Equilibrium and kinetic modelling of cadmium(II) biosorption by nonliving algal biomass *Oedogonium* sp. from aqueous phase

V.K. Gupta [*], A. Rastogi

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

Abstract

The biosorption of cadmium(II) ions on *Oedogonium* sp. is studied in a batch system with respect to initial pH, algal dose, contact time and the temperature. The algal biomass exhibited the highest cadmium(II) uptake capacity at 25 °C, at the initial pH value of 5.0 in 55 min and at the initial cadmium(II) ion concentration of 200 mg L^{-1}. Biosorption capacity decreased from 88.9 to 80.4 mg g^{-1} with an increase in temperature from 25 to 45 °C at this initial cadmium(II) concentration. 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. FTIR analysis of algal biomass revealed the presence of amino, carboxyl, hydroxyl and carbonyl groups, which are responsible for biosorption of metal ions. Acid pretreatments did not substantially increase metal sorption capacity but alkali like NaOH pretreatment slightly enhanced the metal removal ability of the biomass. During repeated sorption/desorption cycles at the end of fifth cycle, Cd(II) sorption decreased by 18%, with 15–20% loss of biomass. Nevertheless, *Oedogonium* sp. appears to be a good sorbent for removing metal Cd(II) from aqueous phase.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Biosorption; *Oedogonium* sp.; Cadmium; Langmuir model; Kinetics; Sorption/desorption

1. Introduction

It is well recognized that the presence of heavy metals in the environment can be detrimental to a variety of living species, including man. Cadmium is one of the most toxic metals affecting the environment. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [1]. Cadmium has been recognized for its negative effects on the environment where it readily accumulates in living systems. Adverse health effects due to cadmium are well documented and it has been reported to cause renal disturbances, lung insufficiency, bone lesions, cancer and hypertension in humans [2,3]. The permissible limits of Cadmium discharge in wastewater and drinking water are 0.1 and 0.05 mg L^{-1}, respectively. Methods proposed for Cd removal from waste waters are those employed for most heavy metals, which include chemical precipitation, chemical oxidation or reduction, evaporation, adsorption and ion exchange. These processes may be ineffective or extremely expensive, especially when concentrations of dissolved metal(s) are in the order 1–100 mg L^{-1}. Therefore, it is necessary to find new technologies or materials for removing heavy metal ions from wastewater.

Biosorption as a wastewater treatment process has been found to be an economically feasible alternative for metal removal. Basically, it can be based on the following mechanisms: physical adsorption, ion exchange, complexation and precipitation. Biosorption may not necessarily consist of a single mechanism. In many sorption processes, several mechanisms often act in combination and it is difficult to distinguish between the single steps [4]. Biosorption utilizes the ability of biological materials to accumulate heavy metals from waste streams by either metabolically mediated or purely physico-chemical pathways of uptake [5].

The biological materials that have been investigated for cadmium uptake include fungi [5,6], bacteria [7,8], yeast [9,10],

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

algae [11–15] and others [16–18]. However, these reports do not satisfactorily define conditions for maximizing metal sorption by these organisms. Similarly, conditions suitable for desorbing heavy metals from metal-loaded biomass have not been adequately described for many algae tested. Also, there are no reports on the sorption ability of test alga, i.e. *Oedogonium* sp. So, the present work reports the study of the cadmium(II) binding to raw biomass of *Oedogonium* sp.

Besides the influence of pH and biomass concentration, the sorption biomass uptake has also been quantified by means of two sorption models: Langmuir and Freundlich. Finally, the work incorporates the pretreatment of the algal biomass with selected chemicals and also a desorption study using eight different eluents was carried out and the possibility of reusing the biomass in different sorption–desorption cycles.

2. Material and methods

2.1. Test alga

Oedogonium sp. was collected from a stream near Roorkee, India. It is an unbranched filamentous yellowish green alga with cylindrical cells, which can form dense mats of coiled filaments, epilithic or epiphytic on submerged surfaces in streams. For biosorption studies, the algal biomass was washed in running tap water for 1–2 h and then thoroughly washed with Milli-Q water 4–5 times, and then eventually kept on a filter paper to reduce the water content. The biomass was then sun dried for four days followed by drying in an oven at 70 °C for 24 h. Subsequently, it was ground on an igate stone pestle mortar and sieved, to select the particles between 150 and 250 mesh sizes for use.

