



Biosorption of Pb (II) by *Spirogyra communis*: Kinetics and Isotherm Model Studies

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ABSTRACT

Biosorption of Pb(II) using immobilized beads of green algae, *Spirogyra communis* to evaluate biosorption potential was studied. The experimental results showed that Pb(II) biosorption was dependent on equilibrium pH, biosorbent dose, initial metal ion concentration and contact time. Langmuir and Freundlich adsorption isotherms were employed to analyze the experimental data. To determine the best fit kinetic equation for the biosorption of Pb(II) ions onto the algal beads two sorption kinetic models, viz., pseudo-first- and pseudo-second-order equations were also used. Analysis of FTIR spectra indicated the presence of electronegative functional groups on surface of *S. communis* responsible for binding of Pb(II) ions.

Keywords: Pb(II), Biosorption, Algae, Immobilization, Kinetics, *S. communis*

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INTRODUCTION

Environmental contamination by heavy metals is a serious problem due to their incremental accumulation in the food chain. Unlike most organic wastes and the microbial load in aquatic bodies, metal contaminants are not biodegradable, tending to accumulate in living organisms, thus becoming a permanent burden on ecosystems [1]. Most heavy metals are transition elements with incompletely filled d-orbitals. These d-orbitals provide heavy metal cations with the ability to form complex compounds. Trace amounts ($\mu\text{g l}^{-1}$) of some metal ions such as copper, zinc, cobalt, iron, nickel are required by living organisms as cofactors for the enzymatic activities. However, heavy metal ion concentrations at ppm (mg l^{-1}) level are known to be toxic to the organisms because of irreversible inhibition of many enzymes by the heavy metal ions. Lead has been cited as one of the the most toxic heavy metal that have long-term negative impacts on health, causing anemia, encephalopathy, hepatitis and nephritic syndrome. The process of accumulation and adsorption of metals by algae involves adsorption onto the cell surface (wall, membrane or external polysaccharides) and binding to cytoplasmic ligands, phytochelatins and metallothioneins, and other intracellular molecules. The algal cell wall has many functional groups, such as hydroxyl (OH), phosphoryl (PO_3O_2), amino (NH_2), carboxyl (COOH), sulphhydryl (SH), etc., which confer negative charge to the cell surface [2, 3]. Since metal ions in water are generally in the cationic form, they are adsorbed onto the cell surface [4, 5, 6, 7]. Freshly available data regarding the capacity of filamentous green algae, such as *Spirogyra* and *Cladophora* to adsorb heavy metal ions, such as Cd and Cu, etc. has opened the doors to new optimism [8]. They are easily available in terms of amount of biomass especially in tropical freshwater bodies. These algae are relatively newly known in this context and their potential to establish as better and cost-effective biosorbents in this scenario needs further exploration. The well-known understanding of filamentous green algae regarding their ability to bind metal ions and the functional groups in the cellulose of their cell wall makes them potential candidates as priority biosorbents for toxic metal cations.

In the present study biosorption of Pb(II) ions using immobilized beads of green algae, *Spirogyra communis* was studied, as a function of initial metal ion concentration, biosorbent dose, contact time and pH. Langmuir and Freundlich isotherm models were used for the expression of adsorption equilibrium.

Furthermore, to analyze the experimental data pseudo-first order and pseudo-second order kinetic models were also calculated.

MATERIALS AND METHODS

Biosorbent collection and its modification

Filaments of *Spirogyra communis*, were collected from ponds located in Fisheries College, G.B. Pant University, Pantnagar, India and tested for their biosorptive capacity for Pb(II) ion. The algal biomass was washed thoroughly in running tap water 4–5 times. To reduce water content it was sun dried for 4 days followed by drying in an oven and then grounded on aagate stone pistol mortar. To enhance the biosorption capacity of algae it was by entrapping powdered *Spirogyra communis* in an alginate matrix produced by ionic polymerization in calcium chloride solution, according to the following procedures [9]: the powdered algal cells were suspended in a 2% sodium alginate (BDH, UK) solution kept at a temperature of 60°C. The mixture was then dropped into a 2% calcium chloride (BDH, UK) solution using a peristaltic pump. The drops of Na-alginate solution gelled into 3.5±0.1 mm diameter beads upon contact with calcium chloride solution. The beads were washed well and then rinsed in deionized water and stored at 4°C. For blank alginate beads, similar procedures were followed, but without algae.

Preparation of heavy metal stock solutions

Stock solution of Pb(II) ion was prepared by dissolving lead nitrate $Pb(NO_3)_2$ in distilled water. From this stock solution different concentration of Pb(II) were prepared (10, 30, 50, 70 and 90 mg L⁻¹).

