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Biosorption of lead from aqueous solutions by green algae *Spirogyra* species: Kinetics and equilibrium studies

V.K. Gupta*, A. Rastogi

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247667, India

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Abstract

Biosorption is the effective method for the removal of heavy metal ions from wastewaters. Results are presented showing the sorption of Pb(II) from solutions by biomass of commonly available, filamentous green algae *Spirogyra* sp. Batch experiments were conducted to determine the biosorption properties of the biomass and it was observed that the maximum adsorption capacity of Pb(II) ion was around 140 mg metal/g of biomass at pH 5.0 in 100 min with 200 mg/L of initial concentration. Temperature change in the range 20–40 °C affected the adsorption capacity and the nature of the reaction was found to be endothermic in nature. Uptake kinetics follows the pseudo-second-order model and equilibrium is well described by Langmuir isotherm. Isotherms have been used to determine thermodynamic parameters of the process, viz., free energy change, enthalpy change and entropy change. Various properties of the algae, as adsorbent, explored in the characterization part were chemical composition of the adsorbent, thermal analysis by TGA, surface area calculation by BET method, surface morphology with scanning electron microscope images and surface functionality by FTIR. FTIR analysis of algal biomass revealed the presence of amino, carboxyl, hydroxyl and carbonyl groups, which are responsible for biosorption of metal ions. The results indicated that the biomass of *Spirogyra* sp. is an efficient biosorbent for the removal of Pb(II) from aqueous solutions.

Keywords: Biosorption; Kinetics; *Spirogyra* sp.; Langmuir model; Thermodynamic parameters; Characterization

1. Introduction

The presence of heavy metals in aqueous water streams has become a problem due to their harmful effects on human health and on the flora and fauna of receiving water bodies. It is recognized that finding methods for removal of heavy metals from aqueous water is of great importance. Lead is among the most toxic heavy metal ion affecting the environment [1]. It comes into water through the combustion of fossil fuels and the smelting of sulphide ore, and into lakes and streams by acid mine drainage. Process industries, such as battery manufacturing and metal plating and finishing are also prime source of Pb pollution. The current EPA and WHO drinking water standard for lead is 0.05 mg/L and 10 μg/L, respectively. Lead accumulates mainly in bones, brain, kidney and muscles and may cause many serious disorders like anaemia, kidney diseases, nervous disorders and sickness even death [2]. It is therefore, essential to remove Pb(II) from wastewater before disposal.

Several different conventional methods applied to remove excessive heavy metals from aqueous solutions include chemical precipitation, ion exchange, evaporation, electroplating and membrane processes. However, these methods are either inefficient or expensive when heavy metals exist in low concentrations [3,4]. Consequently, it is urgent to find new technologies or biomaterials for removing heavy metal ions from wastewater. So, biosorption can be a promising alternative method to treat industrial effluents, mainly because of its low cost, high metal binding capacity, high efficiency in dilute effluents and environmental friendly [5].

Biosorption utilizes the ability of biological materials to accumulate heavy metals from wastewater by either metabolically mediated, or physico-chemical pathways of uptake [6]. Application of biosorbents/biomass from various microbial sources, moss, aquatic plants and leaf-based adsorbents was reported by various investigators [7–12] with the aim of finding more efficient and cost-effective metal-removal biosorbent. Among them,

* Corresponding author. Tel.: +91 1332 285801; fax: +91 1332 273560.
E-mail address: vinodfcy@iitr.ernet.in (V.K. Gupta).

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algae have proved to possess high metal binding capacities [13] due to the presence of polysaccharides, proteins or lipid on the surface of their cell walls containing some functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals [14,15].

There are many reports and reviews on the biosorption of lead metal ion on marine algae [16–19], green seaweed [20–22], and freshwater green algal species [23–26] with varying removal efficiencies, maximum adsorption capacities (q_{max}) and binding constants. Among the algal biomass used for biosorption, *Spirogyra* sp. is a green filamentous, readily available source of biomass for heavy metal removal from wastewater. Investigations conducted by several researchers demonstrated that *Spirogyra* sp. is capable of accumulating heavy metals like copper, chromium, zinc and fluoride [27–30], but still there is lots of scope available to use this abundantly available alga for the removal of other heavy metal ions from wastewaters. In the same sequence in this investigation, biosorption studies for the removal of Pb metal ion from wastewater by *Spirogyra* sp. is carried out. The biosorbent was characterized by employing instrumental techniques, viz., Fourier transform infrared spectroscopy (FTIR), thermo gravimetric analysis (TGA) and scanning electron microscope (SEM). The equilibrium and kinetics were obtained from batch experiments. The adsorption capacities were evaluated from equilibrium adsorption isotherms and the results indicated, on comparing its adsorption capacity with some of the other adsorbents, that it is the suitable material for the development of high capacity biosorbent for Pb(II) removal.