2.2. Preparation and analysis of metal solution

Metal stock solution for sorption was prepared in Milli-Q water with analytical-grade salt of Cd(II) [Cd(NO$_3$)$_2$·4H$_2$O] from Merck, Germany. The stock solution (200 mg L^{-1}) was diluted with milli-Q water in order to prepare solutions of the desired concentrations. Biosorption studies were performed in 100 mL Erlenmeyer flasks previously rinsed with HNO$_3$ in order to remove any metal that remained adsorbed on the glass wall. Pre-weighed dried biomass was added to each flask and constantly agitated at 25 ± 2 °C, until the equilibrium was reached. At the end of adsorption, 1 mL sample was collected and centrifuged at 1500 rpm for 10 min on a centrifuge (Eppendorf Centrifuge model HM-150 IV, Korea). The filtrate was collected in polythene tubes and diluted before analysis. Metal content in the filtrate was determined by an atomic absorption spectrophotometer model Z-7000 (Hitachi, Japan) at a wavelength of 228.8 nm. The adsorption capacities were obtained by mass balance calculations. All the experiments were performed in a batch set up taking three replicates and average values were 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.

2.3. Biosorption studies

The biosorption of Cd(II) ions on the algal biomass *Oedogonium* sp. was investigated in batch biosorption—equilibrium experiments. The effect of solution pH, biosorbent dose, contact time and temperature on the biosorption rate and capacity were studied. The effect of pH was studied using a pH meter (model cyberscan 510, Singapore) in the range 2.99–6.05 and the desired pH of the suspensions was maintained by adding HCl or NaOH at the beginning of the experiment and not controlled afterwards. To determine the effect of biosorbent dose, different dose of biosorbent 0.2–1.6 g L^{-1} were varied and suspended in Cd(II) solutions of fixed initial concentration. The adsorption procedure was the same as described earlier.

To obtain adsorption isotherms the biosorbent (1.0 g L^{-1}) was suspended in cadmium solutions (conc. range 20–200 mg L^{-1}). The experiments were carried out at three different temperatures, i.e. 25, 35 and 45 °C. Kinetic studies of adsorption by alga under study was also carried out at two initial cadmium concentrations (100 and 200 mg L^{-1}) at 25 °C wherein the extent of adsorption was analyzed at regular time interval.

2.4. Effects of biomass pretreatments on metal removal

With a view to enhance metal sorption capacity of the biomass, it was subjected to various pretreatments, such as, with 0.1 mM HCl, 0.1 mM HNO$_3$, 0.1 mM NaOH, 0.1 mM ammonium acetate, 5% (v/v) HCHO, 90% (v/v) methanol, 90% (v/v) acetone, and hot water (60 °C). Many of these chemicals are inexpensive and readily available, and have been tried with other biomass types for enhancing their metal sorption potential [19]. For pretreatment, the dry algal biomass was suspended in 10 mL of the treating agent for 55 min at 25 ± 2 °C, and agitated on a shaker. For hot water treatment, the biomass was kept in a water bath for 15 min at the specified temperature. After various treatments, the algal biomass was separated and washed with Milli-Q water till the pH of the washings reached neutrality. After washing, the biomass was again dried in a hot air oven and tested for metal sorption capacity. The biomass was incubated for 30 min in a solution containing 100 mg L^{-1} Cd(II). After incubation, the algal biomass was separated from the metal solution and the filtrate was analyzed for metal content.

2.5. Efficacy of metal desorbing agents and successive sorption/desorption cycles

In order to determine the reusability of the biosorbent, consecutive biosorption–desorption cycles were repeated five times. Therefore, different chemical agents (0.1 M of HCl, HNO$_3$, H$_2$SO$_4$, NaOH, CaCl$_2$, Na$_2$CO$_3$, EDTA and Milli-Q water) were evaluated for their capacity to desorb the test metal from the metal-loaded biomass. The algal biomass loaded with heavy metal ions was placed in the desorbing medium and was constantly stirred on a rotatory shaker for an hour at 25 °C. After each cycle of adsorption and desorption, the algal biomass was washed with Milli-Q water and reconditioned for adsorption in the succeeding cycle.

2.6. IR spectrum of Oedogonium sp.

The IR spectrum of the biosorbent with that loaded with Cd(II) were recorded on a Perkin Elmer FTIR, Spectrophotometer model −1600 (Perkin Elmer, USA). For FTIR studies dried algal biomass (about 0.1 g) was mixed with KBr (0.1 g) and compacted in pellet form.

3. Results and discussion

3.1. Surface area and composition

The surface area of the algal biomass *Oedogonium* sp. was observed to be $1.22 \, m^2 \, g^{-1}$ by Brunauer Emmett and Teller method (BET method) and the elemental analysis of the alga showed composition of carbon, nitrogen and sulphur as 25.4, 3.06 and 1.77%, respectively.