Biosorption Evaluation

100 mL of Pb(II) solution was taken in 150 mL Erlenmeyer flasks (at concentrations of 10, 30, 50, 70 and 90 mg L⁻¹). The immobilized beads of the free cells equivalent to different biomass concentration (0.1, 0.2, 0.3, 0.4, 0.5, 1.0 and 1.15 g) were suspended in the above mentioned flasks separately. These biomass dosages were also introduced in a separate set of flasks containing distilled water only, as control. The flasks were maintained under constant agitation on a rotator shaker (180 rpm) for different contact time (15, 30, 60, 120 and 180 min). The experiments were conducted at varying pH, ranging from 2.0 to 8.0, adjusted using 0.2N HNO₃ and 0.1N NaOH. The Pb(II) ion concentration of the samples were determined by Atomic Absorption Spectrophotometer. The amount of adsorbed Pb (II) ions (mg metal ions/g biomass) were calculated from the formula:

$$q = (C_i - C_e) V/m$$

Where C_i and C_e are the initial and final metal concentrations in mg L⁻¹ respectively, V is the volume of the metal solution in ml, m is the weight of the biomass in g.

Fourier Transform Infra-red Spectroscopy (FTIR)

For FTIR spectroscopy, tablets of algal biomass were prepared in a Graseby-Specac Press, using algal mass mixed with Potassium Bromide (KBr, 1:100 p/p). The following samples were subjected to FTIR.

-Algal biomass cleaned by HNO₃ treatment and deionized water (control)

-Metal loaded *S. communis* biomass

Mathematical modeling and interpretation of data

The data collected as a result of biosorption studies were tested by conventionally used adsorption isotherms, such as Langmuir and Freundlich isotherms for adsorption. Moreover, kinetic modelling was also carried out.

Desorption Studies

In order to show the reusability of the biosorbents, adsorption–desorption cycles of Pb were repeated five times with 1.0 mol/L HCl by using the beads of *S. communis*. For batch desorption experiments a series of 250 ml Erlenmeyer flasks containing 50 ml HCl solution of known concentration (1.0 mol/L) was contacted with metal-loaded biosorbent at room temperature (25±2°C). The mixtures were agitated on orbital shaker at 150 rpm for 30 min. The biosorbent was removed and supernatant was analysed for heavy metal concentration by AAS.

RESULTS AND DISCUSSION

FTIR spectroscopy

FTIR spectra for *S. communis* is given in Fig. 1. The region between 3200-3500 cm⁻¹ exhibits the stretching vibration of O-H and N-H which confirms the presence of hydroxyl and amine functional groups in alga. The region between 3000-2800 cm⁻¹ shows the C-H stretching vibrations of sp³ hybridized C in CH₃ and CH₂ functional groups. The peaks at 1652 cm⁻¹ reveal the presence of carbonyl group. The presence of amide in the structure of alga is confirmed by the peak at 1545 cm⁻¹. The absorption peaks around 1240 cm⁻¹ and 1150 cm⁻¹ indicate the phosphate esters in *S. communis*. The phosphate esters are the source of phospholipids. The absorption peaks at the respective frequencies of 1026 cm⁻¹ confirm the presence of sulfoxides in *S. communis*. The observed frequencies in FTIR spectra of the algae used indicate

the presence of amine ($R-NH_2$), amide ($R_1(CO)NR_2R_3$) (aminoacids, proteins, glycoproteins, etc.), carboxylic acids (fatty acids, lipopolysaccharides, etc.), sulfoxides (in case of *S. communis*) and phosphates.