2. Materials and methods

2.1. Chemicals

All chemicals used in this study were of analytical grade obtained either from Merck, Germany or SD Fine Chem. Ltd., India. Stock solution of lead was prepared using lead nitrate in double distilled water. Purified water was prepared using a Millipore Milli-Q (Bedford, MA, USA) water purification system. Pb(II) solutions of different concentrations were obtained by diluting the stock solution. Standard solution of Pb(II) (1000 mg/L) for atomic adsorption spectrophotometer was obtained from Merck, Germany. Standard acid and base solutions (0.1N HCl and 0.1N NaOH) were used for pH adjustments.

2.2. Equipment

pH measurements were made using a pH meter (model cyberscan 510, Singapore). The lead solutions were analyzed using an atomic adsorption spectrophotometer model Z-7000 (Hitachi, Japan) at a wavelength of 283.3 nm. LEO 435 VP (Leo Elektronenmikroskopie GmbH, Germany) was used for scanning electron microscopy. Carbon content was measured by Elementar CHNS analyzer model Vario EL III (Vario EL, Elementar Analyser systeme. GmbH, Hanau, Germany). TGA studies were carried out on Perkin Elmer (Pyris Diamond model, USA) in the temperature range 20–750 °C and BET surface area was measured using quantasorb surface analyzer. Infra red spectra of the samples were recorded on a Perkin Elmer FTIR, Spectrophotometer model-1600 (Perkin Elmer, USA).

2.3. Biosorbent

Fresh algal biomass was collected from pond near Roorkee, India. Before use, it was washed with distilled water to remove dirt and was kept on a filter paper to reduce the water content. The biomass was then sun dried for 4 days followed by drying in a oven at 70 °C for 24 h and then ground on a igate stone pistol mortar. The biomass was then sieved to select the particles between 150 and 250 mesh size for use.

2.4. Batch adsorption studies

The adsorption features of the biosorbent *Spirogyra* sp. were investigated as a function of initial pH, initial heavy metal concentration, biosorbent dose, contact time and temperature. The equilibrium and kinetics were obtained from batch experiments, using 250 mL flasks containing 100 mL of heavy metal solutions and 0.05 g of biomass kept at room temperature (298 K). The pH value was adjusted to the required value with 0.1 M HCl or 0.1 M NaOH hourly throughout the experiment. A magnetic stirrer was used to agitate the solution continuously. At the end of adsorption, 1 mL sample was collected and centrifuged at 1500 rpm for 10 min on a centrifuge. The remaining concentration of lead in residual solution was analyzed by taking absorbance on the atomic absorption spectrophotometer. Each experiment was run in triplicate and mean values are reported. Standard deviations were found to be within ±1.3%. Further, the error bars for the figures were so small as to be smaller than the symbols used to plot the graphs and, hence, not shown.

3. Results and discussion

3.1. Characterization of the biosorbent

The scanning electron micrograph clearly revealed the surface texture and morphology of the biosorbent (Fig. 1) at different magnifications. It was evident from the micrographs that the biosorbent showed a tangled mass of filaments in net format (500× and 1.0k×). At 2.5k× and 5.0k× magnifications, the single filament of the biosorbent was focused, where an uneven surface texture along with lot of irregular surface format was observed. The surface area of the algal biomass *Spirogyra* sp. was observed to be 1.31 m^2/g by BET method. The algal biosorbent subjected to elemental analysis showed composition of carbon, nitrogen and sulphur as 36, 5.016 and 0.57%, respectively.

Besides this, to evaluate the thermal stability of the biosorbent, i.e. *Spirogyra* sp., thermal analysis was performed by TGA/DTA curves in an air atmosphere with a constant flow rate of 200 mL/min and a heating rate of 10 °C min^{-1} (figure not shown). The temperature scanning was conducted in the range 20–750 °C with a 10.5 ± 0.5 mg biosorbent which shows two