3.2. IR spectrum of Oedogonium sp.

The absorbance spectrum of *Oedogonium* sp. (native) with that loaded with Cd(II) (conc.200 $mg \, L^{-1}$) is shown in Fig. 1. It can be observed from the IR spectra that the absorbance of peaks in the Cd(II) treated algal biomass is slightly lower than that of the native one. Some intense characteristic bands were obtained from the functional groups presented in proteins and polysaccharides. Display of strong broadband in the region 3362.54 and $2917.14 \, cm^{-1}$ is due to O–H stretch of carboxylic groups and carboxylic/phenolic stretching, respectively. The bands appearing in the region $1650.40 \, cm^{-1}$ might be attributed to >C=N, >C=C and C=O stretch whereas in the region $1421.57 \, cm^{-1}$ might represent OH bonds. Now the band appearing in the region $1082.41 \, cm^{-1}$ was due to C–O existence. Some bands in fingerprint region could be attributed to the phosphate groups. After adsorbing Cd(II), significant changes in the wave numbers 3362.54, 1650.40 and $1082.41 \, cm^{-1}$ was observed as these
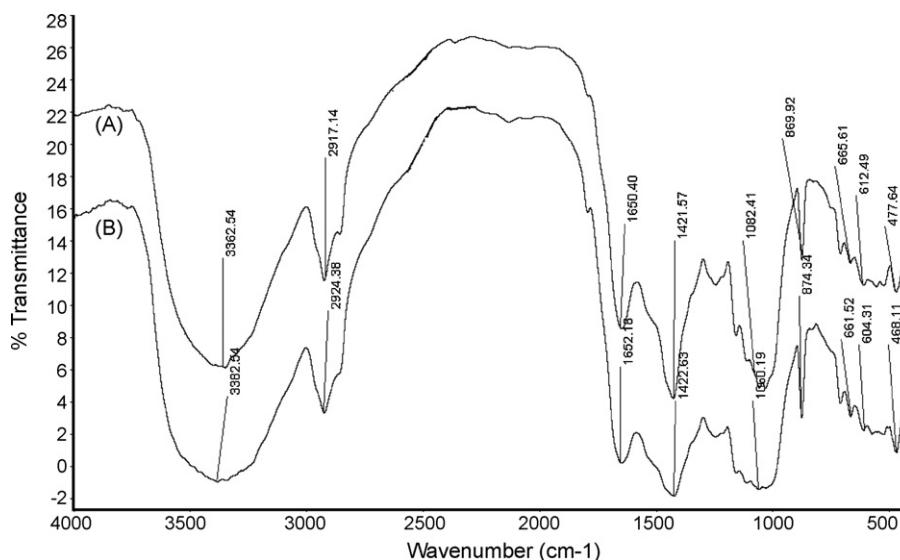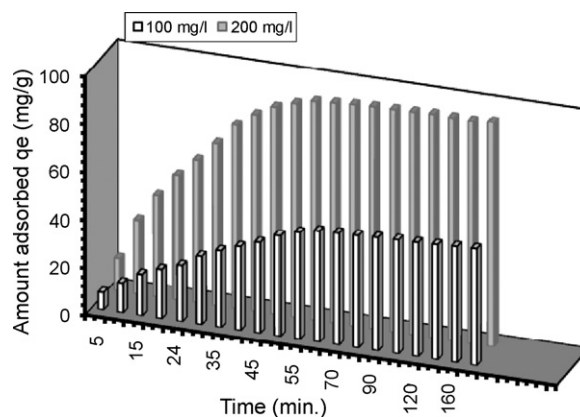
Fig. 2. Effect of contact time on the biosorption of Cd(II) ions on algal biomass *Oedogonium* sp. from aqueous solutions: temperature 25 °C; initial concentration Cd(II) ions 200 $mg \, L^{-1}$; algal dose 1.0 $g \, L^{-1}$. (Average value of three tests, error < 1.3%).

shifted to 3382.54, 1652.10 and $1080.16 \, cm^{-1}$, respectively, which suggested amido, hydroxy, C=O and C–O could combine intensively with Cd(II). 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 and also on the mechanism of adsorption which is dependent on functional groups especially carboxyl.

3.3. Biosorption of heavy metal ion

3.3.1. Effect of contact time

Contact time is one of the important parameters for successful biosorption application. Fig. 2 shows the effect of contact time on the extent of adsorption of cadmium on algal biomass, i.e. *Oedogonium* sp. (at two different initial cadmium concentrations). The plot indicates that the remaining concentration of

Fig. 1. FTIR spectra of algal biomass *Oedogonium* sp. (a) Native; (b) Cd(II) treated (Cd(II): 200 L^{-1}).

metal ion becomes asymptotic to the time axis such that there is no appreciable change in the remaining metal ion concentration after 55 min. This represents the equilibrium time at which an equilibrium metal ion concentration is presumed to have been attained. The data obtained from this experiment was further used successfully to evaluate the kinetics of the adsorption process.

