



Removal of Pb(II) From Aqueous Solutions by *Caesalpinia bonducella* Leaf Powder(CBLP)

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Received 25th May 2013, Revised 11th June 2013; Accepted 15th June 2013.

ABSTRACT

Biosorption of Pb(II) ions from aqueous solutions by Caesalpinia bonducella leaf powder (CBLP) was investigated as a function of initial pH, biosorbent dose, initial metal ion concentration and temperature. The FTIR spectrum shows the involvement of different functional groups (hydroxyl, amine, carboxyl and carbonyl groups) in Pb(II) biosorption. Kinetic data were best fitted with the pseudo-second-order kinetic model. The batch equilibrium data were fitted well by Langmuir isotherm. The monolayer maximum biosorption capacity, calculated from Langmuir isotherm model, was found 116.27 mg/g at 323 K.

Keywords: *Biosorption; Lead; Caesalpinia bonducella leaf powder; Kinetics; Isotherms*

1. INTRODUCTION

Lead, one of the most toxic heavy metals, is attracting ample attention of environmentalists owing to its acute and chronic toxic effects on animal and human health. In addition, lead poisoning in human causes deleterious damage to the kidney, liver, reproductive and nervous systems [1,2]. According to the guidelines recommended by the World Health Organization (WHO), the maximum level for Pb(II) in drinking water is 0.05 mg/L [3].

Removal of Pb(II) is very important with respect to environmental and economical considerations. Conventional processes such as precipitation [4, 5], solvent extraction, ion exchange, chelating or impregnated resins [6,] and membranes processes [7] are facing technical and/or economical limitations, especially for dilute effluents. There is a dire need for developing/using alternative materials for the treatment of low-concentration effluents [8]. Therefore, an alternative technology is required to reduce the level of metal ion concentration from the effluents to the permissible limit. Biosorption is a relatively new technology to remove heavy metals from industrial wastewater. Hence there is a need to search for new biosorbents, especially of low cost biological origin. Low cost biosorbents could be produced from many raw materials such as agricultural by-products and industrial wastes. Many researchers evaluated some low-cost and environmental-secure substitutes such as rice husk [9,10], orange [11] and citrus [12] wastes, nut shells [13], wheat shells [14], Areca catechu powder [15], grape stalk

waste[16] for their potential in the removal of heavy metals from aqueous solutions.

Caesalpinia bonducella commonly known as fever nut belongs to the family Fabaceae, a prickly shrub found throughout the hotter parts of India, Myanmar and Srilanka. *Caesalpinia bonducella* leaves which are disposed as waste in several countries and hence they, are easily available with no cost. In this study we have utilized these waste material as biosorbent for removal of Pb(II) from wastewater by preparing the biosorbent with simple treatment of washing with water.

The aim of the present study was to investigate the Pb(II) removal from aqueous solution by *Caesalpinia bonducella* leaf powder. Effect of experimental parameters such as pH, dose, initial metal ion concentration and temperature on removal of Pb(II) was studied. The pseudo-first order, pseudo-second-order and intra particle diffusion models were studied to analyze the kinetic data. Langmuir and Freundlich isotherms were used to fit the equilibrium data.

2. EXPERIMENTAL

2.1. Preparation of biosorbent material

Caesalpinia bonducella leaves were collected from Somala, Chittoor District, Andhra Pradesh, India. Before use, the leaves were sun-dried and washed with distilled water several times to remove surface impurities, and then dried in an oven at 323 K for 2 days. The dried leaves were ground into a fine powdered form using a blender. Twenty-five grams of the powder was placed in a round bottom flask

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and washed with double distilled water until the washings were free of color and turbidity. Finally, it was dried in a hot air oven at 323 K for 24 h and stored in an airtight container in order to avoid moisture. The obtained product was named "CBLP" (*Caesalpinia bonducella* leaf powder) for further biosorption studies [17].

2.2. Chemicals and reagents

All the reagents were of analytical reagent grade and used without further purification. Distilled water was used to prepare all the solutions. Pb(II) stock solution was prepared (1000 mg/L) by dissolving accurately weighed amount of $\text{Pb}(\text{NO}_3)_2$ (purity > 99.99%) in 1000 mL of distilled water. The stock solution was diluted to the required concentration, and pH of the diluted solution was adjusted with NaOH or HCL.

