

Kinetics, Equilibrium, and Thermodynamics Studies of the Biosorption of Lead(II) and Chromium(III) by *Basella alba* L.

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ABSTRACT

The ability of a fast growing plant (*Basella alba* L.) to remove lead(II) and chromium(III) ions from aqueous solutions has been studied in a batch system. The effects of various parameters such as pH, biomass dosage, agitation time; and initial metal concentration were examined and have been found to have direct influence on the uptake of the metals by the biosorbent. Time-dependence experiments for the metal ions showed that optimum binding to the *Basella alba* L. occurred within 30 min. and 7 min. for Pb²⁺ and Cr³⁺, respectively.

Metal uptake decreased with increase in biosorbent dose for the two metals. The kinetic data fitted well to the pseudo-second-order model. The values of the rate constant, k_2 , for both metals were found to be 0.5644g mg⁻¹min⁻¹ and 22.303 gm⁻¹min⁻¹ for Pb²⁺ and Cr³⁺, respectively. Equilibrium data followed both Langmuir and Freundlich models. Using the thermodynamic equilibrium coefficients obtained at different temperatures, the thermodynamic parameters of each biosorption process were evaluated. The biosorption of Pb²⁺ was found to be endothermic with ΔH° of 18.96 kJmol⁻¹ while that of Cr³⁺ was exothermic with ΔH° of -4.137 kJmol⁻¹. The changes in entropy (ΔS°) of biosorption values obtained were 0.079 and -0.013 kJK⁻¹mol⁻¹ for Pb²⁺ and Cr³⁺, respectively. The values of ΔG° obtained for the two metals were -4.574 and -0.280 kJmol⁻¹, respectively. The values indicate the feasibility and spontaneous nature of the biosorption process.

(Keywords: biosorption, lead, chromium, kinetics, thermodynamics, *Basella alba* Linn.)

INTRODUCTION

Pollution of the environment due to technological development is one of the most significant problems of this century (Park et al., 2006). The presence of heavy metals in the effluents released from industries is a major threat to the environment. It is a well known fact that heavy metals can be toxic. They damage nerves, liver cells, and bones and they block functional groups of vital enzymes (Ewan and Pamphlett, 1996; Baik et al., 2002).

Among the heavy metals, mercury, lead, and cadmium are three of the most toxic with the greatest potential hazard to humans and the environment (Volesky, 1994). Heavy metals such as lead, chromium, cadmium and zinc are released into the environment via effluents from manufacturing industries, especially plating and those manufacturing batteries, pigments, and ammunition (Al-Garni, 2005). Lead and chromium are potent neurotoxic metals (Puranik and Pakniker, 1997). Cadmium has been observed to accumulate throughout the food chain (Volesky, B. 1990; Wase & Forster, 1997), while the presence of lead in drinking water above the permissible limit (5 ng/ml) causes adverse health effects such as hepatitis, encephalopathy, anemia, and nephritic syndrome (Lo et al., 1999).

Conventional techniques, such as chemical precipitation, solvent extraction, ion exchange, electroplating, activated carbon adsorption and membrane separation process have been employed to remove heavy metals from wastewater (Matheickal & Yu, 1999; Yan and Viraraghavan, 2001; Rorrer, 1998). These methods have become inefficient and expensive especially when the heavy metal concentration is

less than 100 ppm (Leusch et al., 1995; Eccles, 1999).

Alternatively, biosorption of heavy metals by bacterial, fungal or algal biomass and agricultural waste biomass have been identified as one of the most promising technologies involved in the removal of toxic metals from industrial waste streams and natural water (Singh et al., 2003; Feng and Aldrich, 2004; Vegilo et al., 1998). Biosorption is a process whereby certain types of inactive, dead biomass may bind and concentrate heavy metals from aqueous solutions (Naja et al., 2005; Volesky, B. 2003). The use of non-expensive waste biomass, the low cost of biomass immobilization, competitive performance, heavy metal selectivity, no sludge generation and the possibility of biomass regeneration are some of the advantages of biosorption over other conventional techniques (Gasbarro, 1997; Quintelas and Tavares, 2002; Siegel et al., 1990).

