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Biosorption of lead ions (Pb^{2+}) from simulated wastewater using residual biomass of microalgae

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ABSTRACT

Presence of different heavy metals in the industrial effluents poses a great problem to the researchers/ technologist dealing with environmental pollution. The present study investigates the suitability of the residual biomass of green algae *Phormidium* sp.—a microalgal strain meant for biodiesel production to remove lead (Pb^{2+}) ions from aqueous solution in both batch type stirred system and a semi-batch-packed bed adsorber. The influences of adsorbent dosage, temperature, pH, contact time, and initial metal ion concentration of solution on biosorption have been investigated. The biosorption equilibrium has been established in 40 min. Thermodynamic, kinetic, and isotherm studies have been carried out for the biosorption of Pb^{2+} ions on *Phormidium* sp. The values of mean enthalpy (ΔH) and the mean entropy (ΔS) have been determined to be −22.75 kJ/mol and 85.24 J/mol K, respectively. The value of Gibbs free energy, ΔG, has been observed to decrease with increasing temperature. The maximum removal efficiency of Pb^{2+} on *Phormidium* sp. at equilibrium has been observed to be 92.2% at pH 5.0, initial Pb^{2+} concentration of 10 mg/L, and an adsorbent dosage of 4 g/L. Experimental breakthrough curves obtained using different flow rate (2–4.5 mL/min), initial concentration (10–30 mg/L), and bed heights (0.1–0.2 cm) have been analyzed.

Keywords: Microalgal strain; Thermodynamics; Kinetics; Isotherm; Breakthrough curves

1. Introduction

The removal of heavy metal from industrial effluent is one of the most challenging tasks faced by the scientific community. Our ecosystem is getting severely affected due to the indiscriminate discharge of effluents containing heavy metals into its system by many industries [1]. These substances are stable and persistent environmental contaminants as they cannot be degraded or destroyed [2]. On the other hand, due to severe energy crisis, a lot of research works are directed toward the development of non-conventional fuels posing no competition with food and ensuring least CO_2 emission. Microalgal biodiesel, a third-generation biofuel, is one such fuel. Besides having the unique property to store oil, microalgae have been reported to be capable of removing the heavy metals. Therefore, biosorbents may be developed using the residual solids remaining after the extraction of algal

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oil from microalgae. This ensures simultaneous production of biofuel and biosorbent from any suitable microalgal cultures.

Lead (Pb^{2+}) is one of the heavy metals with high toxicity when in excess. In children, lead causes a decrease in intelligence quotient score, retardation of physical growth, hearing impairment, impaired learning, as well as decreased attention, and classroom performance. In individual of all ages, lead can cause anemia, kidney malfunctions, brain diseases, and impaired function of peripheral nervous system, high blood pressure, reproduction abnormality, developmental defects, abnormal vitamin D metabolism, colic-like abnormal pains, dementia, madness, and in some situations death [3]. Extensive research works on lead removal have been carried out in the past few years using biosorption. Biosorption is a term that describes the removal of adsorbates by passive binding to non-living biomass from an aqueous solution such that the removal mechanism is not metabolically controlled [4]. The effectiveness of biosorbents depends to a large extent on their biochemical composition, particularly on functional groups available in cell wall polysaccharides[5]. Choice of biosorbent plays an important role with respect to the economic viability of the process. Cost and stability are usually considered to be most vital parameters for the selection of biosorbents. Cost-effective and abundant biomaterials may serve as biosorbents, if the heavy metals under consideration have affinity toward their active sites. Biosorbents, such as *Ficus religiosa* leaves [6], *Caulerpa lentillifera* [7], bagasse fly ash [8], coir [9], *Aspergilus niger* [10], groundnut hull [11], protonated citrus peel [12], and pre-treated orange peels [13], have been successfully used for this purpose.

In the recent past, extensive studies have been carried out on the utilization of microalgal biomass as biosorbent for the removal of heavy metals [14–18]. *Phormidium* sp. is one of the microalgae on which extensive research works were conducted among our laboratory microalgae; *Phormidium* sp. was used for the generation of biodiesel [19]. In the present study, biosorption of Pb^{2+} was carried out using defatted algal biomass (*Phormidium* sp.).

The studies were carried out to find out the effective use of *Phormidium* sp. (negatively charged) as an inexpensive biosorbent for the removal of lead from the simulated industrial effluent. In addition, dense distribution of anions was observed over the surface of *Phormidium* sp., which might be responsible for the higher adsorption capacity as compared to the various other algal species [17]. The effects of operating parameters such as initial metal ion concentration, pH, and temperature on the biosorption process were also studied in batch mode. Kinetic, isothermal, and thermodynamic modeling was carried out from the data obtained from the batch experiments. Breakthrough curves were analyzed when the experiments were carried out in semi-batch mode. Fourier Transform Infrared spectroscopy (FTIR) studies were also performed in order to characterize the distribution of functional groups on the sorbent surface.

