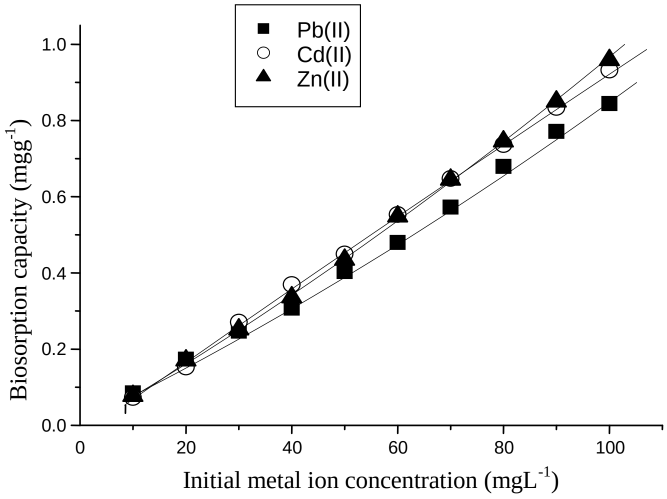

Fig. 9: Dependence of biosorption capacity on initial metal concentration for the biosorption of Pb(II), Cd(II) and Zn(II) by lemon grass at 25 °C

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (7)$$

Where k_2 is the equilibrium rate constant of pseudo-second-order biosorption process (g mg^{-1} min^{-1}). However, plots of *t* versus t/q_t showed good fitness of experimental data with the pseudo-second-order kinetic model as presented in Figure 5. The kinetic parameters are presented in Table 2. The data were equally analysed with the Elovich kinetic model is shown in Eq. 8

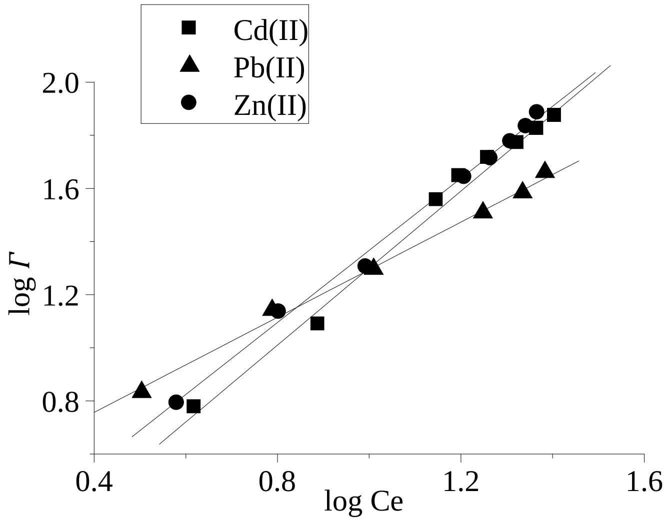

Fig. 10: Freundlich isotherm for biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass

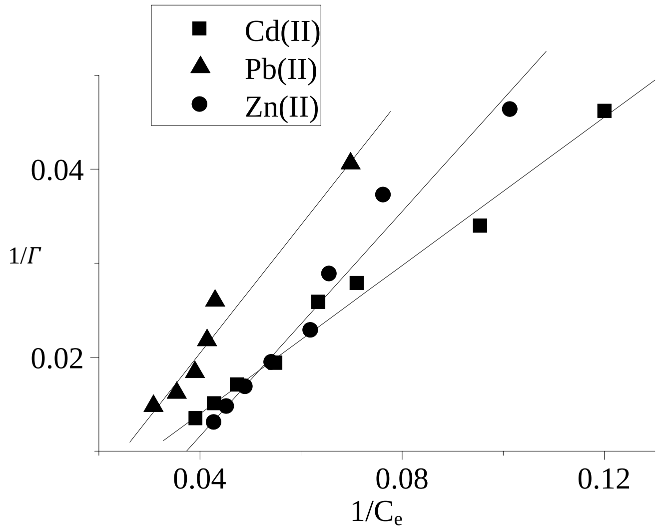

Fig. 11: Langmuir Isotherm for biosorption of Cd(II), Pb(II) and Zn(II) by lemon grass

$$q_t = A + B\ln t \qquad (8)$$

Where, q_e is the amount (mgL^{-1}) of metal ion biosorbed after a given time *t*. The Elovich kinetic plot is presented in Figure 6 while the kinetic parameters are presented in Table 2. The intraparticle diffusion equation was also applied to the kinetic data (Eq. 9)

$$R = K_d t^b \qquad (9)$$

Table 1: FTIR spectra characteristics of Lemon grass (*Cymbopogon citratus*) before and after biosorption of Pb(II), Cd(II) and Zn(II) for 4 hours