Many types of biomass have been reported to have high uptake capacities for heavy metals, including lead and chromium (Bailey et al., 1999; Wase and Forster, 1997; Babarinde et al., 2006). Some agricultural waste/materials that have been investigated for heavy metal uptake include waste maize bran (Singh et al., 2006), maize leaf (Babarinde et al., 2006), sugarcane bagasse (Karnitz et al., 2007), banana pith (Low et al., 1995), coconut copra meal (Ofomaja and Ho, 2006), and rice bran (Zafar et al., 2006). All of these biomaterials have shown adequate heavy metal sorption capacity to be considered for process applications.

Lead and chromium are the focus of this study. The aim of the work was to determine the ability of *Basella alba* L. to remove lead(II) and chromium (III) from aqueous solutions. and to study its kinetics and thermodynamic properties. *Basella alba* L. (Malabar spinach) is a fast growing plant that is spread throughout the tropical world including Africa. It is one of the best tropical spinach widely adapted to a variety of soils and climates (Palada & Crossman, 1999). Due to the ability of this plant to accumulate water in its tissue, it is hoped that the plant could serve as an effective biomaterial in the removal of heavy metals, especially lead and chromium from industrial waste water. First the effects of pH, agitation time, biosorbent dose, and initial metal ion concentration were studied. Furthermore, the data obtained were fitted using two kinetic models (pseudo-first-order and pseudo-second-order) and

two equilibrium models (Langmuir and Freundlich). The thermodynamics of the biosorption system were also investigated.

METHODS

Materials

Fresh leaves of *Basella alba* L. (Malabar spinach) used for the biosorption test were harvested from a household garden near University of Ibadan, Ibadan, South-Western Nigeria. After rinsing with running tap water and de-ionized water, the leaves were oven dried, pulverized and then sifted with a 150 size mesh screen. The resulting dried biomass was later stored in air-tight polyethylene bags and used for the different experiments in this study.

Preparation of Stock Solutions

Lead and chromium solutions with different initial concentrations were prepared by dissolving known masses of $Pb(NO_3)_2$ and $Cr(NO_3)_3 \cdot 9H_2O$ in de-ionized water, respectively. Each was made up to the mark in appropriate standard volumetric flask. The precise concentrations of these metals were determined using Atomic Absorption Spectroscopy (AAS).

Biosorption Experiments

The effect of pH on the biosorption of lead and chromium was studied by adding 30 mg of the prepared biosorbent (*Basella alba* L.) to 15 mL of 0.3 mM solutions of each of lead(II) and chromium(III) in 250 mL plastic bottles at 25 °C. The bottles with the mixtures were agitated on a thermostated shaker at 200 rpm for 2 hours and then centrifuged at 8,000 rpm for 10 min to separate the supernatant. The experiments were carried out at pH range of 2 to 8. Adjustments to different pH values were made with 0.1 M HNO_3 and 0.1 M NaOH solutions using a glass electrode (Jenway 3510 model) pH meter.

Effect of biosorbent dosage was studied with different adsorbent doses (10, 30, 50, 70, 90 and 110 mg) in 15 mL of 0.3 mM each of lead(II) and chromium(III) solutions, adjusted to pH 6. These were then agitated at 200 rpm for 2 hours and centrifuged at 8,000 rpm for 10 min. to separate the supernatants.

To determine the contact time required for equilibrium biosorption, 30 mg of the biosorbent was contacted with 15 mL of 0.3 mM solutions of metal ion in 250 mL plastic bottles and under constant agitation at 200 rpm in a thermostatic shaker at temperature of 25 °C. The pH values of the solutions were adjusted to the optimum value for each metal. Samples were withdrawn from the shaker at different time intervals of 5, 10, 20, 30, 60, and 120 min for lead and 2, 5, 10, 20, 30, 60, and 120 min for chromium (Parvathi et al., 2007; Zafar et al., 2006).

In studying the effect of initial metal ion concentration, 30 mg of the biosorbent was shaken with 15 mL of lead(II) and chromium (III) solutions of varied concentration (0.1, 0.3, 0.5, 0.75, 1 and 2 mM) in different plastic bottles in a thermostated shaker at a constant speed of 200 rpm, temperature of 25 °C and at the predetermined agitation time for each metal. The supernatants were then separated by centrifugation at 8,000 rpm for 10 min.