2. Materials and methods

2.1. Chemicals

Lead nitrate (MERCK), hydrochloric acid (MERCK), and sodium hydroxide pellets were used. All chemicals used were of analytical reagent grade.

2.2. Analytical instruments

FTIR spectroscopy (Shimadzu 0,119) was used for the characterization of the adsorbent; Spectroquant (MERCK Pharo 300) was used to analyze the concentration of metal ion.

2.3. Adsorbent preparation

Phormidium sp. was used as the biosorbent which was cultivated in our laboratory for the production of biodiesel. The algae collected were thoroughly centrifuged in a Superspin R-V/m. They were then dried in a hot air oven at 90–100°C for 3 h. The dried biomasses were crushed into powder using a pestle. The washed and dried material was then passed through a sieve to obtain a particle size of 150 μm.

2.4. Batch experiments

2.4.1. Effect of adsorbent dosage

The effect of adsorbent dosage on removal of Pb^{2+} was studied by adding 0.05, 0.1, 0.15, 0.2, and 0.25 g of the biomass separately to glass flasks containing 50 mL of Lead nitrate solution having a concentration of 10 mg/L. The pH and the temperature were kept constant at 5 and 25°C, respectively. The flasks were kept under constantly stirred condition for 24 h at 200 rpm. Concentration after 24 h was measured using Spectroquant (Pharo 300). The concentration of Pb^{2+} in the sorbent phase was calculated by mass balance. The following equation was used to determine the concentration of Pb^{2+}:

$$q_e = \frac{V_{\text{solution}}(C_0 - C_e)}{M_{\text{sorbent}}} \tag{1}$$

2.4.2. Effect of temperature

In order to study the effect of temperature, same experiments were conducted at different temperature (25, 35, and 40˚C) keeping the adsorbent dosage and pH constant at 4 and 5 g/L, respectively. The initial metal ion concentration was kept at 10 mg/L.

2.4.3. Effect of pH

The effect of pH on the biosorption of Pb^{2+} was investigated by adjusting the pH values to 2, 3, 4, 5, 6, and 7 keeping the adsorbent dosage, temperature, and initial metal concentration constant at 4 g/L, 25˚C, and 10 mg/L, respectively.

2.4.4. Isotherm studies

Isotherms were generated using the saturation concentration of Pb^{2+} in sorbent phase corresponding to different initial concentrations (10, 15, 20, 25, and 30 mg/L) at an adsorbent dosage of 4 g/L at temperature 25˚C and pH 5.

2.4.5. Adsorption kinetics

Kinetic studies were carried out in a constantly stirred vessel at room temperature (~25˚C). Accurately weighed amounts of biomass (0.2 g) were added to a set of 10 glass flasks containing 50 mL of Lead solution at specified concentration of 10 mg/L. The pH was adjusted to 5 using 0.1 N HCl and 0.1 N NaOH. Flasks were taken out of the incubator at 10 min interval spanning from 0 to 90 min. Contents of each flask were filtered through Whatman filter paper (70 mm diameter and 2.5 μm pore size) and were analyzed to determine the Pb^{2+} concentration. Concentration of metal ion in the solid phase was determined using Eq. (1).

The following equation was used to evaluate the removal efficiency (%) of Pb^{2+} through biosorption:

$$A(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

2.5. Semi-batch packed bed adsorption

Removal of Pb^{2+} in semi-batch mode (continuous with respect to liquid phase and batch with respect to adsorbent) was carried out in a cylindrical 15 cm high glass column of 4.8 cm internal diameter. Crushed *Phormidium* sp. (particle size 150 microns) was used as the adsorbent. Adsorbent bed was placed in between two non-adsorbing zones made of ceramic wool. This arrangement was made to avoid carrying over of active adsorbent with liquid solution. Simulated wastewater containing Pb^{2+} ions was passed up through the bed using a peristaltic pump. The adsorbent dosage was varied from 0.5 to 2 g. On the other hand, initial concentration of Pb^{2+} and volumetric flow rate of simulated wastewater were varied in the range of 10 –30 mg/L and 2 –4.5 mL/min, respectively. For experiments, varying the inlet concentration of Pb^{2+}, flow rate was maintained at 2 mL/min. Similarly, inlet concentration was maintained at 10 mg/L during the experiments, varying the flow rate of simulated water to isolate the effect of one parameter from the other on the overall removal of Pb^{2+} through biosorption using *Phormidium* sp.

3. Equations used

3.1. Thermodynamics of biosorption

The thermodynamic parameters namely Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for the adsorption process may be obtained using the following relations:

$$\log\left(\frac{q_e}{C_e}\right) = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \tag{3}$$

$$\Delta G = \Delta H - T\Delta S \tag{4}$$

where the ratio, q_e/C_e is known as the sorption affinity of the biosorbent. The values of ΔH and ΔS have been determined using Eq. (3) through the regression analysis using the adsorption data generated from experimental runs, as described in Section 2. Gibbs free energy, ΔG of adsorption has been evaluated using Eq. (4).