Metal ion	Absorption band (cm^{-1})			Functional groups
	before	after	difference	
Cd(II)	1255.70	1377.22	121.52	C=O, Stretch (Ester)
Pb(III)	1255.70	1251.84	3.86	C=O, Stretch (Ester)
Zn(II)	1255.70	1251.84	3.86	C=O, Stretch (Ester)
Cd(II)	1161.19	1251.84	90.25	C-O Stretch (Carboxylic)
Pb(III)	1161.19	1161.19	0	C-O Stretch (Carboxylic)
Zn(II)	1161.19	1161.19	0	C-O Stretch (Carboxylic)
Cd(II)	2144.91	2137.20	7.71	C≡N stretch
Pb(III)	2144.91	2110.19	34.72	C≡N stretch
Zn(II)	2144.91	2129.48	15.43	C≡N stretch
Cd(II)	3396.76	3421.83	25.07	O-H stretch
Pb(III)	3396.76	3396.76	0	O-H stretch
Zn(II)	3396.76	3396.76	0	O-H stretch

Table 2: Kinetic parameters for the biosorption of Cd(II), Pb(II) and Zn(II), onto lemon grass at 100 mgL^{-1}

Kinetic model	Parameters	Cd(II)	Pb(II)	Zn(II)
First-order	$q_e(mgg^{-1})$	64.42	35.37	59.32
	k_1 (min^{-1})	1.52×10^{-2}	4.63×10^{-2}	1.82×10^{-2}
	R^2	0.998	0.973	0.975
Second-order	$q_{e,\,cal}(mgg^{-1})$	83.40	65.44	82.85
	$k_2(g\ mg^{-1}min^{-1})$	2.36×10^{-4}	3.55×10^{-3}	5.53×10^{-4}
	R^2	0.992	0.999	0.993
Elovich	A	-33.25	31.23	-8.53
	B	18.67	6.56	15.77
	R^2	0.976	0.888	0.984
Intraparticle diffusion	$K_d(mgg^{-1}min^{-½})$	7.32	36.05	15.69
	B	0.42	0.12	0.30
	R^2	0.976	0.826	0.968

The intraparticle diffusion equation has been used to indicate the behaviour of intraparticule diffusion as the rate limiting step in the biosorption process. R is the percent metal ions biosorbed, K_d is the intraparticle diffusion constant, t is the contact time, while b is the gradient of the linear plot. In the linear form, equation (9) turns to 10.

$$\log R = b \log t + \log K_d \qquad (10)$$

The Intraparticle kinetic plot is presented in Figure 7 while the kinetic parameters are presented in Table 2.

For the four kinetic model tested, the kinetic parameters are presented in Table 2. On comparison of the values of R^2 for the experimental points, the correlation coefficients obtained were found to be highest for the pseudo-second-order kinetics. They were found to be in excess of 0.99 for each metal ions in the order Pb(II) > Zn(II) > Cd(II). The pseudo-second-order kinetic model is therefore, the best kinetic model to predict the dynamic biosorption of

Cd(II), Pb(II) and Zn(II) on lemon grass. The biosorption capacity is in the order Cd(II) > Zn(II) > Pb(II).

Effect of biomass dosage on biosorption

Figure 8 presents the results of the influence of lemon grass dosage on the percentage removal and the amount of Pb(II), Cd(II) and Zn(II) biosorbed at equilibrium (mgL^{-1}). The general trend of increase in the three metal ions 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 fact that increase in biomass dosage leads to increase in the number of active sites available for biosorption. 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 (mgg^{-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. This trend has been reported for other biosorbents (Miranda et al., 2010).