For the thermodynamic study, biosorption of 15 mL of 0.3 mM each of lead(II) and chromium (III) solutions by 30 mg biosorbent was carried out at 15, 25, 37 and 50 °C in a thermostatic shaker bath for the predetermined agitation time for each metal, and then centrifuged. In all the studies, the resulting residual metal ion concentration of the supernatants were determined using AAS and each experiment was carried out in duplicate.

Metal uptake was determined using the following equation:

$$q = \frac{(C_o - C_e)V}{S} \quad (1)$$

where, q is the metal uptake (mg/g); V is the solution volume (L); C_o is the initial concentration of metal in solution (mg/L); C_e is the final concentration of metal in solution (mg/L); and S is the mass of biosorbent added (g) (Vijayaraghavan et al., 2006; Vieira & Volesky, 2003).

RESULTS AND DISCUSSION

Effect of pH on biosorption

The removal of metal ions from aqueous solutions by biosorption is dependent on the solution's pH because it affects biosorbent surface charge, the degree of ionization, and the species of

biosorbates (Karnitz et al., 2006; Yin et al., 1999). pH effect on biosorption equilibrium has been reported to be necessary for an accurate evaluation of biosorption process (Wase and Forster, 1997). Figures 1 and 2 show the dependence of lead and chromium uptake by *Basella alba* L. on the pH of the solution.

Investigation of the capability of this biosorbent to remove lead and chromium at different values of pH (2–6) showed that biosorption of Pb²⁺ ion increases with increase in pH. Maximum uptake of Pb²⁺ was observed at pH 6. The biosorption experiments were not performed beyond pH 6 because at pH above this, precipitation of the metals is said to occur (Parvathi et al., 2006; Mahamadi et al., 2007). For Pb²⁺ ion biosorption, metal uptake of up to 76% was obtained at pH 6 which served as the optimum pH for this study. From pH 5 to 6, effect of pH became apparent, and an increase in metal uptake was observed. Karnitz et al. (2006) have also reported pH 6 in the biosorption of Pb²⁺ using chemically modified sugarcane bagasse.

For chromium uptake, the optimum pH was found at pH 5 as shown in Figure 2.

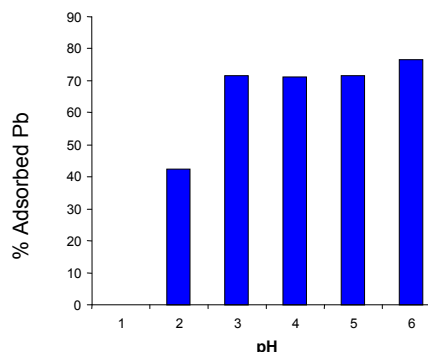


Figure 1: Effect of pH on Biosorption of Lead by *Basella alba* L. (conc., 62.2 mg/l; temp., 25°C)

Effect of biosorbent dose

Figures 3 and 4 illustrate typical sets of results obtained by varying biosorbent dosage during lead and chromium biosorption by *Basella alba* L. It has been reported that dose of biomass added into the solution determine the number of binding sites available for biosorption (Zafar et al., 2006). For Pb²⁺ ion, metal uptake decreased with increase in biomass dosage. A similar pattern of result was obtained for the biosorption of chromium. This may be due to complex

interactions of several factors. An increase in biosorbent quantities strongly affects the quantities of metal removed from aqueous solutions. This could be attributed to the fact that at high biosorbent dosages the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, usually resulting into low metal uptake (Vijayaraghavan et al., 2006; Fourest & Roux, 1992). Similar observations were reported by other researchers (Al-Asheh & Duvnjak, 1995; Sampedro et al., 1995). But for the purpose of this present study, biomass dose of 30 mg was selected for further studies.

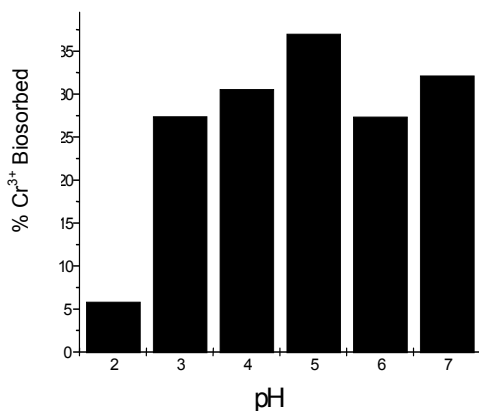


Figure 2: Effect of pH on Biosorption of Chromium by *Basella alba L.* (conc., 15.6 mg/l; temp., 25°C).