3.2. Kinetic equations

Both pseudo-first-order and pseudo-second-order kinetics have been attempted for kinetics of biosorption of Pb^{2+} on *Phormidium* sp. Pseudo-first-order model is given as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{5}$$

where q_e and q_t are the amounts of biosorbed (mg/g) at equilibrium and at time, t respectively, and k_1 is the rate constant of pseudo-first-order biosorption (min^{-1}).

Pseudo–second-order model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 is the rate constant of pseudo-second-order biosorption (g/mg min).

Model parameters have been determined by non-linear regression analysis through minimization of square of differences between the predicted and experimental data for $q(t)$.

3.3. Model isotherms

Biosorption isotherms describe how adsorbate interacts with biosorbents and equilibrium is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during the surface biosorption. Equilibrium isotherms are determined to quantify the adsorption capacity of the biosorbent with respect to an adsorbate. The most common types of models describing this type of system are the Langmuir and Freundlich isotherms.

Langmuir isotherm assumes monolayer coverage of adsorbate over a homogeneous adsorbent surface, and that the adsorption of each molecule onto the surface has equal activation energy. On the other hand, Freundlich isotherm considers a heterogeneous surface with a non uniform distribution of heat of biosorption over the surface, and a multilayer biosorption is assumed. The Langmuir equation is represented as follows [20]·

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{7}$$

where $q_{\max}$ is the monolayer capacity of the biosorbent (mg/g) and b is the biosorption constant (L/mg).

The Freundlich equation may be expressed as follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{8}$$

where K_F and $1/n$ are the constants of Freundlich isotherm constants related to biosorption capacity and intensity of biosorption, respectively.

4. Results and discussion

4.1. Batch experiments

Efficacy of removal (%) of Pb^{2+} from simulated waste water has been analyzed with respect to adsorbent dosage, temperature, pH, contact time, and initial metal ion concentration. This is described in the following subsection.

4.1.1. Effect of adsorbent dose on Pb^{2+} uptake

The effect of adsorbent dose on Pb^{2+} sorption on the algae (*Phormidium* sp.) has been determined by varying the biomass concentration from 1 to 5 g/L. From the experimental data (figure not shown), it may be inferred that adsorbent dose strongly affects the removal of lead. The adsorption of Pb^{2+} is found to increase with the concentration of the biosorbent up to 4 g/L. Maximum adsorption of 92.2% is achieved. Any further increase in biomass concentration over 4 g/L does not improve the extent of biosorption yield due to the saturation of the biosorbent surface with Pb^{2+} ions. It may be attributed to the fact that at high sorbent dosage, the available metal ions are insufficient to cover all the exchangeable sites on the biosorbent, resulting in the saturation of percentage biosorption.

4.1.2. Effect of temperature

Temperature also plays a vital role in the Pb^{2+} sorption. It has been observed that, with increasing temperature (25–40˚C), the percentage adsorption decreases (92–85%). This can be justified by the fact that with rise in temperature the adsorbent sites tend to shrink significantly reducing the uptake amount and percentage of adsorption.

Using Eq. (3), the value of adsorption enthalpy value (ΔH) has been calculated as −22.75 kJ/mol. This shows that the interaction between Pb^{2+} and the biomass was endothermic. The enthalpy changes are considerable to suggest that the interactions are chemical in nature. The mean entropy change of biosorption of lead on the biomass was calculated as 85.24 J/mol K. The Gibbs free energy (Eq. (4)) has been found to decrease from −24.998 to −26.702 kJ/mol with the increase in temperature from 25 to 40˚C (Table 1). This shows that the metal–adsorbent complex is stable in nature. It is to be noted that in all the cases the changes in Gibbs free energy are small in magnitude compared wih that reported in the literature. Values of Gibbs energy have been reported as −26.92, −28.15, −29.37, and −230.77 kJ/mol at 293, 303, 313, and 323 K, respectively, for adsorption of Pb^{2+} on an agricultural byproduct, *C.annuum* seeds [21]. It may be noted that the small discrepancies may be due to the differences in affinities of the cations toward the functional groups present in the biosorbents.