Effect of initial metal ion concentration on biosorption

Typically, 0.5 g of lemon grass was added to each tube containing 25 ml of a metal ion solution with varying initial metal ion concentrations (10-100 mgL^{-1}) at optimal pH. The results show that the initial concentration of metal ions in the solution remarkably influenced the equilibrium uptake of Pb(II), Cd(II) and Zn(II). It was noted that as the initial concentration increased, the sorption of the three metal ions also increased, as it is generally expected due to equilibrium process (Figure 9). This increase in uptake capacity of the biosorbents with the increased initial metal ion concentrations is due to higher availability of Pb(II), Cd(II) and Zn(II) for the sorption. Moreover, higher initial metal ion concentrations provides increased driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phase resulting in higher probability of collision between the three metal ions and lemon grass. This also results in higher metal ion uptake (Farghali et al., 2013). The sorption capacity at equilibrium, q_e, (mgg^{-1}) was calculated from the Eq. 11.

$$q_e = V(C_0 - C_e)/m \tag{11}$$

Where, q_e is the equilibrium biosorption capacity (mgg^{-1}) in mg (of the metal ion) per g (of the biosorbent), C_o is the initial concentration of metal ion before biosorption (mgL^{-1}), C_e is the equilibrium concentration of metal ion (mgL^{-1}), V is the volume of the metal ion solution (litre), and m is the mass of the biosorbent (g) .

Several isotherm equations are available for equilibrium modeling of biosorption processes. In this study, Freundlich, Langmuir, Temkin and Dubinin-Radushkevich (D-R) isotherms were employed to calculate the biosorption capacity because they are the most widely used in the literature, due to their simplicity, good agreement with experimental data and better analysis of the biosorption process (Batista et al., 2009, Bishnoi et al., 2007, Kavitha and Namasivayam, 2007). The Freundlich isotherm model is based on the assumption that adsorption occurs on a heterogenous surface. It proposes a monolayer sorption with a heterogenous energetic distribution of active sites, accompanied by interactions between sorbed molecules (Uluozlu et al., 2008). The Freundlich isotherm is expressed in Eq. 12.

$$\log \Gamma = \frac{1}{n}\log C_e + \log K_f \tag{12}$$

Where, K_f and n are the Freundlich constants related to the biosorption capacity (mgg^{-1}) and biosorption intensity of the biosorbent, respectively. Saxena et al., (2006) demonstrated that if n > 1, the sorption is favourable. Figures 10 illustrates the biosorption isotherm of metal ions onto lemon grass (*Cymbopogon citratus*). The equilibrium biosorption capacity, q_e, increases with increase in the three metal ions concentration. The isothermal parameters are presented in Table 3.

The Langmuir isotherm model assumes a monolayer adsorption in which all absorbed ions do not interact with each other and once a metal ion occupies a site, no further adsorption can take place on that site. The linearized form is based on the assumption that the maximum sorption occurs when a monolayer of solute molecules is present on the sorption surface and the energy of sorption is constant with no migration of sorbate molecule in surface plane (Bishnol et al., 2007). The model can take the following linear form (Eq. 13).

$$\frac{1}{q_e} = \frac{1}{q_{\max} K_L}\frac{1}{C_e} + \frac{1}{q_{\max}} \tag{13}$$

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 bisorption 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.

$$R_L = \frac{1}{1 + K_L C_i} \tag{14}$$

Table 3: Isothermal parameters for the biosorption of Cd(II), Pb(II) and Zn(II) onto lemon grass

Kinetic model	Parameters	Cd(II)	Pb(II)	Zn(II)
Freundlich	n	6.90×10^{-1}	11.09	7.38×10^{-1}
	K_f $(mgg^{-1})(Lmg^{-1})^{1/n}$	7.28×10^{-1}	2.49	1.02
	R^2	0.991	0.995	0.996
Langmuir	$q_{max}(mgg^{-1})$	-699.30	-152.67	-8.17
	$K_L(L\ mg^{-1})$	2.55	1.46	1.68
	R^2	0.985	0.967	0.972
Temkin	A	-90.92	-139.21	-192.20
	$B(mgg^{-1})$	49.79	59.24	84.32
	R^2	0.9776	0.967	0.991
D-R	q_m (mgg^{-1})	137.50	160.04	291.39
	$\beta(mol^2J^{-2})$	7.19×10^{-3}	1.14×10^{-2}	1.31×10^{-2}
	$E(Jmol^{-1})$	8.34	6.62	6.17
	R^2	0.956	0.994	0.989