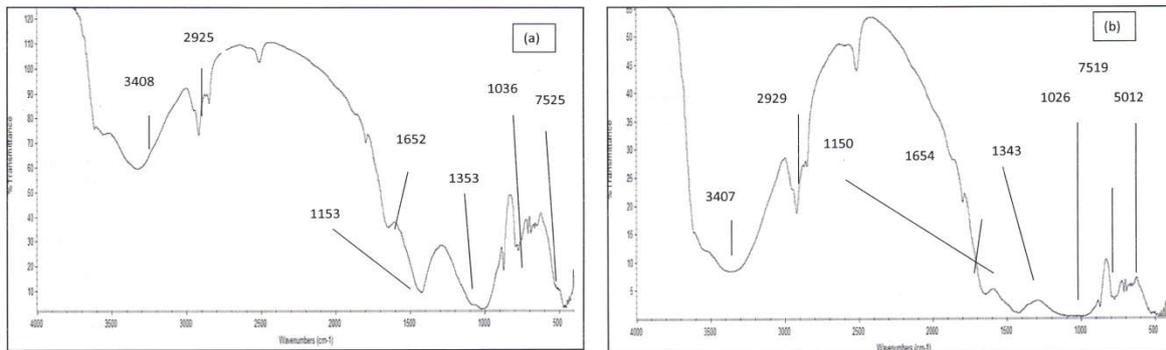


Fig. 1: FTIR spectra of *S. communis* (a) native (b) Pb- loaded

Effect of parameters on biosorption potential

Fig. 2 illustrates the biosorption of Pb(II) ions by immobilized algal beads as a function of contact time. The equilibrium time for Pb removal (97.94%) by algal beads was observed to be 60 min. A further increase in the contact time has a negligible effect on the removal percentage because the active sites of the biosorbent gets exhausted due to the repulsive forces between the metal ions in the solid and bulk phases [10]. The metal uptake by the sorbent surface was rapid initially and geared as the competition for the decreasing availability of active sites intensified by the metal ions remaining in the solution [11, 12]. The maximum removal of Pb(II) by *S. communis* was obtained at 50 mg L⁻¹ of initial metal ion concentration (Fig. 2). Removal of Pb by biosorbent increased with increase in initial concentration of the metal, up to a certain concentration (50 mg L⁻¹), but with further increase in metal concentration (>50mg L⁻¹), metal removal efficiency of the biosorbent got saturated or declined slightly. increasing the initial metal concentration results in an increase in the biosorption capacity because it provides a driving force to overcome mass transfer resistance between the biosorbent and biosorption medium [13].

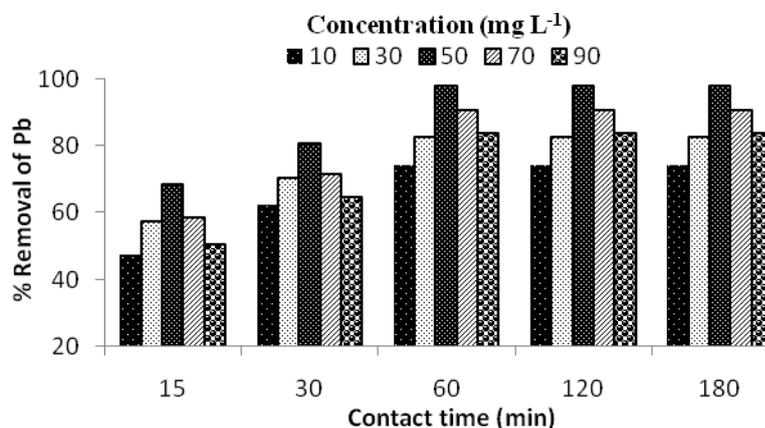


Fig. 2 The effect of contact time and initial metal ion concentration on biosorption of Pb(II) by algal beads of *S. communis*

The maximum removal of Pb (96.54%) was recorded at 0.5 g equivalent algal beads. (Fig. 3). However, it has been observed that there was no change in the extent of heavy metal adsorption, when the algal dose was increased further beyond its optimum value (0.5 g). For a fixed metal initial concentration, increasing the adsorbent dose provides greater surface area and availability of more active sites, thus leading to the enhancement of metal ion uptake [14, 15].

The maximum removal efficiency for Pb was observed at pH 6 (Fig. 4). At low pH values the concentration of hydrogen ion was high, effectively competing for binding sites, resulting in a reduced uptake capacity [16]. As the pH increased, more functional groups were dissociated and became available for metal binding [17], but as the pH increased further metal began to deposit and refused to be adsorbed.

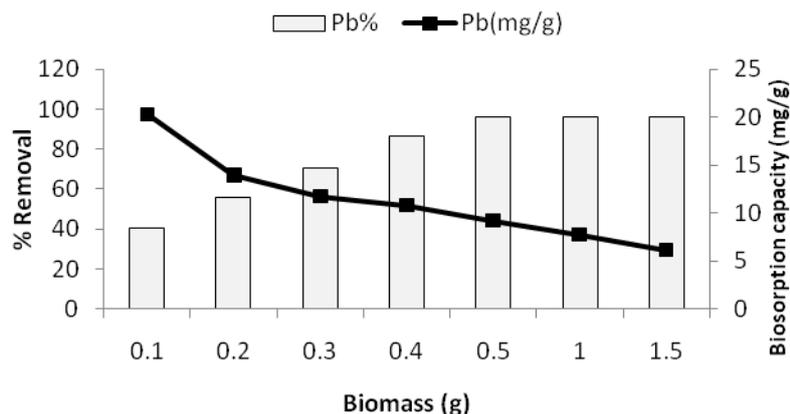


Fig. 3 The effect of biosorbent dose(g) on biosorption of Pb(II) by algal beads of *S. communis*