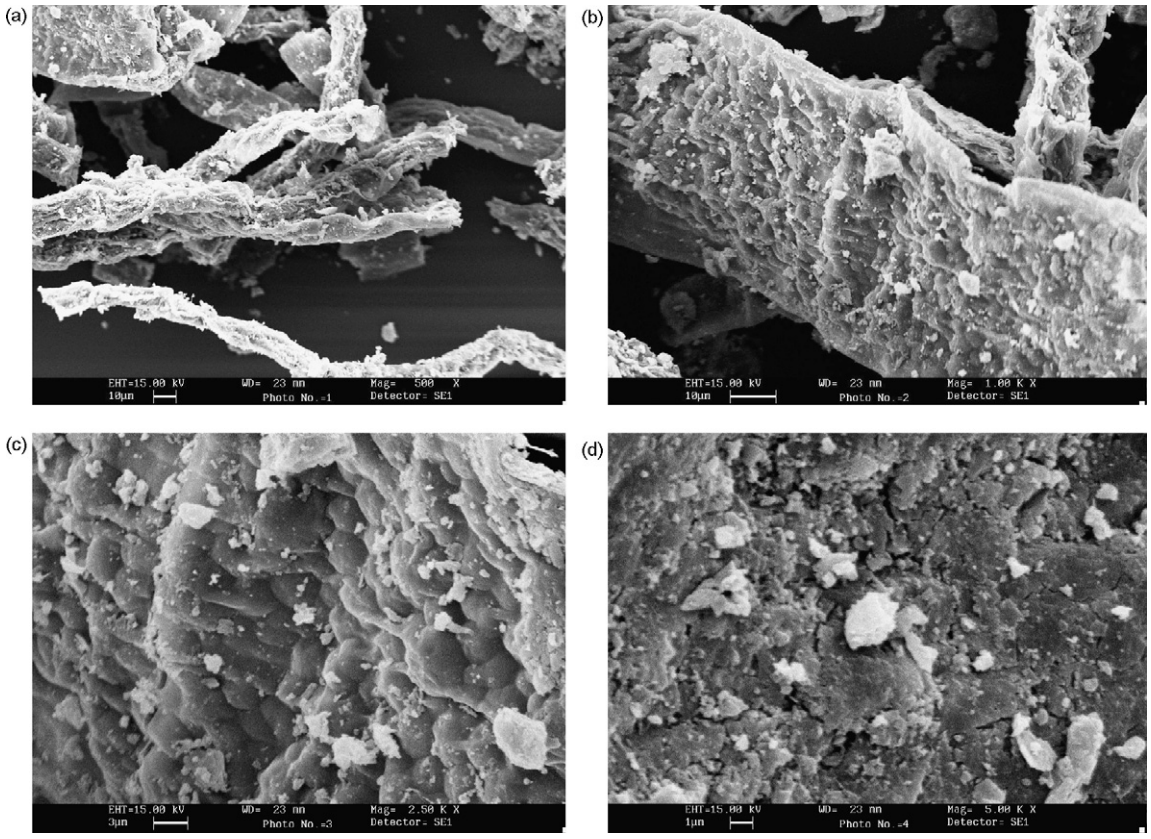

Fig. 1. SEM photo of algal biomass (*Spirogyra* sp.) at different magnifications: (i) 500×; (ii) 1.0k×; (iii) 2.5k×; (iv) 5.0k×.

steps decomposition process. These results are similar to the results as obtained by other workers [30].

For FTIR studies dried algal biomass (about 0.1 g) was mixed with KBr (0.1 g). The functional groups responsible for heavy metal ion biosorption on *Spirogyra* sp. is confirmed by FTIR spectra. The FTIR spectra of native and Pb(II) treated algal biomass (Fig. 2) indicate the presence of amino, carboxylic, hydroxyl and carbonyl groups. Display of strong broad O–H stretch carboxylic bands in the region 3408 cm^{-1} and carboxylic/phenolic stretching bands in the region of 2925 cm^{-1} was observed. The peaks appearing in the region 1652 cm^{-1} might be attributed to >C=N, >C=C and C=O stretch whereas the peaks appearing in the region 1538 and 1442 cm^{-1} might represent quinine OH bonds. Now the peaks appearing in the