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

Metal ion	ΔH^o $(kJmol^{-1})$	ΔS^o $(JK^{-1}mol^{-1})$	R^2	A $(kJmol^{-1})$ @ (303K)	A $(kJmol^{-1})$ @ (318K)
Cd(II)	+26.54	+98.08	0.994	2.55	2.67
Pb(II)	+15.59	+58.61	0.994	2.53	2.66
Zn(II)	+19.26	+74.64	0.997	2.54	2.66

Where, C_i is the initial concentration (mgL^{-1}) and K_L is the Langmuir equilibrium constant (Lmg^{-1}) and it is related to the energy of sorption, which quantitatively reflects the affinity between the sorbent and sorbate (Batista et al., 2009). 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 Figure 11 while the evaluated constants are given in Table 3.

The Temkin Isotherm model assumes that adsorption is characterized by a uniform distribution of binding energies up to some maximum binding energy. 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.

$$q = B \ln A + B \ln C_e \tag{15}$$

Where, C_e is concentration of the biosorbate at equilibrium (mgL^{-1}), q_e is the amount (mgg^{-1}) of adsorbate adsorbed at equilibrium. $RT/b_T = B$ where *T* is the temperature (K) and R is the ideal gas constant ($8.314 Jmol^{-1}K^{-1}$) and *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.

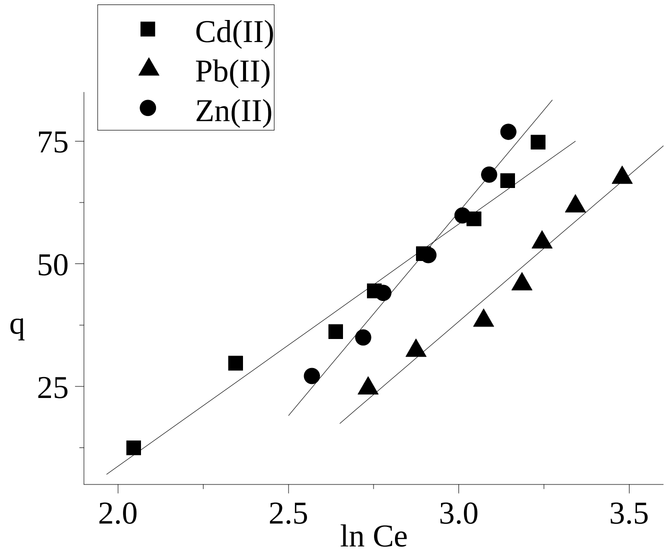

Fig. 12: Temkin Isotherm for biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass

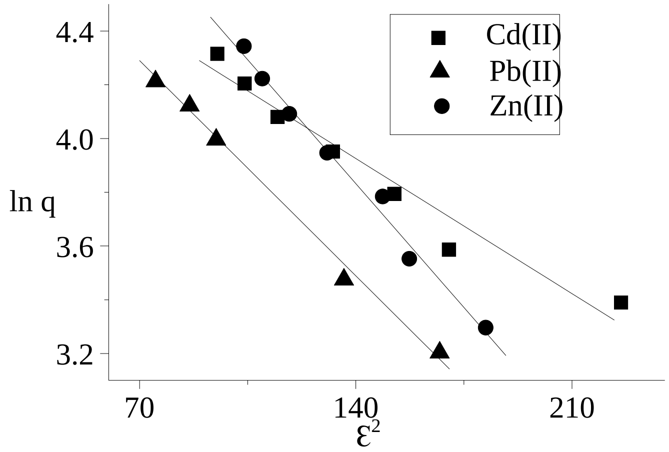

Fig. 13: D-R Isotherm for biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass

The Temkin isotherm is presented in Figure 12 while the evaluated constants are given in Table 3. The Dubinin-Radushkevich (D-R) isotherm model proposes a Gaussian distribution of energy sites and distinguishes between physical and chemical sorption as a function of biosorption heterogeneity (Saxena et al., 2006). It was used to estimate the heterogeneity of the surface energies. The D-R isotherm equation is linearly represented as shown in Eqs. 16-17 (Dubinin, 1960)

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

$$\varepsilon = RT ln(1 + \frac{1}{C_e}) \qquad (17)$$

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 (mol^{2}J^{-2}), and ε is the polanyl potential, C_e is the equilibrium concentration of adsorbate in solution (mol/L), R (Jmol^{-1}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 lnq_e versus ε^2 of Figure 13 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).

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

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 isothermal parameters for the four isotherm applied are presented in Table 3. On comparison of the values of R^2 for the experimental points, the correlation coeffficents obtained were found to be highest for the Freundlich isotherm and were found to be in excess of 0.99 for each metal ion in the order Zn(II) > Pb(II) > Cd(II). The Freundlich isotherm is therefore, the best isotherm to predict the dynamic biosorption of the three metal ions on lemon grass. The value of E is less than 1 kJmol^{-1} for each metal ion implying that each metal biosorption process proceeded via physicosorption.

Biosorption efficiency

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

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

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 ion concentration on biosorption efficiency is shown in Figure 14. The plots show that the biosorption efficiency of the biomass 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. The increase in biosorption efficiency with the increase in initial metal ion concentration might be due to increase in the number of active sites available for biosorption as the dosage increases.

Thermodynamics of the biosorption process

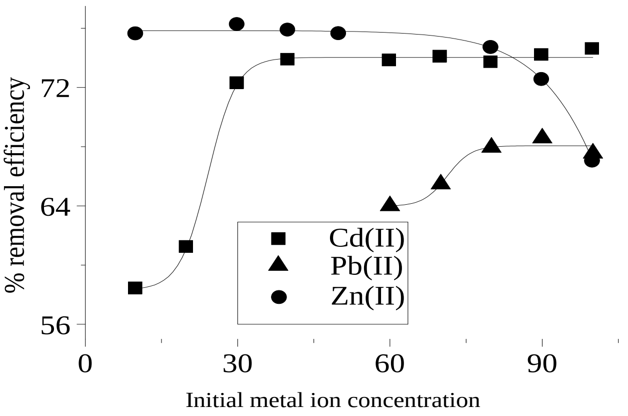

Fig. 14: Percentage Efficiency plot for the biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass

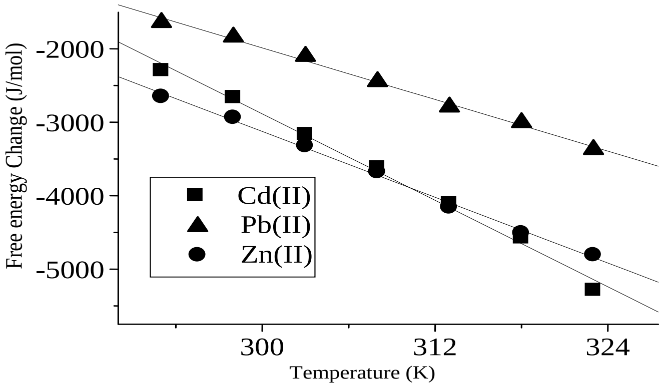

Fig. 15: Thermodynamic plots for the biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass at 100 mgL^{-1} initial metal ion concentration

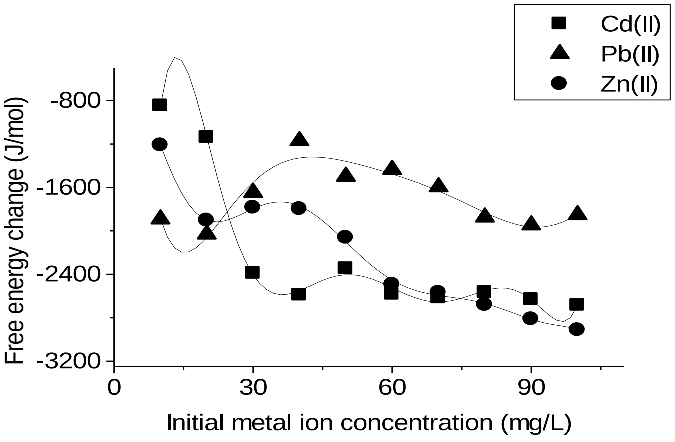

Fig. 16: Free energy profile for the biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass at varying initial metal ion concentration