3.3.2. Influence of biosorbent dose

The effect of biosorbent dosage on the biosorption of Cd(II) ions was studied using different biomass dosage in the range, 0.2–1.6 g L^{-1} as shown in Fig. 3. Results showed that the biosorption efficiency is highly dependent on the increase in biomass dosage of the solution. To determine the effect of adsorbent dose, different amounts of adsorbent were suspended in 10 mL cadmium solution in which the concentration of cadmium was 200 mg L^{-1} and pH 5.0. The maximum biosorption of the metal ions was attained at about biomass dosage, 1.0 g L^{-1} and it was almost same (changed by about 10%) at higher dosages. This trend could be explained as a consequence of partial aggregation of biomass at higher biomass concentration, which results in a decrease in effective surface area for the biosorption [20]. Furthermore, higher adsorbent dose will result in lower adsorption capacity ($q_e = 12$ mg g^{-1} at 1.6 g L^{-1} dosage) value at a fixed cadmium concentration (200 mg L^{-1}), as shown in Fig. 3. Therefore, the optimum biomass dosage was selected as 1.0 g L^{-1} for further experiments.

3.3.3. Effect of pH

Earlier studies on heavy metal biosorption have shown that pH is an important parameter affecting the biosorption process. Cadmium(II) uptake by *Oedogonium* sp. is also a function of solution pH. The effect of initial solution pH in the range 2.99–6.05 pH on Cd(II) uptake capacity of *Oedogonium* sp. was studied at 25 °C and initial cadmium(II) ion concentration of 100 and 200 mg L^{-1}. As seen from Fig. 4 the biosorption of

Fig. 4. Effect of pH on biosorption of Cd(II) ions on algal biomass *Oedogonium* sp. from aqueous solutions: temperature 25 °C; initial concentration Cd(II) ions 200 mg L^{-1}; algal dose 1.0 g L^{-1} (Average value of three tests, error < 1.3%).

Cd(II) increases from pH 2.99–5.0 and then declined with further increase in pH. The maximum equilibrium uptake value was found as 72.0 and 80.0 mg g^{-1} at pH 5.0 for 100 and 200 mg L^{-1} Cd(II) ion concentrations. The equilibrium binding capacity decreased at pH 6.0–28.0 and 35.0 mg g^{-1}, respectively, for 100 and 200 mg L^{-1} Cd(II) ion concentrations. Solution pH influences both cell surface metal binding sites and metal chemistry in water. At low pH, cell wall ligands were closely associated with the hydronium ions H$_3$O$^-$ and restricted the approach of metal cations as a result of the repulsive force. As the pH increased, more ligands such as carboxyl, phosphate, imidazole and amino groups would be exposed and carried negative charges with subsequent attraction of metallic ions with positive charge and biosorption onto the cell surface [21,22]. The decrease of the fixation for pH upper than 5.0 is due to the complexation of cadmium(II) by OH$^-$ groups which would prevent the metal adsorption.

3.3.4. Effect of temperature

The isotherms of cadmium adsorption on the biosorbent, at three different temperatures (25, 35 and 45 °C) are given in Fig. 5. For an increase in temperature from 25 to 45 °C, a
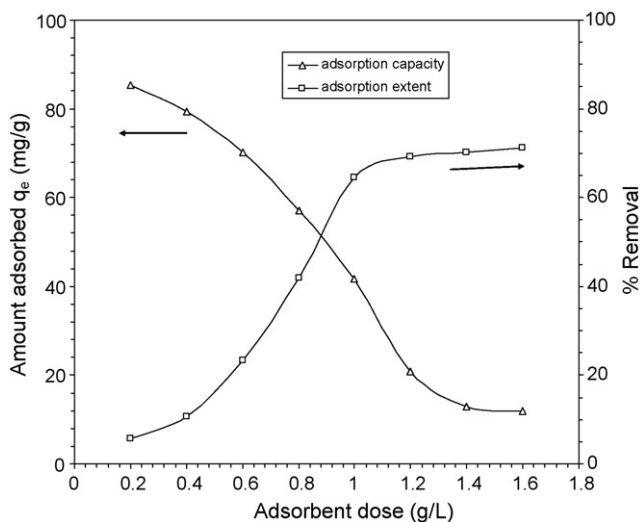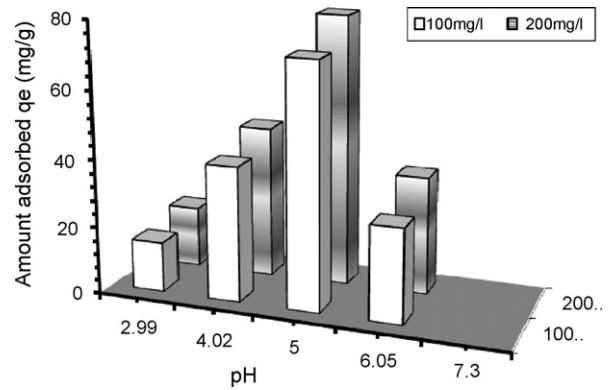