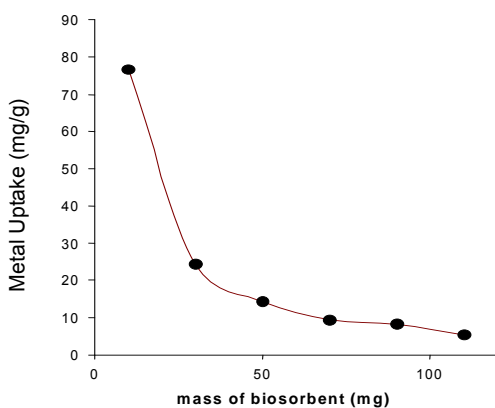


Figure 3: Effect of Biosorbent Dosage on Biosorption of Lead by *Basella alba L.* (pH 6; conc., 62.2 mg/l; temp., 25°C)

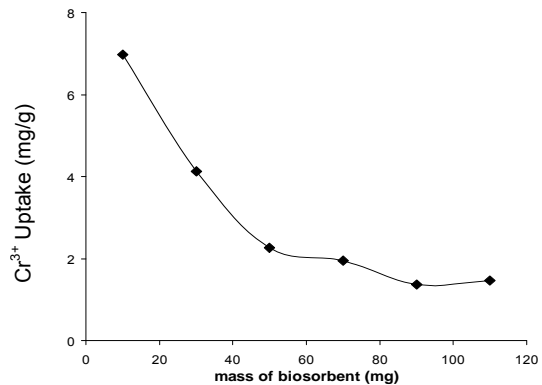


Figure 4: Effect of Biosorbent Dose on Biosorption of Chromium by *Basella alba L.* (pH 5; conc., 15.6 mg/l; temp., 25 °C)

Effect of contact time

Agitation time is another factor that greatly affected the biosorption of lead and cadmium by *Basella alba L.* as illustrated in Figures 5 and 6.

For Pb²⁺, biosorption equilibrium was reached after 30 min of agitation. For chromium, maximum biosorption was observed in within 7min of agitation, after which a slight decrease in metal uptake was noticed until equilibrium was reached from 60 min. These optimum agitation times were subsequently used for each metal under this study.

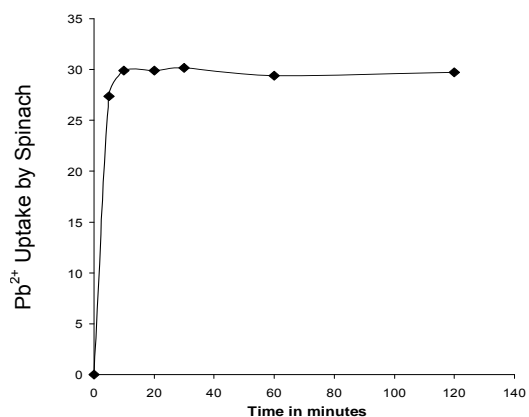


Figure 5: Effect of Agitation Time on the Biosorption of Lead by *Basella alba L.* (pH 6; conc., 62.2 mg/l; biomass dose, 30mg; temp., 25°C)

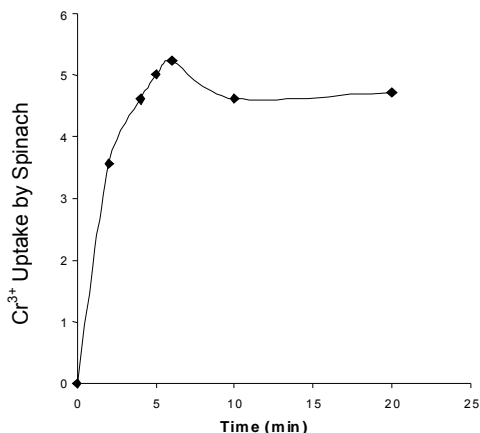


Figure 6: Effect of Agitation Time on the Biosorption of Chromium by *Basella alba* L. (pH 5; conc., 15.6 mg/l; biomass dose, 30mg; temp., 25 °C)