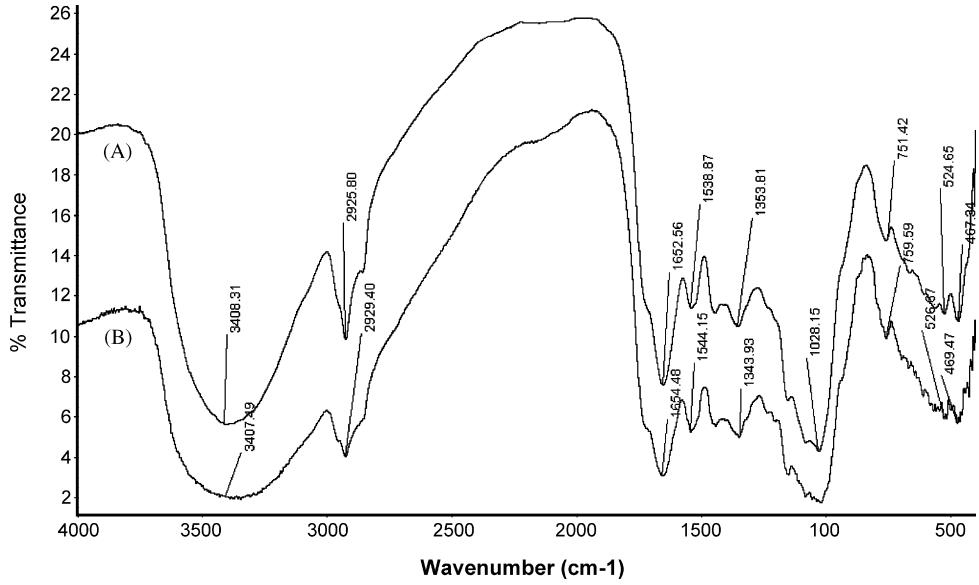

Fig. 2. FTIR spectra of algal biomass *Spirogyra* sp. (a) Native; (b) Pb(II) treated (Pb(II): 100 mg/L).

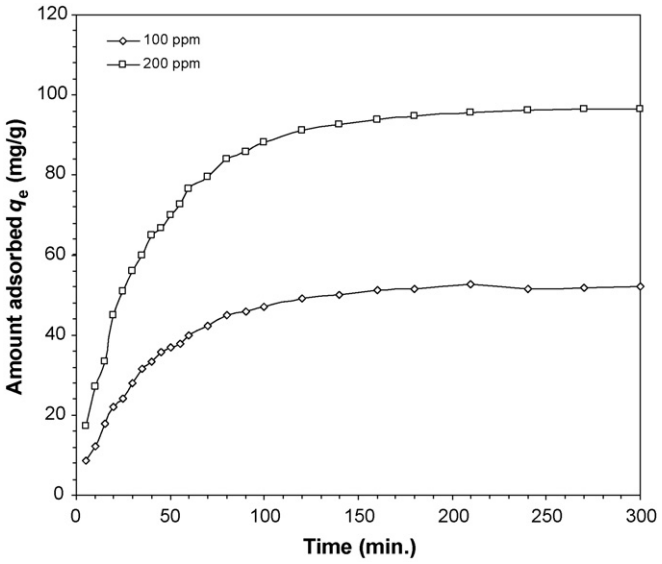

Fig. 3. Effect of contact time on the extent of biosorptions at two initial lead concentration: 100 and 200 mg/L.

region 1353, 1078 and 1028 cm^{-1} represents N–H bending, $–CH_3$ wagging and C–OH stretching vibrations, respectively, are due to the several functional groups present on the algal cell walls. The peaks at 524 and 467 cm^{-1} are caused by C–N–S scissoring, which are found in polypeptide structure. As seen in Fig. 2, the absorbance of the peaks in the Pb(II) treated algal biomass is slightly lower than that in the native one. The analysis of the FTIR spectra showed the presence of ionisable functional groups (i.e. carboxyl, amino, amide and hydroxyl) able to interact with protons or metal ions. The above results obtained give an idea about the presence of functional groups on the algal cell surfaces.

3.2. Biosorption of heavy metal ion

3.2.1. Effect of contact time

Fig. 3 shows the effect of contact time on the extent of adsorption of lead on algal biomass, i.e. *Spirogyra* sp. (at two different initial lead concentration). It has been observed that maximum adsorption took place within first 100 min. The data obtained from this experiment was further used successfully to evaluate the kinetics of the adsorption process.

3.2.2. Influence of biosorbent dose

To determine the effect of adsorbent dose, different amounts (0.05–10.0 g/L) of adsorbent were suspended in 10 mL lead solution in which the concentration of lead was 100 and 200 mg/L. The effect of adsorbent dose on the extent of removal of lead at optimum pH (5.0) is shown in Fig. 4. The amount of adsorbent significantly influenced the extent of lead adsorption. The extent of lead biosorption was 31.2% for 0.05 g/L of algal biomass, while it was greatly increased to 80% for 10 g/L of adsorbent. However, there was only a slow change in the extent of lead adsorption when the adsorbent dose was over 5 g/L. Furthermore, higher adsorbent dose will result in lower adsorption capacity (q_e = 12 mg/g) value at a fixed lead concentration (150 mg/L), as shown in Fig. 4. At low algal dose, all types of sites are entirely exposed and the adsorption on the surface is saturated faster, showing a higher q_e value (q_e = 93.5 mg/g at 0.05 g/L algal biomass). But at higher adsorbent dose, the availability of higher energy sites decreases with a larger fraction of lower energy sites occupied, resulting in a lower q_e value.