Fig. 3. Effect of adsorbent dose on the biosorption of Cd(II) ions on *Oedogonium* sp. from aqueous solutions: temperature 25 °C; initial concentration Cd(II) ions 200 mg L^{-1} (Average value of three tests, error < 1.3%).
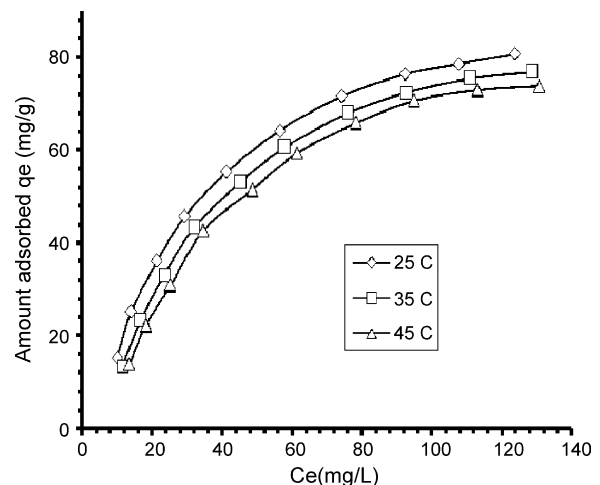

Fig. 5. Adsorption isotherms at three different temperatures for algal biomass *Oedogonium* sp. (Average value of three tests, error < 1.3%).
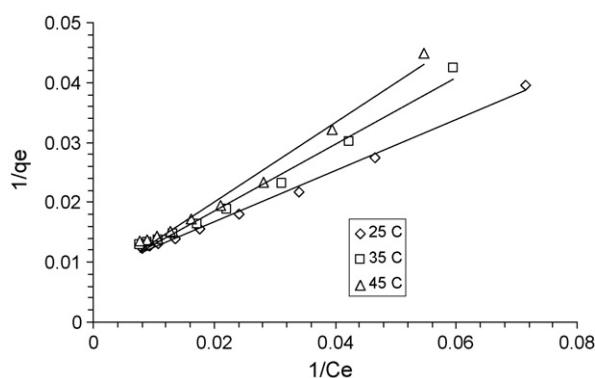
Fig. 6. Langmuir fitting of adsorption isotherms of Cd(II) on algal biomass *Oedogonium* sp.

decrease in adsorption of cadmium from 88.9 to 80.4 mg g^{-1} at 200 mg L^{-1}, initial cadmium concentration was observed. These adsorption data were further fitted to two adsorption models to find out the suitable model.

The effect of temperature on the biosorption process found in the literature presents different and opposite behaviours. Some of the researchers have reported [16,23] higher uptake capacities of cadmium in different organisms as temperature increases. On the other hand, few have reported [24–26] temperature-independent effect of Cd(II) uptake on biosorption capacity. In contrast, there are also reports [22,27] showing a decrease in the uptake capacity with temperature increase. Even a more complex situation was described by Benguella and Benaissa [28] for the adsorption of cadmium by chitin where an initial increase in the capacity of sorption was followed by a subsequent reduction.

3.4. Isotherms modelling

Langmuir and Freundlich isotherms were used to quantitatively describe metal sorption by the test alga. The Langmuir model is expressed by the equation:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{bQ_0C_e} \tag{1}$$

where q_e is the amount adsorbed (mg g^{-1}), C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), Q_0 is the Langmuir constants related to maximum monolayer adsorption capacity (mg g^{-1}) 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* $1/C_e$ were drawn as shown in Fig. 6 for three different temperatures to calculate these constants whereas Table 1 depicts the linearized form of the isotherms at all temperature over the whole concentration range studied and the extremely high correlation coefficients. These values of the correlation coefficients strongly support the fact that the cadmium–algal biomass biosorption data closely follow the Langmuir model of sorption.

The Freundlich model is represented by the equation:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{2}$$

Table 1
Langmuir and Freundlich isotherm constants for the biosorption of cadmium on algal biomass (*Oedogonium* sp.) at different temperatures

Temperature (°C)	Langmuir constant			Freundlich constant		
	b (L mg^{-1})	Q_0 (mg g^{-1})	R^2	n	K_F (mg g^{-1})	R^2
25	0.019	88.2	0.995	1.627	4.894	0.934
35	0.013	77.5	0.986	1.476	3.462	0.927
45	0.010	69.3	0.984	1.433	2.968	0.923

where K_F and n are constants related to the sorption capacity and intensity, respectively. The plots of $\ln q_e$ *versus* $\ln C_e$ (Fig. not shown) 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, and the correlation coefficients indicate, the data are not well correlated to Freundlich correlation coefficients compared to the Langmuir correlation coefficients. Earlier, satisfactory fitting of the Langmuir model to the adsorption isotherms of cadmium was obtained on Gelidium algae [29] and marine algal biomass [30].

3.5. Thermodynamic study

The free energy change (($G°$), enthalpy change (($H°$) and entropy change (($S°$) for adsorption process were calculated using following equations:

$$\Delta G° = -RT \ln(b) \tag{3}$$

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

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

The values of these parameters are summarized in Table 2. The enthalpy change ($H°$ is negative (exothermic) due to decrease in adsorption on successive increase in temperature. Further, negative ($G°$ values dictate spontaneous process. The positive value of ($S°$ reveals the increased randomness at the solid–solution interface during the fixation of the cadmium ion on the active sites of the biosorbent.