Kinetic studies

Kinetic models have been used to investigate the mechanism of the biosorption of lead and chromium ions by *Basella alba* L. The two models used were pseudo-first-order and pseudo-second-order model (Ho and McKay, 1998). The pseudo-first-order model is based on sorbent capacity and considers that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. The pseudo-second-order equation is also based on the adsorption capacity of the solid phase (Aksu and Tunc 2005). The linearized forms of the pseudo-first-order and pseudo-second-order model are represented below by Equations 2 and 3, respectively (Ho and McKay, 1998).

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where, q_e is the amount of metal biosorbed at equilibrium (mg/g); q_t is the amount of metal biosorbed at time, t (mg/g); k_1 is the rate constant of pseudo-first-order biosorption (min^{-1}); k_2 is the rate constant of pseudo-second-order biosorption (g/mg min.).

The two models were applied to the biosorption of the metals in this study. For pseudo-first-order kinetics, the straight-line plots of $\log (q_e - q_t)$ against t were made, but the pseudo-first-order

model was found not to achieve a good fitting for the biosorption of both metals. This is because the coefficient of correlation for pseudo-first-order kinetic model was far less than one ($\ll 1$). In most cases in the literature, the pseudo-first-order model does not fit the kinetic data well for the whole range of contact time, and generally underestimate the q_e values (Ho and McKay, 1998; Reddad et al., 2002).

The best fits, in the data range for the two metals, were found to be the pseudo-second-order model as reported in Figures 7 and 8. The pseudo second-order model is based on the assumption that rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Zafar et al., 2006).

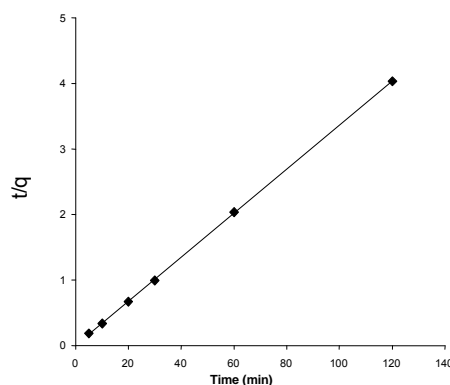


Figure 7: The Pseudo-Second-Order Plot for the Kinetic study of Pb^{2+} Biosorption by *Basella alba* L. (pH 6; conc., 62.2 mg/l; biomass dose, 30 mg; agitation time, 60 min.; temp., 25°C)

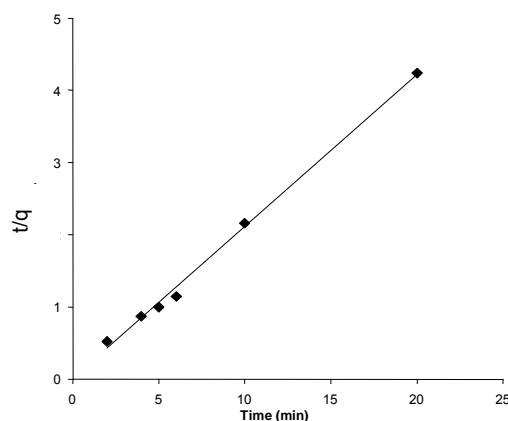


Figure 8: The Pseudo-Second-Order Plot for the Kinetic Study of Cr^{3+} Biosorption by *Basella alba* L. (pH 5; conc., 15.6 mg/l; biomass dose, 30 mg; agitation time, 6 min.; temp., 25°C)

The values of the parameters, k_2 and q_e , for the two metals and their correlation coefficients, R_2 , are presented in Table 1. The correlation coefficients obtained are approximately one ($R^2 \approx 1$), and the adequate fitting of theoretical and experimental q_e values for all the metals suggest the applicability of second-order kinetic model based on the assumption that the rate limiting step may be the biosorption of metal and *Basella alba* L. in explaining the kinetics of biosorption (Donmez et al., 2002).

Table 1: The Pseudo-Second-Order Parameters for the Kinetic Study of Pb^{2+} and Cr^{3+} Biosorption by *Basella alba* L.