Table 1
Thermodynamic parameters

Temp. (°C)	C_e (mg/L)	%adsorption	$(C_0 - C_e)$ (mg/L)	q_e (mg/g)	q_e/C_e	Log (q_e/C_e)	$1/T$ (K^{-1})	ΔG (kJ/mol)
25	0.78	92.2	9.22	2.305	2.955	0.471	0.003	−24.998
35	1.16	88.4	8.84	2.210	1.905	0.280	0.003	−25.85
40	1.47	85.3	8.53	2.133	1.450	0.162	0.003	−26.702

4.1.3. Effect of pH

It is very well known that pH is one of the main parameters, which plays an important role in the sorption of heavy metals on the biosorbent surface. The effect of pH has been studied by varying the pH values from 2 to 7. It has been observed that sorption capacity was highly dependent on pH. It has been observed that the biosorption increases up to pH 5 but beyond pH 5 the sorption remains nearly constant (Fig. 1). The low level of Pb^{2+} biosorption at pH below 3 may be due to the protonation of active biosorption sites resulting in a competition between H^+ and Pb^{2+} for occupancy of the binding sites. There is a sharp increase in biosorption from pH 3 to 5. The increase in metal removal may be due to decrease in competition between protons and metal cations for the same functional groups on the adsorbent surface, and decrease in the positive surface charge resulting in a lower electrostatic repulsion between the surface and metal ions. Beyond pH 5, the lead uptake may decrease mainly due to metal precipitation.

4.1.4. Sorption kinetics

Fundamental information about the rate of biosorption of Pb^{2+} has been obtained from the experimental data dedicated to the adsorption kinetic. Time histories of concentration of Pb^{2+} in the adsorbent phase indicate that the amount of biosorption sharply increases with the contact time in the initial stage (0–20 min), and then gradually increases to reach an equilibrium value in approximately 40 min (Fig. 2). A further increase in contact time had a negligible effect on the amount of biosorption. According to these results, the shaking time has been fixed at 24 h for the rest of the batch experiments to make sure that the equilibrium is reached.

The second-order model shows much better fit as compared with the first-order model with $R^2 > 0.99$. The second order constants, namely q_e and k_2 have been evaluated to be 2.38 mg/g and 0.448 min^{-1}, respectively.

The validity of pseudo-second-order kinetic model signifies that the rate-limiting step may be chemical sorption involving valance forces either through sharing or exchange of electrons between heavy metal ions and the adsorbent [22]. Based on theoretical considerations, the following expressions may suitably describe the reaction of a divalent metal ion M binding to two free binding sites B:

$$M + B \leftrightarrow B_2\text{Mr} = k[M][B]^2 \tag{9}$$

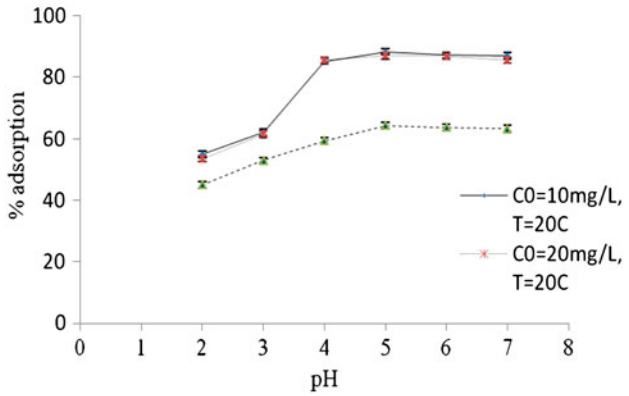

Fig. 1. Variation of adsorption profile of Pb^{2+} ions on *Phormidium* sp. with pH (initial lead concentration = 10 and 20 mg/L, temperature = 25˚C, adsorbent = 4 g/L, time = 24 h).

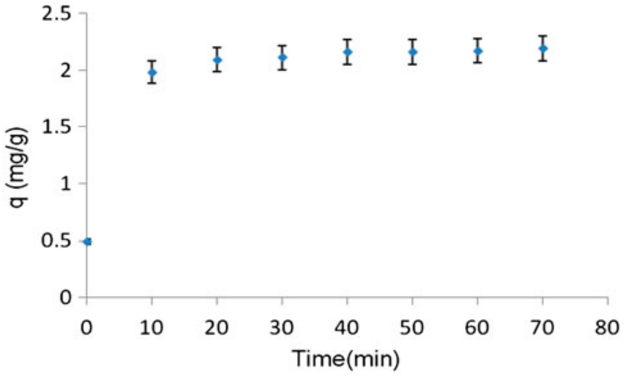

Fig. 2. Variation in the amount of uptake q (mg/g) of *Phormidium* sp. with time (initial lead concentration = 10 mg/L, temperature = 25˚C, adsorbent = 4 g/L).

This indicates that the sorption rate would be proportional to the metal concentration, and the square of the number of free sites which corresponds to the term $(q_e - q)^2$ in the second-order model. The better fit of the second-order model, therefore indicates that a 1:2 binding stoichiometry applies, where one divalent metal binds to two monovalent binding sites. However, the second-order model does not take into account the effect of metal concentration on reaction rate.