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 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 favoured by increase in temperature while the contrary holds for the exothermic side. The corresponding free energy change was calculated from the relation (Eq. 20) (de la Rosa et al., 2008; Sun et al., 2008).

$$\Delta G^{\circ} = -RT \ln K_c \qquad (20)$$

Where, T (K) is the absolute temperature. The equilibrium constant (K_c) was calculated from the following relationship (Eq. 21).

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

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 Pb(II), Cd(II) and Zn(II) onto lemon grass 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 (Ertugay and Bayhan, 2008; Uluozlu et al., 2010). The change in free energy is related to other thermodynamic properties (Eqs. 22-23)

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (22)$$

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

Where, T is the absolute temperature (K); R is the gas constant (8.314 Jmol^{-1}.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 Figure 15 while the thermodynamic parameters are presented in Table 4

The negative values of ΔG° indicate spontaneity of each biosorption process, with the order of spontaneity being Zn(II) > Cd(II) > Pb(II). The positive value of ΔH° for the biosorption of the each of the metal ions 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 these metal ions indicate an increase in randomness at the solid/solution interface during their biosorption. The order of decreasing disorder being Cd(II) > Zn(II) > Pb(II).

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; Vimonses et al., 2009). In the present study, the overall ΔG° has values ranging from −7.5 to −3.5 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 (Arias and Sen, 2009; Vimonses 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 has been calculated using the following relation shown in Eq. 24.

$$A = \Delta H^{\circ} + RT \tag{24}$$

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.

Free energy and initial metal ions concentration

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 as presented in Eq. 25.

$$\Delta G^{\circ} = -RT \ln K_c \tag{25}$$

Where, T (K) is the absolute temperature. The equilibrium constant (K_c) was calculated from the following relationship (Eq. 26).

$$K_c = \frac{C_{ad}}{C_e} \tag{26}$$

Where, ΔG is the Gibbs free energy for the reaction and K_c is the reaction quotient. When a reaction is at equilibrium = K_c. The Van't Hoff isotherm can help estimate the equilibrium reaction shift. When $\Delta G<0$, the reaction moves in the forward reaction. When, $\Delta G>0$, the reaction moves in the backward reaction.

The large negative value of ΔG obtained shows the spontainety of each biosorption process. The value is comparable to those earlier reported (Kavitha and Namasivayam, 2007). Batch biosorption shows that the free energy change is dependent on the initial concentrations as shown in figure 16. The result shows decrease in free energy change with increase in initial concentration until a minimum was reached at the concentration of 40 mgL^{-1}, 50 mg L^{-1} and 60 mg L^{-1} for Cd(II), Pb(II) and Zn(II) respectively. Thermodynamically, the process was most spontaneous at this concentration at the temperature of 25°C.

CONCLUSIONS

Biosorption of Pb(II), Cd(II) and Zn(II) using lemon grass (*Cymbopogon citratus*) biomass is found to be influenced by the solution pH, contact time, biosorbent dose, initial metal ion concentration and temperature. The FTIR spectra studies of the biosorbent before and after been loaded by the metals revealed carboxylate, hydroxyl and amine functional groups may be involved in the sorption process as the intensities and wave numbers of these bands changed after the biosoorption. The biosorption process was best described by pseudo-second-order model based on the assumption that the rate limiting step may be a chemical sorption process. Out of the four isotherm tested, Freundlich isotherm gave the best fit. The thermodynamic parameters calculated indicated that the process is feasible and spontaneous and therefore industrially applicable while the positive value of enthalpy change (ΔH) indicates an endothermic process. Hence lemon grass (*Cymbopogon citratus*) can be employed as good biosorbent for the removal of Pb(III), Cd(II) and Zn(II) from aqueous solutions and as an alternative method of their removal from industrial effluent.

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