Metal	R^2	k_2 (g mg ⁻¹ min ⁻¹)	q_e (calc)	q_e (expt)
Pb ²⁺	0.9999	0.5644	29.762	30.19
Cr ³⁺	0.9969	22.303	4.735	5.24

Effect of initial metal concentration

The biosorption experiments conducted in a series of aqueous solutions of lead and chromium with different initial concentrations showed that biosorption capacity of *Basella alba* L. increased from 7.7 mg/g to 154.3 mg/g for lead(II) ion and 2 mg/g to 12 mg/g for chromium. This sorption characteristic indicated that surface saturation was dependent on the initial metal ion concentrations. At low concentrations, sorption sites took up the available metal more quickly. However, at higher concentrations, metal needed to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate (Zafar et al., 2006).

Equilibrium studies

The lead and cadmium uptake capacity of the *Basella alba* L. was evaluated using the Freundlich (1907) and Langmuir (1918) isotherm models. These two models are the earliest, most common and simplest known relationships describing the ad/bio-sorption phenomenon (Jalali et al., 2002). The Langmuir equation is widely used for modeling the adsorption equilibrium, which is valid for monolayer sorption onto a surface with finite number of binding sites. These are homogeneously distributed over the adsorbent surface (Aksu and Tunc, 2005). These binding sites have the same affinity for adsorption of a

single molecular layer and there is no interaction between adsorbed molecules (Langmuir, 1918).

The empirical Freundlich model also takes into account the monomolecular layer coverage of solute by the sorbent, but it assumes that the sorbent has a heterogeneous surface, which means that binding sites are not equivalent and/or independent (Freundlich, 1907). The linearized forms of the Freundlich and Langmuir isotherm models are represented below by equations 4 and 5 respectively:

$$\log q = \log K_f + \left(\frac{1}{n}\right) \log C_e \quad (4)$$

$$\frac{1}{q} = \frac{1}{q_{max}} + \frac{b}{q_{max} C_e} \quad (5)$$

where, q is the heavy metal biosorbed on the biosorbent (mg/g dry weight); C_e is the final concentration of metal (mg/L) in the solution; K_f is an empirical constant that provides an indication of the adsorption capacity of biosorbent; n is an empirical constant that provides an indication of the intensity of adsorption; b is the equilibrium constant related to the affinity of the binding sites for the metals; and q_{max} is the maximum possible amount of metallic ion adsorbed per unit weight of adsorbent.

For the Freundlich isotherm model, the adsorption constants (K_f and $1/n$) were obtained by plotting $\log q$ as a function of $\log C_e$. While the adsorption constants (q_{max} and b) for the Langmuir isotherm model were obtained by plotting $1/q$ as a function of $1/C_e$ (Parvathi et al, 2007). The experimental data points for the biosorption of lead and chromium by *Basella alba* L., at temperature of 25 °C were fitted to Langmuir and Freundlich isotherm equations. As illustrated in Figures 9 to 12, the Langmuir and Freundlich models present good fits of the experimental data and are both adequate for modeling the isotherm of sorption.

Table 2 shows the different parameter (R^2 , q_{max} , b , K_f , n) obtained from both Langmuir and Freundlich isotherm models. The parameter q_{max} represents the maximum metal adsorption and b is an affinity parameter (a high value of b reflects the high affinity of the biosorbent for the sorbate), K_f relates to biosorption capacity, and n is an

empirical parameter that varies with the degree of heterogeneity.

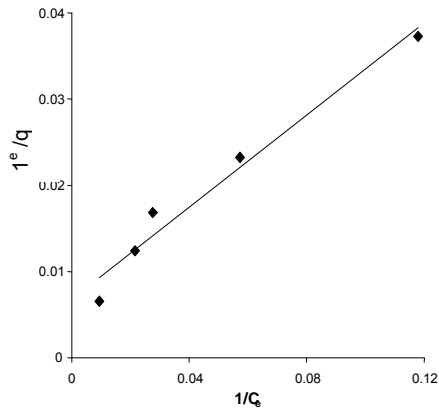


Figure 9: Langmuir Isotherm for the Biosorption of Lead by *Basella alba L.* (pH 6; biomass dose, 30 mg; agitation time, 60 min; temp., 25°C)