3.6. Kinetic modelling

In order to conclude about the controlling mechanism of the biosorption process, kinetic models are used to test the experimental data. The high heterogeneity of surface groups on alga cell wall (carboxyl, hydroxyl, phosphate, imidazole and amino

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

Algae	Temperature (°C)	$\Delta G°$ (KJ mol^{-1})	$\Delta S°$ (KJ mol^{-1} K^{-1})	$\Delta H°$ [a] (KJ mol^{-1})
Oedogonium sp.	25	−18.347	0.070	
	35	−18.960	0.069	−2.527
	45	−18.570	0.066	

[a] Measured between 25 and 45 °C.

Table 3
Adsorption rate constants, q_e estimated and coefficient of correlation associated to the Lagergren pseudo-first and second-order adsorption for the algal biomass *Oedogonium* sp.

Algae	Initial conc. (mg L^{-1})	$q_{e\,exp.}$ (mg g^{-1})	First-order model			Second-order model		
			$k_1\,10^{-3}$ (min^{-1})	$q_{e\,cal.}$ (mg g^{-1})	R^2	$k_2 \times 10^{-3}$ (g mg^{-1} min^{-1})	$q_{e\,cal.}$ (mg g^{-1})	R^2
Oedogonium sp.	100	58.4	17.963	30.22	0.903	0.797	63.29	0.996
	200	110.2	21.418	48.17	0.937	0.643	117.60	0.998

groups) suggests that there are many types of biosorbent–metal ion interactions. The two-sorption kinetic models used in this study are pseudo-first-order and pseudo-second-order models. The pseudo-first-order, rate expression of Lagergren is given as [31]

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

where q_t (mg g^{-1}) is the amount of adsorbed cadmium on the algal biomass at time t and $k_{1,ads}$ (min^{-1}) is the rate constant of first-order adsorption, q_e 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 upto a certain time (Fig. not shown) 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 [32] in its integrated and linearized form has been used.

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

where $k_{2,ads}$ (g mg^{-1} min^{-1}) is the rate constant of second-order adsorption. The plot t/q *versus* t (Fig. 7) 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. Table 3 lists the results of rate constant studies for different initial cadmium concentrations by the pseudo-first-order and pseudo-second-order models. The values of correlation coefficient R^2 for the pseudo-second-order adsorption model is relatively high (>0.995), and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for the
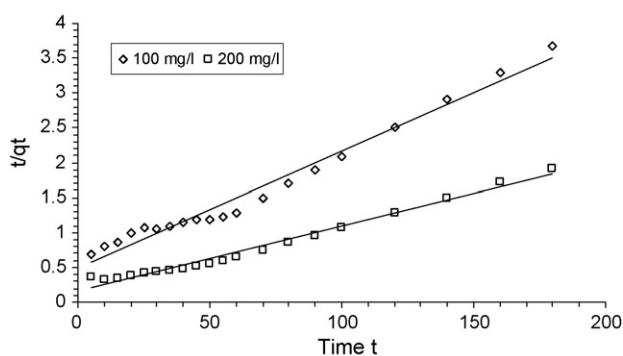
pseudo-first-order are not satisfactory. Therefore, it has been concluded that the pseudo-second-order adsorption model is more suitable to describe the adsorption kinetics of cadmium over algal biomass.

3.7. Comparison with other adsorbents

Table 4 compares maximum adsorption capacities obtained in this study with some other values reported in the literature. The adsorption capacity for cadmium using the algal biomass *Oedogonium* sp. is of the same order of magnitude or greater than that has been found using similar biosorbents [33–37,16,22,26,29].

3.8. Effects of biomass pretreatments on metal removal

Efforts were made to enhance the removal of Cd(II) by pretreating the oven-dried, i.e. nonliving biomass of *Oedogonium* sp. with selected chemicals as shown in Table 5. As evident from the table, acid pretreatment did not substantially increase metal sorption capacity of *Oedogonium* sp., except for a 9% and 3% increase in Cd(II) sorption capacity following HCl and HNO$_3$ treatment. This observation does not agree with Mehta et al. [38] who have reported 39% increase in metal binding capacity following acid pretreatment. As acids do not deteriorate *Oedogonium* sp. biomass, this finding may have considerable bearing on the use of acids for metal desorption.

3.9. Adsorption–desorption/reuse studies

Adsorption–desorption experiments are useful in elucidation of the mechanism of sorption reaction and also to assess the regeneration capacity of the adsorbent for reuse in a more

Fig. 7. Second-order kinetic modelling of Cd(II) ions biosorption on algal biomass *Oedogonium* sp.