4.1.5. Effect of inlet concentration and sorption isotherm

Variation of biosorption with different initial concentration has been studied using the same biomass loading (4 g/L). It has been observed that with the increase in the initial concentration the biosorption decreases to a great extent. This can be attributed to the fact that the adsorbent site gets blocked due to clustering of metal ions at high initial metal concentration inhibiting the adsorbent sites to adsorb more metal ions (Fig. 3).

Biosorption isotherms describe how adsorbate interacts with biosorbents and equilibrium is established between adsorbed metal ions on the biosorbent and the residual metal ions in the solution during the surface biosorption. The nature of equilibrium isotherms has been investigated to determine the capacity of the biosorbent for metal ions. The most common types of models describing this type of system are the Langmuir and Freundlich isotherms.

The Langmuir model fits well with $R^2 > 0.99$. The Langmuir constants such as q_{mon} and K_L have been calculated as 5.1546 mg/g and 0.8432 L/mg. Since the fitting of experimental data with Langmuir isotherm is better compared with Freundlich isotherm, it is expected that monolayer coverage of adsorbate over a homogeneous adsorbent surface is occurring and the biosorption of each molecule onto the surface has equal biosorption activation energy. The Freundlich isotherm fitting had $R^2 < 0.99$. The Freundlich constants "n" and K_F have been evaluated as 3.649 and 2.52 mg L/g, respectively.

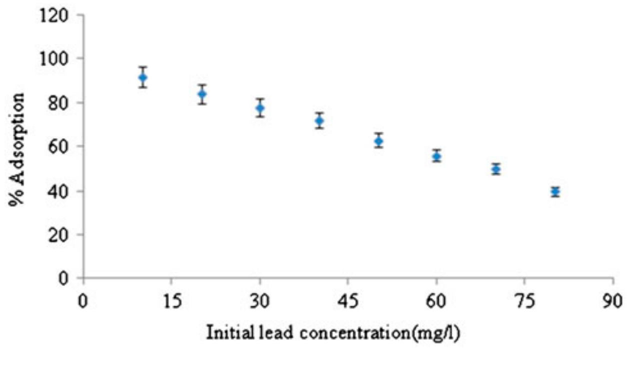

Fig. 3. Adsorption profile of *Phormidium* sp. with initial concentration of Pb^{2+} ions (temperature = 25˚C, adsorbent = 4 g/L, time = 24 h).

4.2. Semi-batch packed bed adsorption

4.2.1. Breakthrough phenomenon

When an adsorbate solution is passed through a fixed adsorbent bed, a point is reached where the effluent concentration reaches some limiting permissible value. This point is termed as the breakthrough point. After progression of a certain adsorption time, the effluent concentration suddenly shoots and ultimately reaches the value almost equal to the inlet concentration. The point of shooting is known as the breakthrough point and the other one is known as the exhaustion point. According to Treybal [23], the break point is often taken as a relative concentration of 0.05 or 0.1, and since only the last portion of the fluid processed has this high a concentration, the average fraction of solute removed from the start to the break point is often 0.99 or higher. However, it has been reported in literature [24–26] that, in case of semi-batch adsorbers for wastewater treatment, the effluent concentration at breakthrough and exhaustion points are approximately 35 and 92%, respecively, of that of the inlet concentration .

4.2.1.1. Effect of flow rate. Flow rate plays a very vital role in evaluating the performance of adsorption process for semi-batch treatment of industrial effluent. The flow rate is inversely proportional to the space-time i.e. with increasing flow rate the retention time decreases. Experiments have been carried out by varying the flow rate between 2 and 4.5 mL/min to determine the effect of flow rate of lead adsorption on the green algae. During these experiments, the initial Pb^{2+} concentration, pH, and initial adsorbent dosage were maintained at 10 mg/L, 5, and 0.5 g, respectively. The effect of flow rate on breakthrough performance at the above-operating conditions is shown in Fig. 4. In the present study, the breakthrough times and the exhaust times correspond to C/C_0 equal to 0.35 and 0.94, respectively, where C and C_0 are the Pb^{2+} concentration in the inlet and outlet of the column, respectively. For the flow rates 2, 3.5, and 4.5 mL/min, the breakthrough time was observed to be 180, 120, and 90 min, respectively. The saturation time has been determined as 330, 270, and 240 min, respectively. From these

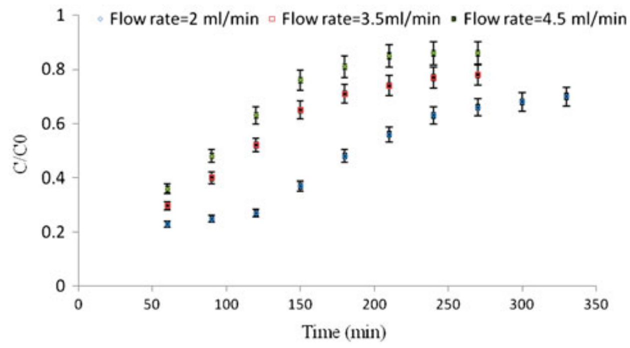

Fig. 4. Breakthrough curves for lead adsorption on*Phormidium* sp. at different flow rates (♦ 2 mL/min, ■ 3.5 mL/min, ▲ 4.5 mL/min).