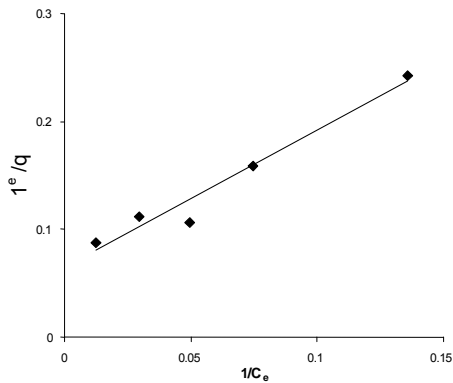


Figure 10: Langmuir Isotherm for the Biosorption of Chromium by *Basella alba L.* (pH 5; biomass dose, 30 mg; agitation time, 6 min; temp., 25°C)

Thermodynamic studies

The thermodynamic parameters such as standard Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were estimated to evaluate the feasibility and nature of the biosorption of lead and chromium by *Basella alba L.* Experiments were carried out at different temperatures in the range of 288 – 323 K and the following relationships have been used to evaluate the thermodynamic parameters:

$$\Delta G^\circ = -RT \ln K_c \quad (6)$$

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (7)$$

where, T is temperature in K, R is ideal gas constant having value as $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and K_c is thermodynamic equilibrium constant.

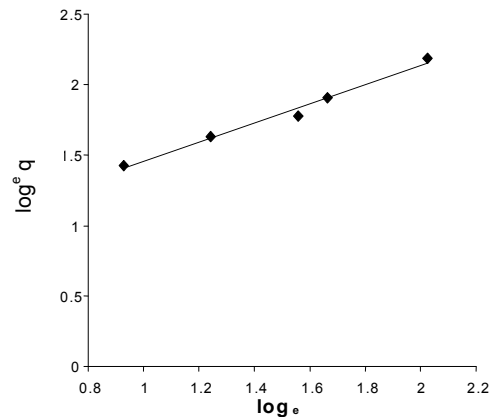


Figure 11: Freundlich Isotherm for the Biosorption of Lead by *Basella alba L.* (pH 6; biomass dose, 30 mg; agitation time, 60 min; temp., 25°C).

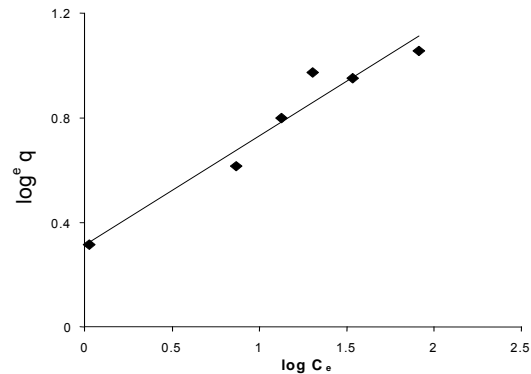


Figure 12: Freundlich Isotherm for the Biosorption of Chromium by *Basella alba L.* (pH 5; biomass dose, 30 mg; agitation time, 6 min; temp., 25°C).

Table 2: Langmuir and Freundlich Isotherms Parameters for the Biosorption of Pb²⁺ and Cr³⁺ by *Basella alba* L.

Metal ion	LANGMUIR R ²	LANGMUIR q _{max}	LANGMUIR K _L	FREUNDLICH R ²	FREUNDLICH K _f	FREUNDLICH N
Pb ²⁺	0.9696	149.25	0.0250	0.9832	6.028	1.474
Cr ³⁺	0.9594	15.36	0.0514	0.9483	2.057	2.389

The values of enthalpy change (ΔH°) and entropy change (ΔS°) were calculated from the slope and intercept of van, t Hoff plot of $\ln K_c$ versus $1/T$ (Sarin et al., 2006).

The thermodynamic equilibrium constant, K_c , was determined as follows

$$K_c = \frac{C_a}{C_e} \quad (8)$$

Where, C_a is mg of adsorbate adsorbed per liter, and C_e is the equilibrium concentration of solution, mg/l (Sarin et al, 2006). The standard Gibb's free energies of the biosorption of the metals at different temperatures are presented in Table 3. The negative values of ΔG° confirm the feasibility and spontaneous nature of the biosorption process (Aksu and Tunc, 2005). The change in free energy decreased with increase in temperature (from 288K-310K) for Pb²⁺. This shows that increase in temperature favors the biosorption process. However, there was increase in free energy change with increase in temperature (from 288K-310K) was observed for the biosorption of Cr³⁺. This indicates that the biosorption of the metal ions exhibited a decrease in biosorption with rise in temperature.