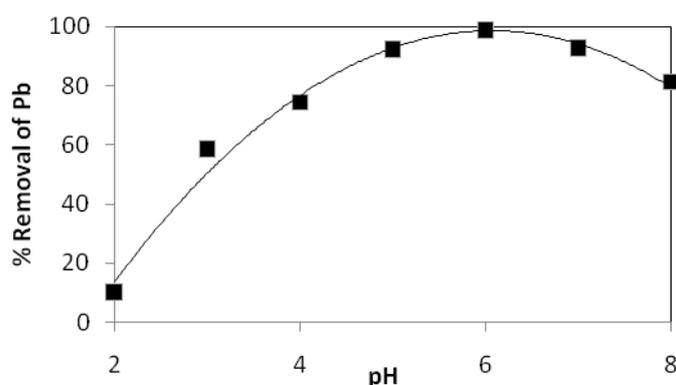


Fig. 4 The effect of pH on biosorption of Pb(II) by algal beads of *S. communis*

Kinetics and Isotherm

In the present study all the data on the sorption of Pb(II) ions fitted better in Freundlich isotherm than the Langmuir isotherm as it is evident from values of correlation coefficient listed in Table 1. Better fitting of equilibrium data in the Freundlich isotherm confirms the heterogeneous adsorption of Pb(II) on to the surface of biosorbents. Freundlich adsorption isotherm presumes that adsorption of metal is mainly by the process of ion exchange. Thus, it is assumed that during the present study ion-exchange may have played major role in metal adsorption. The Langmuir model assumes a definite number of homogenous binding sites on the surface, and this model does not allow interaction among sites. The values of the pseudo-second-order equation parameters together with the correlation coefficients were listed in Table 2. The correlation coefficient (R^2) for the pseudo-second-order kinetic model was 0.99. These values being very close to one, suggesting that the data on the biosorption of Pb by *S. communis* showed a good fit to the second order reaction kinetics model, which relies on the assumption that biosorption may be the rate limiting step, which could be chemisorption involving valence forces through the exchange of electrons between sorbent and sorbate, complexation, coordination and/or chelation [18].

Table 1. Langmuir model constants and correlation coefficients for sorption of Pb(II) on *S. communis* beads

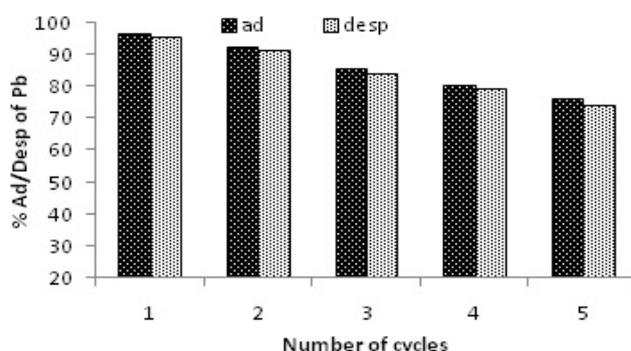
Metal	Langmuir			Freundlich		
	q_{\max} (mg g^{-1})	b (L mg^{-1})	R^2	K_f (mg g^{-1})	N	R^2
Pb	-4.94	-0.10	0.667	3.77	0.50	0.944

Table 2. Kinetic model constants and correlation coefficients for sorption of Pb on *S. communis* beads

Metal	Pseudo-first-order kinetic model			Pseudo-second-order kinetic model		
	K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g/mg/min)	q_e (mg/g)	R^2
Pb	0.029	2.53	0.633	0.074	10.09	0.986

Desorption

Maximum desorption of Pb(II) ion (95.32%) was observed by *S. communis* beads during 1st adsorption-desorption cycle (Fig. 5). In order to show the reusability of the biosorbents, adsorption-desorption cycle of Pb was repeated five times by using *S. communis* beads. It was observed that the adsorption capacities of the biosorbents did not change so much during repeated adsorption-desorption operations (Fig. 5). These results show that the alga under investigation could be repeatedly used for adsorption of Pb without significant losses in its initial adsorption capacity.

**Fig. 5: Adsorption/Desorption cycles for Pb(II) by *S. communis* beads**

CONCLUSION

Heavy metal biosorption by *S. communis* beads revealed that the rate and extent of heavy metal uptake were influenced by initial metal ion concentration and contact time, biomass dose and pH. Maximum removal of heavy metals by algal beads was obtained at 0.5 g of *S. communis* biomass. The optimum pH value for uptake of Pb was found to be 6.0. The equilibrium time for Pb(II) removal was 60 min by algal beads at 50 mg L⁻¹ of initial metal ion concentration. All the data on metal sorption fitted better in Freundlich isotherm than Langmuir isotherm and Pseudo-second-order kinetics was suitable for interpretation of data, which is evident by values of correlation coefficient for Pb(II). Desorption studies revealed a high reusability of algae for all the tested heavy metals. FTIR revealed biosorptive binding sites and possible electronegative functional groups, such as carboxyl, hydroxyl, carbonyl, etc., on the surface of algae which could favor the binding of Pb(II) ions. Easy availability and cost effective nature of *S. communis* make it most promising biosorbent over other conventional biosorbents. Biosorption of Pb(II) ion utilizing *S. communis* beads proved promising technique to mitigate water pollution.

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