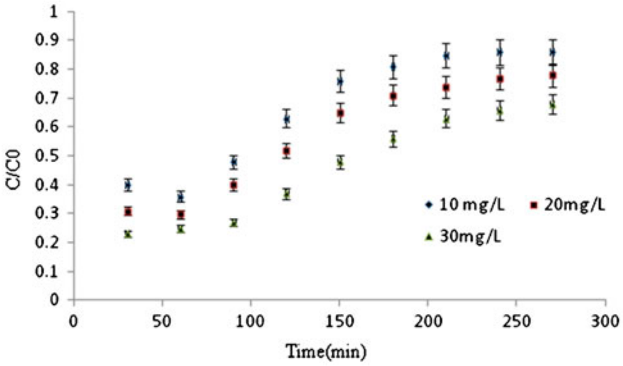

Fig. 5. Breakthrough curves for lead adsorption onto *Phormidium* sp. at different initial Pb^{2+} concentration (♦ 10 mg/L, ■ 20 mg/L, ▲ 30 mg/L).

results it is elucidated that at low flow rate it takes more time to achieve saturation. This can be explained by the fact that at lower flow rates, the residence time of the adsorbate in the column would increase and metal ions have more time to diffuse into the pores of adsorbent through intraparticle diffusion [19–21].

4.2.1.2. Effect of inlet lead concentration. The time for the appearance of breakthrough and shape of the breakthrough curve are the major characteristics for determining the operation and the dynamic response of adsorption column. The general position of the breakthrough curve along the time axis depends on the capacity of column with respect to the feed concentration, bed height, and the flow rate [25]· Break through curves have been obtained by keeping the inlet Pb^{2+} concentration between 10 and 30 mg/L. The other parameters such as pH, adsorbent dosage, and flow rate have been kept constant at 5, 0.5 g, and 2 mL/min, respectively. The adsorption breakthrough curves obtained for adsorbate concentrations of 10, 20, and 30 mg/L are shown in Fig. 5. The breakthrough time was found to decrease from 180 to 120 min due to the saturation of binding sites. The increase in uptake capacity of the biosorbent is due to the fact that high inlet Pb^{2+}concentration provides higher driving force for the transfer process to overcome the mass transfer resistance. The saturation time for biosorbent decreases from 330 to 270 min when the inlet Pb^{2+}concentration increases from 10 to 30 mg/L. At lower inlet concentration, the breakthrough curve is flatter indicating a relatively wide mass transfer zone and film controlled process. On the contrary, the breakthrough curves are sharp at high Pb^{2+} concentration, implying a relatively smaller mass transfer zone and intraparticle diffusion control.

4.2.1.3. Effect of bed height. The sorption performance of the *Phormidium* sp. has been tested at various bed heights (0.1–0.2 cm) as shown in Fig. 6 at a constant volumetric flow rate of 2 mL/min, an initial Pb^{2+} concentration of 10 mg/L, and pH 5. In order to build bed heights of 0.1, 0.15, and 0.2, adsorbent amount of 0.5, 1, and 2 g were taken. Fig. 6 shows the breakthrough profile of lead sorption at different bed heights. The breakthrough time has been observed to be 180, 300, and 450 min and the saturation time has been found as 330, 480, and 660 min for the bed heights 0.1, 0.15, and 0.2, respectively. This clearly implies that the breakthrough time and saturation time increase with increasing bed height. At low bed depths, the axial dispersion phenomena predominate in mass transfer and reduce the diffusion of metal ions. The metal ions do not have enough time to diffuse into the whole of the biosorbent mass, due to which reduction in breakthrough time has occurred. With the increase in bed depth, the residence time of solution in the column increases allowing the metal ions to diffuse deeper inside the biosorbents [24,26].

4.2.2. Models for breakthrough curve analysis

Successful design of a column adsorption process requires prediction of the concentration-time profile. Various mathematical models have been used to describe the fixed bed adsorption. The analysis of breakthrough curve has been done using two models:

(A) Bohart–Adams model [27]
(B) Bed depth service time (BDST) model [28]

Bohart–Adams model [27] has been applied to the experimental data for the description of the initial part

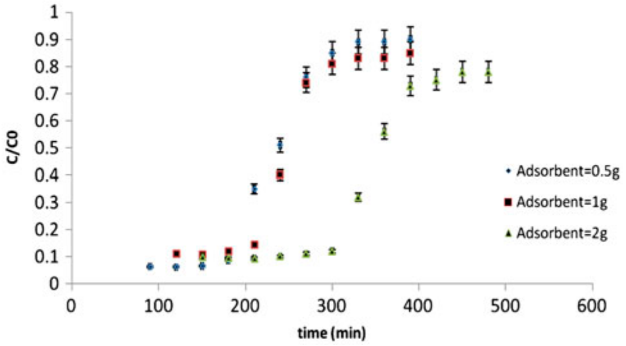

Fig. 6. Breakthrough curves for lead adsorption onto *Phormidium* sp. at different initialbed height (♦ 0.1 cm, ■ 0.15 cm, ▲ 0.2 cm).