Table 4
Adsorption capacities for Cd(II) using different low cost adsorbents (at room temperature)

Adsorbent	q_m[a] (mg g^{-1})	pH	Literature
Pine bark	28.0	7.5	33
Waste tea leaves	31.48	5.0	34
Hazelnut shells	5.42	6.0	35
Peat	22.5	5.0	36
Aquatic moss, *Fontinalis antipyretica*	28.0	5.0	16
Chlorella vulgaris	85.3	4.0	22
Gelidium algae	18.0	5.3	29
Chlamydomonas reinhardtii	42.6	6.0	26
Spirulina platensis	98.04	6.0	37
Oedogonium sp.	88.2	5.0	This study

[a] is the adsorption capacity of various adsorbents at room temperature.

Table 5
Effect of various pretreatments (55 min; 0.1 mM of all the chemicals) on Cd(II)metal sorption ability of *Oedogonium* sp.

Pretreating agent	Percentage change in metal sorption ability
HCl	8.0 ± 1.2[a]
HNO$_3$	3.0 ± 0.3
NaOH	14.3 ± 1.1
Hot water (60 °C) for 15 min	-17.5 ± 1.5
Ammonium acetate	-21.2 ± 1.4
Methanol	-30.5 ± 1.2
Acetone	-35.7 ± 2.6
Formaldehyde	-2.5 ± 1.0

The symbols '+' and '−', respectively, denote increase and decrease relative to the control (untreated biomass).

[a] Data denote, means $\pm$ S.D. of three replicates.

economic manner. Eight different desorption agents (0.1 M) were tested for desorbing the test metal from the metal-loaded biomass of *Oedogonium* sp. (Table 6). The amount of desorption provides an insight into the nature of adsorbent–adsorbate bonding and also on the ion exchange property of the adsorbent. Comparatively effective desorption of cadmium ions from biomass was found in acidic solution. Maximum desorption of Cd(II) [84.8%] occurred with HCl followed in decreasing order by EDTA, H$_2$SO$_4$, HNO$_3$, NaOH, CaCl$_2$·2H$_2$O, Na$_2$CO$_3$ and Milli-Q water. Tuzun et al., [26] have shown ~90% desorption of Cd(II) from microalgae *Chlamydomonas reinhardtii* by HCl. Alkaline reagents (NaOH, Na$_2$CO$_3$ and CaCl$_2$·2H$_2$O) and Milli-Q water could desorb very little of Cd(II) from the Cd(II)–loaded *Oedogonium* sp. This observation has a good agreement with the findings of other workers [39]. These latter authors have shown the superiority of acids over bases for the desorption of metals from the biomass. The present work indicated that EDTA desorbs metals from the biomass with a great efficiency, however, EDTA cannot be used for metal desorption on a large scale as its release in nature may lead to serious environmental problems. On the other hand, HCl is not only efficient in desorbing metal ions but is inexpensive as well.

In order to assess the reusability of *Oedogonium* sp. biomass for Cd(II) removal from aqueous phase, five successive cycles of sorption and desorption were carried out in a batch system. A 200 mg L^{-1} concentration of test metal was selected, as such a high concentration commonly occur in wastewater from smelters and acid mine drainage [40,41]. Metal sorp-

Table 6
Effects of various chemical agents (0.1 M) on desorption of Cd(II) from the metal-loaded biomass of *Oedogonium* sp.

Desorbing agent	Cd(II)% desorption
HCl	84.8 ± 2.2[a]
H$_2$SO$_4$	71.2 ± 2.0
HNO$_3$	69.7 ± 1.9
NaOH	34.1 ± 1.5
CaCl$_2$·2H$_2$O	28.2 ± 1.4
Na$_2$CO$_3$	13.5 ± 1.2
EDTA	80.0 ± 2.6
Milli-Q water	10.5 ± 1.0

[a] Mean $\pm$ S.D. of three replicates.

Table 7
Successive cycles of sorption and desorption of Cd(II) by *Oedogonium* sp. in the batch system

Cycle	Cd(II) sorption	Cd(II) desorption
1.	42.8 ± 1.8[a]	35.6 ± 2.0[a]
2.	40.1 ± 1.5	34.5 ± 1.4
3.	38.8 ± 2.0	32.8 ± 1.6
4.	36.5 ± 1.6	31.0 ± 1.7
5.	34.2 ± 1.8	28.3 ± 1.8

Desorption by HCl (0.1 M); contact time 55 min.

[a] Sorption and desorption data (means $\pm$ S.D. of three replicates) are given as mg metal g^{-1} dry weight.

tion by the biomass decreased slightly after each successive cycle (Table 7). In all the cycles, more than 80% of metal was recovered back by using HCl as the desorbing agent. Furthermore, the present study shows that only 18% decrease in sorption of Cd(II) by the biomass was occurred after five sorption/desorption cycles. If we take into account the loss of biomass (15–20%) at the end of the fifth cycle, it is apparent that the metal sorbing ability of the biomass did not considerably diminish during repeated sorption/desorption cycles. On the other hand, metal sorption potential of other biomass types may substantially decrease following desorption of metals by acids. For instance, acid desorbents caused around 22% decline in sorption of Cd(II) by microalgae *Chlamydomonas reinhardtii* [26], and of Cd and Co by *Phormidium valderianum* [42] during 5–6 sorption/desorption cycles, respectively. Such a decline occurs because acids deteriorate biomass and may dissolve certain polysaccharides that may contain metal binding sites [19]. The regeneration of the algal biomass shows that the biosorption–desorption process using the algal biomass is a reversible process and the algal biomass can be used repeatedly for the removal of heavy metal ions from aqueous solutions.