3. RESULTS AND DISCUSSION

3.1. Characterization of CBLP

Characterization of biosorbent is vital for understanding the metal binding mechanism onto biomass. The physicochemical characterization in terms of moisture content, bulk density, ash content and the PZC of the biosorbent was discussed in our previous publication [17].

3.1.1. FT-IR analysis

In order to study the active functional groups participating in Pb(II) biosorption, FTIR analysis of CBLP were recorded in the frequency range from 4000-500 cm^{-1} . The FTIR spectrum of pure CBLP (Figure 1a) shows a broad peak at 3372 cm^{-1} corresponds to the O-H stretching vibration of hydroxyl groups in the CBLP. The band observed around 2925 cm^{-1} is attributed to the C-H stretching vibrations of $-\text{CH}_2$. The distinct peaks observed at 1741 cm^{-1} and 1644 cm^{-1} characterize the stretching vibration of carbonyl groups from aldehydes and ketones. The band located at 1112 cm^{-1} is due to C-O stretching of alcohols and carboxylic acids. After biosorption of Pb(II) (Figure 1b), the characteristic -OH band at 3372 cm^{-1} shifts to 3427 cm^{-1} . Also the bands shift (lower/higher wavenumber) from 2925, 1741, 1644 and 1112 cm^{-1} to 2927, 1746, 1319, 1262 and 1022, m^{-1} respectively. Thus, it can be reasonably concluded that the hydroxyl, carbonyl and carboxyl groups are involved in Pb(II) biosorption onto CBLP.

3.2. Effect of solution pH

The pH of the solution is an important parameter in biosorption processes. In order to determine the optimum pH for maximum removal efficiency, experiments were carried out in the pH range 2-7. The removal percentage of Pb(II) was increased significantly with the increase in solution pH. This may be due to the fact that at lower solution pH

values, H^+ competes with metal ions for biosorption sites, resulting in the surface of the biosorbent occupied by more H^+ , thus reducing the complexation of metal ions on the surface of the biosorbent. The maximum percent removal of Pb(II) was found to be at pH 5.0. At higher pH values (pH>5.0), a decrease could be noticed. With increasing pH value, the concentration of H^+ ions decreased resulting in greater Pb(II) biosorption. This may be due to the formation of soluble hydroxyl complexes in the solution. Under these conditions, an initial solution pH of 5.0 was considered as an optimum value and was used in all further experiments.

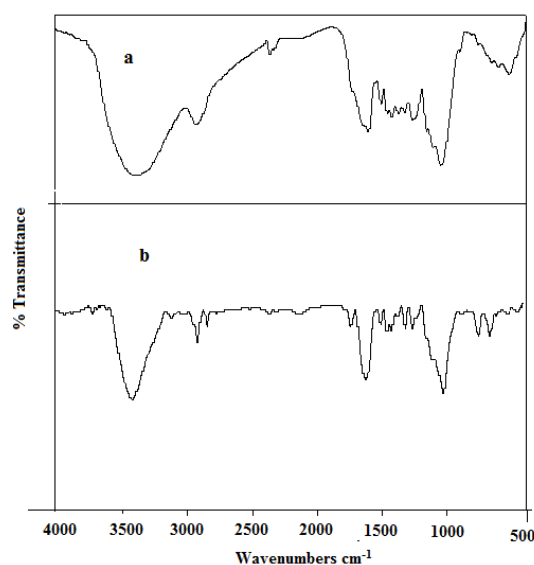


Figure 1. FT-IR spectra of (a) pure CBLP and (b) Pb(II) loaded CBLP.

3.3. Effect of biosorbent dose

One of the parameters that strongly affect the biosorption process in an aqueous solution is the biosorbent dose. The effect of sorbent dose on sorption of Pb (II) was studied by varying the amount of sorbent from 0.01 to 0.08 g/L. The removal percentage of Pb(II) increases with increase in biosorbent dose may be due to the availability of more binding sites present on the biosorbent surface. The maximum Pb(II) removal was attained with 0.06 g/L biosorbent dosage, and further increase in the dose (dose >0.06 g/L) does not significantly change the biosorption yield. Therefore, the optimum biosorbent dose of 0.06 g/L was selected in all the subsequent batch biosorption experiments.

3.4. Effect of contact time and biosorption rate kinetics

Biosorption of Pb(II) with respect to the effect of time was studied in the range of 15-120 minute. The biosorption rate of CBLP was studied at

Table 1: Kinetic parameters for the biosorption of Pb(II) onto CBLP at different metal ion concentrations.