Table 3
Bohart–Adam model parameters

Parameter	$k_{AB} \times 10^4$ (L/mg min)	N_0 (mg/L)	R^2
Flow rate (mL/min)			
2	11	3,473	0.854
3.5	6	5,191.6	0.839
4.5	6	6,470	0.902
Initial Pb^{2+}concentration (mg/L)			
10	11	3,473	0.854
20	2.5	7,480	0.960
30	2	10,033.3	0.925
Bed height (cm)			
0.1	11	3,473	0.854
0.15	11	3,296	0.876
0.2	9	3,519.75	0.941

of breakthrough curve. This approach focuses on the estimation of characteristic parameters such as saturation concentration (N_0, mg/L) and the kinetic constant (k_{AB}, L/mg/min). The model equation is given below

$$\ln\frac{C}{C_0} = k_{AB}C_0 t - k_{AB}N_0\frac{H}{U_0} \tag{10}$$

where C and C_0 are the outlet and inlet adsorbate concentrations, respectively, H is the bed height (cm), and U_o is superficial velocity (cm/min). For evaluation of parameters, the range of time considered is shown in Table 2. The values of $\ln(C/C_0)$ were plotted against different flow rates, initial Pb^{2+} concentrations, and bed heights. The kinetic constant (k_{AB}) and saturation concentration (N_0) have been calculated from the slope and intercept of the curves, respectively, and are shown in Table 3. It is observed from the table that the kinetic constant, k_{AB} decreased with the increase in the flow rate, initial lead concentration, and bed height. Further, it shows that the overall system kinetics is dominated by external mass transfer in the initial part of adsorption in the column. The adsorption capacity (N_0) is observed to increase with flow rate and initial metal ion concentration.

Table 2
Thermodynamic parameters

Parameters	Time (min)	Volume of effluent (L)
Flow rate (mL/min)		
2	330	0.57
3.5	270	0.65
4.5	240	1.00
Initial Pb^{2+} concentration (mg/L)		
10	330	0.57
20	300	0.52
30	270	0.47
Bed height (cm)		
0.1	330	0.572
0.15	480	0.832
0.2	660	1.144

BDST is a simple model for predicting the relationship between the bed depth (H) and service time (t), in terms of process concentrations and adsorption parameters. Hutchins [28] proposed a linear relationship between the bed depth and service time as

$$t = \frac{N_0}{C_0 F/A}H - \frac{1}{K_b C_0}\ln\left(\frac{C_0}{C} - 1\right) \tag{11}$$

where C is the effluent lead concentration (mg/L), C_0 is the influent lead concentration (mg/l), F is the volumetric flow rate in mL/h, N_0 denotes the adsorption capacity (mg/L), K_b depicts the rate constant in BDST model (L/mg h), t represents time (h), and H is the bed depth of the column in centimeter (cm). N_0 and k values were calculated from the slope and intercept of the plot between ln $(C_0/C - 1)$ vs. time t at different adsorption parameters such as flow rate, inlet adsorbate concentration, and bed height and are depicted in Table 4. The slope of the BDST model (m) represents the time required for the sorption zone to travel a unit length through the adsorbent and can be used to predict the performance of the bed at different initial metal ion concentrations [28].

The breakthrough time is defined as the time when the ratio between effluent concentration and inlet concentration of lead reaches 0.35. The bed exhaustion time t_e represents the time when the ratio reaches 0.92 is observed in the effluent. The time difference between t_b and t_e (i.e. Δt) is related to the length of

Table 4
BDST parameters

Parameter	k_{AB} (L/mg min)	N_0 (mg/L)	R^2
Flow rate (mL/min)			
2	0.00199	3,127.34	0.941
3.5	0.002	3,858.1	0.9326
4.5	0.002	3,942.15	0.9337
Initial Pb^{2+} concentration (mg/L)			
10	0.00199	3,127.34	0.941
20	0.0007	4,937.61	0.9779
30	0.0007	6,865.8	0.919
Bed height (cm)			
0.1	0.00199	3,127.34	0.941
0.15	0.00193	3,214.545	0.8992
0.2	0.0018	3,595.14	0.9501

Table 5
Length of the sorption zone (H_m)

Bed height (cm)	t_b (min)	t_e (min)	H_m (cm)
0.1	180	330	0.045
0.15	300	480	0.056
0.2	450	660	0.064

the sorption zone [29]. The length of this zone can be calculated from the following equation:

$$H_m = H\left(1 - \frac{t_b}{t_c}\right) \qquad (12)$$

H is the total length of the sorption bed and H_m is the length of the sorption zone (the critical bed length). This length signifies the minimum bed height required to obtain the breakthrough time at zero. The calculated H_m values for various bed heights are given in Table 5.