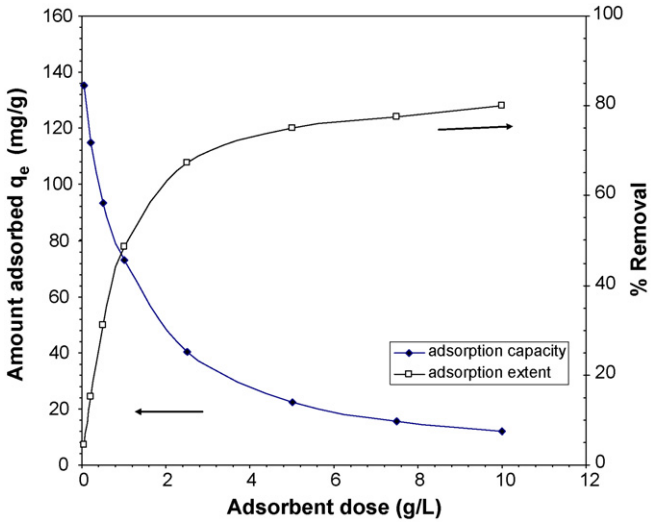

Fig. 4. Effect of adsorbent dose on the removal extent and adsorption capacity of lead.

3.2.3. Effect of pH

It is well known that pH could affect the protonation of the functional groups on the biomass as well as the metal chemistry. The effect of pH on lead adsorption capacity of *Spirogyra* sp. is shown in Fig. 5. As the pH of the lead solution (100 and 200 mg/L) increased from 2.99 to 7.04, the adsorption capacity of lead was changed, i.e. it first increased from 2.99 pH to pH 5.0 and then dramatically decreased up to pH 7.04. At pH higher than 5, the precipitation of insoluble metal hydroxides takes place restricting the true biosorption studies. The results showed strong pH dependence of biosorption. This is consistent with the results obtained for the other adsorbent systems [26,31]. The

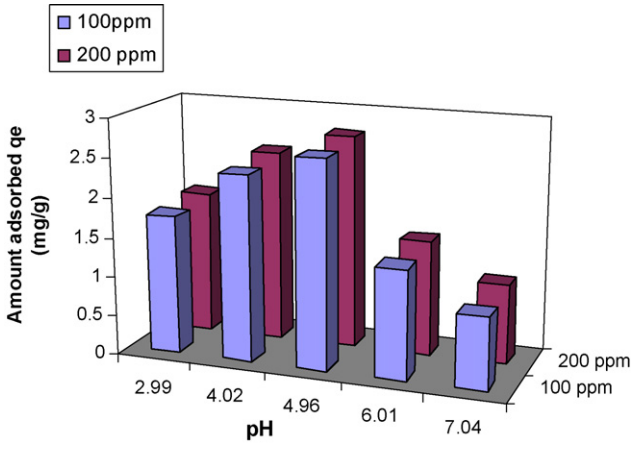

Fig. 5. Effect of pH on the biosorption of lead.

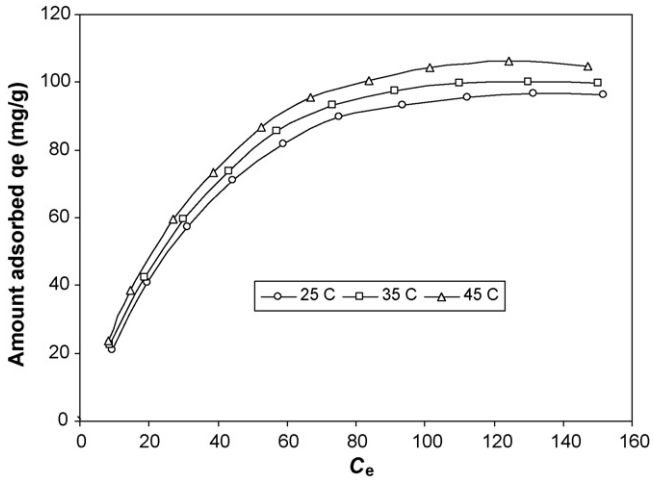

Fig. 6. Adsorption isotherms at three different temperatures.