Pb(II) Conc. (mg/L)	Lagergren-first-order			Pseudo-second-order			Weber and Morris		
	K_1 (1/min)	R^2	SSE	K_2 (g/mg.min)	R^2	SSE	K_{id} (mg/g.min ^{-0.5})	R^2	SSE
50	0.029	0.991	0.9036	0.011	0.999	0.0110	0.174	0.943	0.9435
75	0.034	0.979	0.9906	0.015	0.999	0.0042	0.212	0.962	0.9434
100	0.039	0.976	0.9907	0.021	0.999	0.0016	0.261	0.969	0.9390
125	0.043	0.986	0.9922	0.022	0.999	0.0037	0.307	0.971	0.9460

various initial Pb(II) concentrations (50, 75, 100 and 125 mg/L) while keeping all other parameters (pH 5.0, biosorbent dose 0.06 g/L, agitation speed of 150 min and temperature at 303 K) constant. The rapid initial uptake of the Pb(II) ions onto CBLP is due to the availability of large number of vacant sites available for biosorption. As the active sites were occupied, biosorption slowed down and finally an equilibrium stage was reached. The equilibrium contact time for Pb (II) biosorption was found to be 120 minutes. Three different kinetics models were applied to investigate the kinetics of Pb(II) adsorption namely pseudo-first-order [18], pseudo-second-order [19] and intraparticle diffusion model [20].

The pseudo-first-order rate equation is given as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (1)$$

where q_e (mg/g) and q_t (mg/g) are the amounts of Pb(II) sorbed at equilibrium and at time t . K_1 (min⁻¹) is the rate constant of first order biosorption process. The pseudo-first order kinetic constants were determined from slope of the plot of $\log(q_e - q_t)$ versus t and the values are shown in Table 1.

The pseudo-second order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (2)$$

where q_e and q_t are the amount of the Pb(II) removal per unit mass of biosorbent (mg/g) at equilibrium and at any time t (min), and K_2 (g/mg.min) is the pseudo-second order rate constant. The biosorption rate constant (K_2) is obtained from linear plot of t/q_t versus t and the values are shown in Table 1. Based on the R^2 values, it may be concluded that biosorption of Pb(II) follows the pseudo-second-order reaction rather than pseudo-first-order reaction. The intraparticle diffusion model is expressed as:

$$q_t = K_{id} t^{0.5} + C \quad (3)$$

where q_t (mg/L) is the amount adsorbed at time t (min), K_{id} is the intraparticle diffusion rate constant (mg/g.min^{-0.5}), and C is the intercept

which gives an idea about the thickness of the boundary layer. The values intraparticle diffusion model coefficients, calculated from the plot of qt (mg/g) versus $t^{0.5}$ (min), are given in Table 1. The first sharper portion is due to the mass transfer of solute molecules from the bulk solution to the biosorbent surface; this is also known as instantaneous biosorption. The second portion, the gradual biosorption stage, is limited by intraparticle diffusion. The third portion is the final equilibrium stage, where in intraparticle diffusion starts to slow down due to the extremely low solute concentration in the solution. Besides the SSE test was carried out to support the best fit.

$$SSE = \sum \frac{(q_{t,e} - q_{t,m})^2}{q_{t,e}^2} \quad (4)$$

where $q_{t,e}$ and $q_{t,m}$ are the experimental biosorption capacities of metal ions (mg/g) at time t and the corresponding values that are obtained from the kinetic models. Based on the low SSE values (Table 1) it can be concluded that biosorption Pb(II) onto CBLP follow pseudo-second-order model.

3.5. Effect of temperature

The effect of temperature is a major influencing factor in the biosorption process. The biosorption of Pb(II) ions was studied at 3 different temperatures, 303, 313 and 323 K, using CBLP as a biosorbent. The experimental results showed that the biosorption capacity increases with an increase in the solution temperature. The increase in the rate of biosorption with the increase in temperature may be attributed to the strong of adsorptive forces between the active sites of the biosorbents and adsorbate. This indicates that the biosorption of Pb(II) ions onto CBLP is endothermic in nature.

3.6. Isotherm studies

An equilibrium sorption isotherm describes the interactive behaviour between the metal ion and the biosorbent. The biosorption isotherms of Pb(II) onto CBLP were investigated using two isotherm models: the Langmuir and Freundlich isotherm models.