4.2.3. FTIR Studies

FTIR spectra of green algae before and after adsorption are shown from Figs. 7 to 8. The broad and intense absorption peaks between 3,250–3,300 cm^{-1} correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols, and carboxylic acids, as in pectin, cellulose, and lignin, thus, showing the presence of "free" hydroxyl groups on the adsorbent surface. The peaks in the range of 1,600–1,670 cm^{-1} are due to asymmetric and symmetric stretching vibrations of C=O in ionic carboxylic groups (–COO$^-$), respectively. Aliphatic acid group vibration in the range of 1,400–1,450 cm^{-1} may be assigned to deformation vibration of C=O and stretching formation of -OH of carboxylic acids and phenols. Peaks in the range of 1,000–1050 cm^{-1} may be due to stretching vibration of C–OH of alcoholic groups and carboxylic acids. Some distinct changes are noted in the spectrum of green algae after adsorption. Many of the peaks shifted to a new value indicating that a bond has been developed between the functional group and the sorbate (Fig. 8).

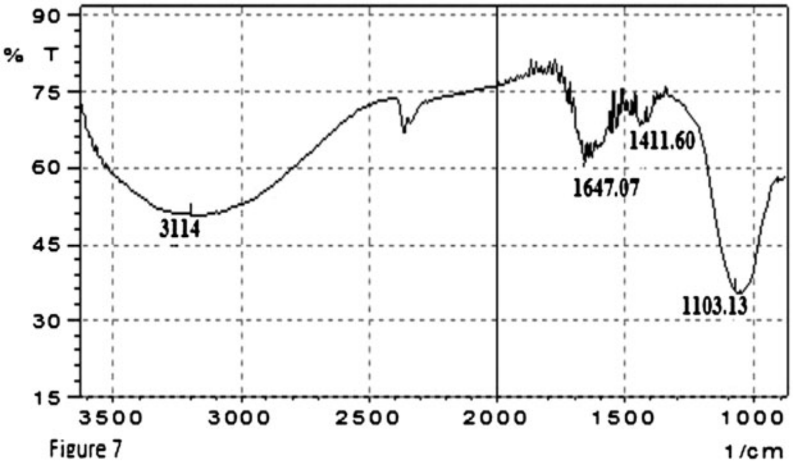

Fig. 7. FTIR spectrum of green algae (*Phormidium* sp.) before adsorption.

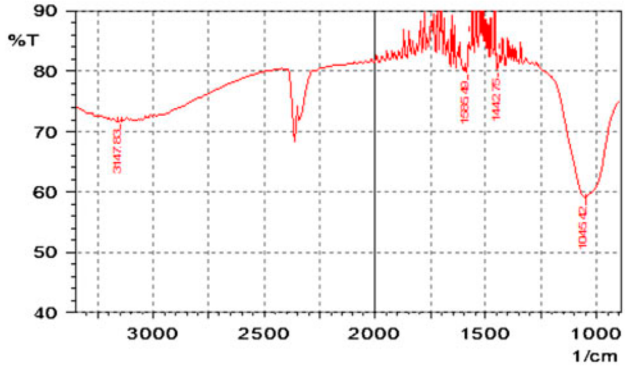

Fig. 8. FTIR spectrum of green algae (*Phormidium* sp.) after adsorption of lead.

5. Conclusions

The present paper deals with the microalgal (*Phormidium* sp.) biomass for the removal of lead (Pb^{2+}) from aqueous solution. Adsorbent dose over 4 g/L does not affect the adsorption significantly. The optimum temperature and pH of adsorption have been determined as 25 and 5˚C, respectively. The equilibrium of adsorption is obtained at 40 min. Adsorption decreases with the increase in the initial concentration of lead ions. At 10 mg/L, the adsorption is the highest (92.2%). The second-order kinetics can explain the chemisorption of lead on the green algae. Langmuir isotherm is found to fit the data well. Dynamic adsorption studies reveal that *Phormidium* sp. can be successfully used as biosorbent for treating effluents containing Pb^{2+}. Flow rate and bed height play a vital role in the semi-batch biosorption process. The Bohart–Adams and the BDST models are successful in describing the breakthrough curves. *Phormidium* sp. can be considered as an effective and low-cost alternative biosorbent material for lead removal from aqueous solution. Kinetic and thermodynamic data obtained from this study may be utilized to develop commercial adsorber for the removal of lead ions from wastewater using microalgal biomass remaining after the extraction of algal oil for the biodiesel production.

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