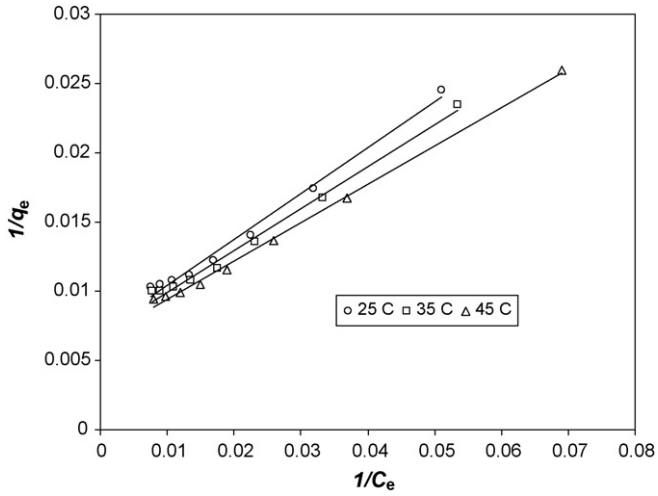

Fig. 7. Langmuir fitting of adsorption isotherms of lead on algal biomass.

cell wall matrix of green algae contains complex heteropolysaccharides that can provide amino, carboxyl and sulphate groups [32]. At low pH, cell wall ligands are protonated and restrict the approach of metal cations as a result of the repulsive force. As pH increases, more ligands such as amino, phosphate and carboxyl groups would be exposed and carry negative charges with subsequent attraction of metal ions [33,34].

3.2.4. Effect of temperature

The isotherms of lead adsorption on the biosorbent, at three different temperatures (298, 308 and 318 K) are given in Fig. 6. For an increase in temperature from 298 to 318 K, an increase in the adsorption of lead was observed. The maximum amount adsorbed increased from 96.4 to 104 mg/g at 150 mg/L, initial lead concentration. These adsorption data were further fitted to two adsorption models to find out the suitable model.

3.2.5. Isotherms modeling

The equilibrium data presented in Fig. 6 were applied to Langmuir and Freundlich isotherms equations. The Langmuir isotherm is the most widely used two-parameter equation, commonly expressed as

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \quad (1)$$

where q_e is the amount adsorbed (mg/g), C_e the equilibrium concentration of the adsorbate (mg/L), Q_0 the Langmuir constants related to maximum monolayer adsorption capacity (mg/g) and b is the constant related to the free energy or net enthalpy of adsorption ($b \propto e^{-\Delta H/RT}$). The plots of $1/q_e$ versus $1/C_e$ (Fig. 7) were drawn for three different temperatures to calculate these constant (Table 1). The linearized forms of the isotherms at all temperature are found to be linear over the whole concentration range studied, and the correlation coefficients were extremely high, as shown in Table 1. These values of the correlation coefficients strongly support the fact that the lead–algal biomass biosorption data closely follow the Langmuir model of sorption. The high degree of correlation for the linearized Langmuir relationship suggests a single surface reaction with constant activation energy is the predominant sorption step and possibly the predominant rate-controlling step.

The Freundlich isotherm was also applied for the biosorption of lead on algal biomass. The logarithmic form of Freundlich model is given by the following equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

Therefore, plots of $\ln q_e$ versus $\ln C_e$ (Fig. 8) were drawn to calculate the values of K_F and $1/n$ which are given in Table 1. It was found that the plots exhibit deviation from linearity at the higher concentration range (>100 mg/L). However, the correlation coefficients in Table 1 indicate the data are not well correlated to Freundlich correlation coefficients compared to the Langmuir correlation coefficients.

By comparing the results presented in Table 1, it can be seen that the Langmuir sorption isotherm can accurately describe the adsorption of lead onto algal biomass in this study. The values of Q_0 calculated by Langmuir equation fitting were all close to those actually determined values at given temperatures. Earlier, satisfactory fitting of the Langmuir model to the adsorption

Table 1
Langmuir and Freundlich isotherms constants for the biosorption of lead on algal biomass (*Spirogyra* sp.) at different temperatures

Temperature (K)	Langmuir constant			Freundlich constant		
	b (L mg^{-1})	Q_0 (mg/g)	R^2	n	K_F (mg/g)	R^2
298	0.021	140.84	0.990	1.870	8.010	0.916
308	0.023	144.927	0.991	1.935	9.123	0.919
318	0.024	151.575	0.997	1.928	9.679	0.933

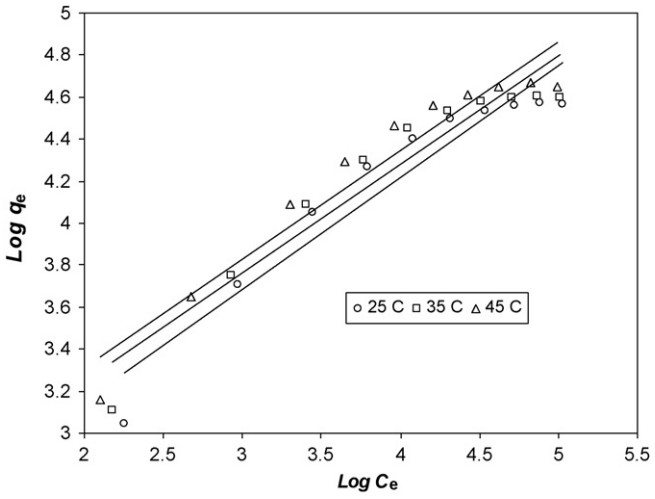

Fig. 8. Freundlich isotherms of lead on algal biomass.