The linearized form of the Langmuir isotherm is:

$$\frac{1}{q_e} = \frac{1}{q_m K} \left[\frac{1}{C_e} \right] + \frac{1}{q_m} \quad (5)$$

where q_e is the equilibrium metal ion concentration on the sorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the maximum monolayer biosorption capacity of the sorbent (mg/g) and b is the Langmuir biosorption constant related with the free energy of sorption. The values of Langmuir constants of q_m and b are given in Table 2. The R^2 values are close to unity for Langmuir isotherm model. The plot of $1/q_e$ versus $1/C_e$ (Figure 2) was used for three temperatures to calculate these constants (Table 2) at all the temperatures.

The essential characteristics of the Langmuir isotherm can be described by a separation factor (R_L), which can be calculated using the following equation:

$$R_L = \frac{1}{1 + b C_0} \quad (6)$$

where b is the Langmuir constant (L/mg) and C_0 is the initial biosorbent concentration of Pb(II) ions (mg/L). The value of R_L indicates isotherm shape and whether the sorption is favorable or not, as per the following criteria: unfavourable ($R_L > 1$), Linear ($R_L = 1$), Favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values were found to be between 0-1 for the present study.

Freundlich isotherm describes the heterogeneous surface energies by multilayer adsorption and is expressed in linear form as;

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (7)$$

where K_f is a constant relating the biosorption capacity and $1/n$ is an empirical parameter relating the biosorption intensity. The values of Freundlich constants K_f and $1/n$ are included in Table 2.

3.6.1. χ^2 analysis

Chi-square test was carried out to identify the suitable isotherm for the biosorption of Pb(II) onto CBLP. The equation for evaluating the best fit model is written as:

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (8)$$

where $q_{e,m}$ is the equilibrium capacity obtained from the model (mg/g) and q_e is the experimental data on the equilibrium capacity (mg/g). The χ^2 values of the two isotherms (Table 2) are comparable and the lower Chi-square values confirm that the biosorption of Pb(II) onto CBLP follows Langmuir isotherm model.

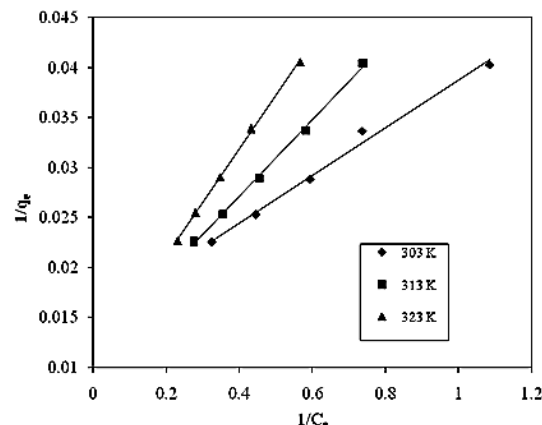


Figure 2: Langmuir isotherm for biosorption of Pb(II) onto *Caesalpinia bonducella* leaf powder at different temperatures.

4. CONCLUSIONS

The biosorption of Pb(II) from aqueous solution by CBLP has been investigated under different experimental conditions in batch mode. Kinetic studies showed that the biosorption of Pb(II) onto CBLP follows pseudo-second-order model. Langmuir isotherm provides the best fit of experimental sorption data for Pb(II) ions onto CBLP. The maximum monolayer capacity of Pb(II) onto CBLP is found to be 116.27 mg/g at pH 5.0, biosorbent dose of 0.06 g/L, contact time 120 min and temperature 323 K.

Acknowledgements

Gutha Yuvaraja is highly thankful to UGC, Government of India, New Delhi for the award of UGC-BSR Fellowship. **Abburri Krishnaiah** is grateful to UGC, Government of India, New Delhi for the award of UGC-BSR Faculty Fellowship.

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Table 2: Langmuir and Freundlich isotherm constants and correlation coefficients for Pb(II) biosorption onto CBLP at different temperatures.

Temp. (K)	Langmuir				Freundlich			
	q _m (mg/g)	B(L/mg)	R ²	χ ²	K _f (mg/g)	1/n	R ²	χ ²
303	86.20	0.351	0.999	8.71	22.85	0.566	0.979	56.53
313	94.33	0.153	0.999	13.38	20.79	0.670	0.989	69.46
323	116.27	0.150	0.999	28.49	18.62	0.633	0.993	86.33

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