Figures 13 and 14 illustrate the plots of $\ln K_c$ versus $1/T$ for the biosorption of the two metal ions by *Basella alba* L. The values of the thermodynamic parameters are presented in Table 3. The positive values of ΔH° for the biosorption of both metal ions suggest the endothermic nature of the biosorption process and possible strong bonding between the metal ion and *Basella alba* L. (Aksu and Tunc, 2005). The positive values of ΔS° for the two metals also shows increased randomness at solid solution interface during the biosorption of the metal ions on *Basella alba* L. (Sarin et al., 2006).

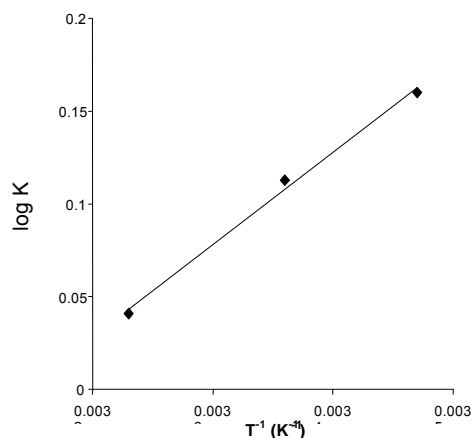


Figure 13: Thermodynamic Plot of the Biosorption of Lead by *Basella alba* L. (pH 6; biomass dose, 30 mg; agitation time, 60 min; conc., 62.2 mg/l; temp., 25°C)

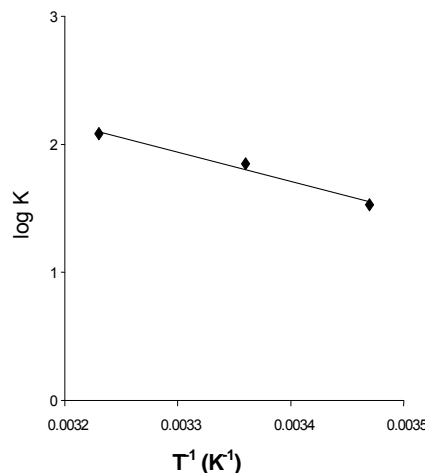


Figure 14: Thermodynamic Plot of the Biosorption of Chromium by *Basella alba* L. (pH 5; biomass dose, 30 mg; agitation time, 6 min; conc., 15.6 mg/l; temp., 25°C)

Table 3: Thermodynamic Parameters for the Biosorption of Pb²⁺ and Cr³⁺ by *Basella alba* L.

Metal ion	R ²	ΔH° (kJmol ⁻¹)	ΔS° (kJK ⁻¹ mol ⁻¹)	ΔG° (kJmol ⁻¹) T ₁ =288K	ΔG° (kJmol ⁻¹) T ₂ =298K	ΔG° (kJmol ⁻¹) T ₃ =310K	ΔG° (kJmol ⁻¹) T ₄ =323K
Pb ²⁺	0.9819	18.963	0.079	-3.661	-4.574	-5.361	-4.042
Cr ³⁺	0.9947	-4.137	-0.013	-0.383	-0.280	-0.106	-0.832

CONCLUSIONS

Basella alba L. was found to be an effective biosorbent for the removal of lead(II) and chromium(III) from aqueous solutions. The biosorbent was found to be a better removal of lead than chromium: at the experimental conditions monitored at 25°C, above 86% of lead was removed, while about 59% of cadmium was removed. The study showed that pH, biomass dosage, agitation time and initial metal concentration highly affected the overall metal uptake capacity of the biosorbent. The fit of the biosorption data into the pseudo-second-order kinetic model indicated that the rate-limiting step may be chemical sorption or chemisorption.

The equilibrium data have been found to follow the Langmuir and Freundlich isotherm models. Thermodynamic studies confirm that the process was spontaneous and endothermic.

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