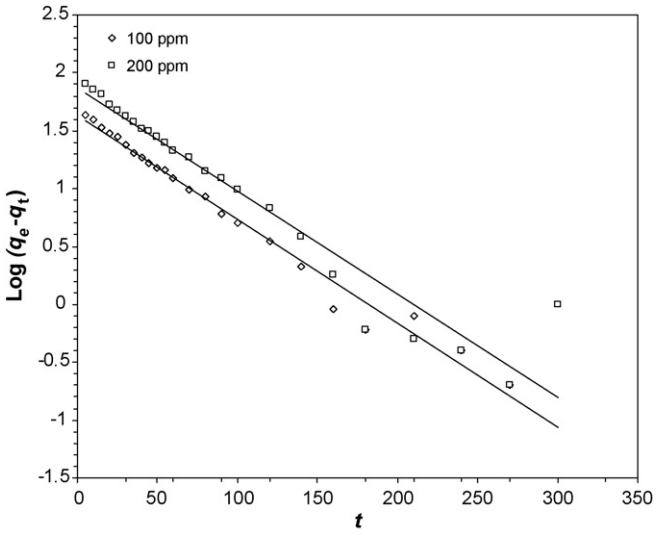

Fig. 9. First-order kinetic modeling of lead adsorption on algal biomass.

isotherms of lead was obtained on brown seaweed *Turbinaria conoides* [35] and pretreated biomass of Australian marine algae *Durvillaea potatorum* and *Ecklonia radiata* [36].

The maximum adsorption capacity obtained from the Langmuir isotherm increased with increasing temperature, and the value of q_m was 140.84 mg/g at 298 K and pH 5.0.

3.2.6. Thermodynamic study

The free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) for adsorption process were calculated using the following equations:

$$\Delta G^\circ = -RT \ln(b) \tag{3}$$

$$\ln\left(\frac{b_2}{b_1}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{5}$$

The values of these parameters are summarized in Table 2. The enthalpy change ΔH° is positive (endothermic) due to increase in adsorption on successive increase in temperature. Further, negative ΔG° values dictate spontaneous process. The positive value of ΔS° reveals the increased randomness at the solid–solution interface during the fixation of the lead ion on the active sites of the biosorbent. Since the adsorption process is endothermic, it follows that under these conditions the process becomes spontaneous because of the positive entropy change.

Table 2
Thermodynamic parameters for the biosorption of lead on algal biomass (*Spirogyra* sp.) at different temperatures

Temperature (K)	ΔG° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔH° (kJ mol^{-1})[a]
298	−20.455	0.0835	
308	−21.322	0.0836	4.0038
318	−22.124	0.0835	

[a] Measured between 298 and 318 K.

3.2.7. Adsorption kinetics

The pseudo-first-order and pseudo second-order models were used to test adsorption kinetics data to investigate the mechanism of biosorption.

The pseudo-first order, rate expression of Lagergren is given as [37]:

$$\log(q_e - q_t) = \log\, q_e - \frac{k_{1,ads}}{2.303}t \tag{6}$$

where q_t (mg/g) is the amount of adsorbed lead on the algal biomass at time t and $k_{1,ads}$ (min^{-1}) the rate constant of first-order adsorption, and q_e is the equilibrium sorption uptake, is extrapolated from the experimental data at time t = infinity. A straight line of $\log(q_e - q_t)$ versus t up to a certain time (Fig. 9) suggests the slightly applicability of this kinetic model. q_e and $k_{1,ads}$ (Table 3) were determined from the intercept and slope of the plot, respectively.

The pseudo second-order kinetic model [38] in its integrated and linearized form has been used:

$$\frac{t}{q} = \frac{1}{k_{2,ads}q_e^2} + \frac{1}{q_e}t \tag{7}$$

where $k_{2,ads}$ (g mg min^{-1}) is the rate constant of second-order adsorption. The plot t/q versus t (Fig. 10) giving a straight line shows, second-order kinetics is applicable and q_e and $k_{2,ads}$ (Table 3) were determined from the slope and intercept of the plot, respectively. It is important to notice that for the application of this model the experimental estimation of q_e is not necessary.

Table 3 lists the results of rate constant studies for different initial lead concentrations by the pseudo-first-order and pseudo-second-order models. The value of correlation coefficient R^2 for the pseudo-second-order adsorption model is relatively high (>0.997), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the pseudo-first-order are not satisfactory. Therefore, it has been concluded that the pseudo-second-order

Table 3
Comparison between adsorption rate constants, q_e estimated and coefficient of correlation associated to the Lagergren pseudo-first- and -second-order adsorption

Initial concentration (mg/L)	$q_{e\,exp.}$ (mg/g)	First-order model			Second-order model		
		k_1 ($\times 10^{-3}$ min^{-1})	$q_{e\,cal.}$ (mg/g)	R^2	K_2 ($\times 10^{-3}$ g mg^{-1} min^{-1})	$q_{e\,cal.}$ (mg/g)	R^2
100	52	20.727	43	0.927	0.545	59.17	0.997
200	98	20.496	73.99	0.932	0.317	111.11	0.998

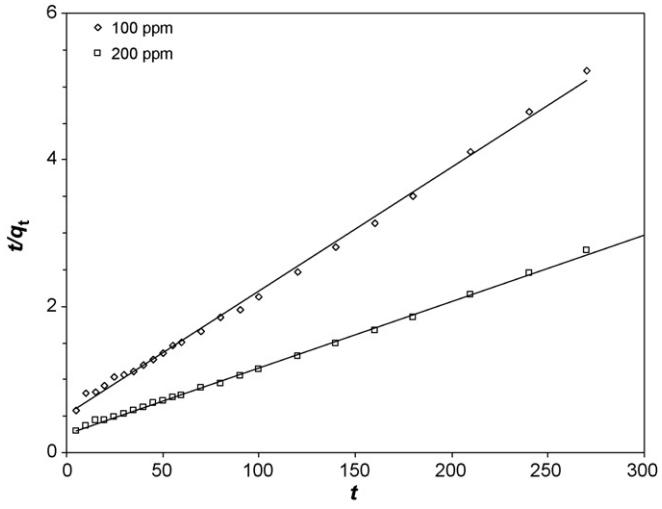

Fig. 10. Second-order kinetic modeling of lead adsorption on algal biomass.

Table 4
Uptake capacities for Pb(II) of various adsorbents (at room temperature)

Adsorbent	q_m (mg/g)	pH	Literature
Crab shell and arca shell	19.83, 18.33	5.5	[39]
Chaff	12.4	5.5	[40]
Powder activated carbon	20.7	–	[41]
Bacillus sp.	92.27	3.0	[42]
Rhizopus arrhizus	2.643	4.5	[43]
Waste bakers yeast in ethanol	17.49	5.0	[44]
Caulerpa lentillifera (Green macroalga)	28.7	5.0	[22]
Gelidium algae	64.0	5.0	[19]
Chlamydomonas reinhardtii	96.3	5.0	[26]
Spirogyra sp.	140.84	5.0	This study

adsorption model is more suitable to describe the adsorption kinetics of lead over algal biomass.

3.3. Comparison with other adsorbents

A comparison between the results of this work and others found in the literature [39–44] is presented in Table 4. The value of Pb(II) uptake found in this work is significantly higher than reported for other biosorbents. Thus, the comparison of adsorption capacities shows that the algae *Spirogyra* sp., is an efficient biosorbent for the uptake of lead metal ion.

4. Conclusion

The batch studies conducted in the present study provides significant information regarding biosorption of lead on green algae *Spirogyra* species in terms of optimum pH and biomass dose for maximum removal of Pb(II) from the aqueous solution. The studies indicate that *Spirogyra* species is an effective biosorbent for Pb(II) removal. The maximum Pb(II) biosorption capacity has been found to be 140.84 mg Pb(II)/g of dry weight of biomass at an algal dose of 0.5 g/L in 100 min of contact time with initial Pb(II) concentration of 200 mg/L and optimum pH of 5.0. The Langmuir and Freundlich adsorption model were used for the mathematical description of the biosorption of Pb(II) ions onto algal biomass and it was found that the adsorption equilibrium data fitted well to the Langmuir model. The biosorption of lead ions on the algal biomass follows second-order biosorption kinetics. With the advantage of high metal biosorption capacity, the biomass of *Spirogyra* has the potential to be used as an efficient and economic biosorbent material for the removal of lead from aqueous solutions.

Acknowledgement

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