4. Conclusion

The batch studies conducted in the present study provides significant information regarding biosorption of cadmium on green algae *Oedogonium* sp. in terms of optimum pH and biomass dose for maximum removal of Cd(II) from the aqueous solution. The studies indicate that *Oedogonium* sp. is an effective biosorbent for Cd(II) removal. The maximum Cd(II) biosorption capacity has been found to be 88.2 mg Cd(II) g^{-1} of dry weight of biomass at an algal dose of 1.0 g L^{-1} in 55 min of contact time with initial Cd(II) concentration of 200 mg L^{-1} and optimum pH of 5.0. The langmuir and Freundlich adsorption model were used for the mathematical description of the biosorption of Cd(II) ions onto algal biomass and it was found that the adsorption equilibrium data fitted well to the Langmuir model. The biosorption of cadmium ions on the algal biomass follows second-order biosorption kinetics. Only alkali pretreatment could slightly enhance the metal sorbing ability of the biomass. HCl efficiently desorbed metal from the metal-loaded biomass, but it did not substantially lessen the metal—loading ability of the biomass during successive sorption/desorption cycles. With the advantage of high metal biosorption capacity, the biomass

of *Oedogonium* sp. has the potential to be used as an efficient and economic biosorbent material for the removal of cadmium from aqueous phase.

Acknowledgement

References

[1] M. Tsezos, Biosorption of metals. The experience accumulated and the outlook for technology development, Hydrometallurgy 59 (2001) 241–243.

[2] J. Yin, H.W. Blanch, A bio-mimetic cadmium adsorbent: design, synthesis, and characterization, Biotechnol. Bioeng. 34 (1989) 180–188.

[3] Y.C. Sharma, Economic treatment of cadmium(II)-rich hazardous waste by indigenous material, J. Appl. Interface Sci. 173 (1995) 66–70.

[4] C. Lacher, R.W. Smith, Sorption of Hg(II) by *Potamogeton natans* dead biomass, Minerals Eng. 15 (2002) 187–191.

[5] E. Fourest, J. Roux, Heavy metal biosorption by fungal mycelial by-products: Mechanism and influence of pH, Appl. Microbiol. Biotechnol. 37 (1992) 399–403.

[6] R. Say, A. Denizli, M.Y. Arica, Biosorption of Cd(II), lead(II) and copper(II) with the filamentous fungus *Phanerochaete chrysosporium*, Biores. Technol. 76 (2001) 67–70.

[7] M. Ziagova, G. Dimitriadis, D. Aslanidou, X. Papaioannou, E.L. Tzannetaki, M.L. Kyriakides, Comparative study of Cd(II) and Cr(VI) biosorption on *Staphylococcus xylosus* and *Pseudomonas* sp. in single and binary mixtures, Biores. Technol. 98 (2007) 2859–2865.

[8] M.I. Ansari, A. Malik, Biosorption of nickel and cadmium by metal resistant bacterial isolates from agricultural soil irrigated with industrial wastewater, Biores. Technol. 98 (2007) 3149–3153.

[9] B. Volesky, H. May, Z.R. Holan, Cadmium biosorption by *Saccharomyces cerevisiae*, Biotechnol. Bioeng. 41 (2004) 826–829.

[10] B. Hadi, A. Margaritis, F. Berruti, M. Bergougnou, Kinetics and equilibrium of cadmium biosorption by yeast cells *S. cerevisiae* and *K. fragilis*, Int. J. Chem. Reactor. Eng. 1 (2003) 1–18.

[11] H. Doshi, A. Ray, I.L. Kothari, Biosorption of cadmium by live and dead *Spirulina*: IR spectroscopic, kinetics, and sem Studies, Cur. Microbiol. 54 (2007) 213–218.

[12] Z. Aksu, G. Do̎nmez, Binary biosorption of cadmium(II) and nickel(II) onto dried Chlorella vulgaris: co-ion effect on mono-component isotherm parameters, Process Biochem. 41 (2006) 860–868.

[13] J.T. Matheickal, Q. Yu, G.M. Woodburn, Biosorption of cadmium(II) from aqueous solutions by pre-treated biomass of marine alga *Durvillaea potatorum*, Water Res. 33 (1999) 335–343.

[14] P. Kaewsarn, Q. Yu, Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga *Padina* sp., Environ. Pollut. 112 (2001) 209–213.

[15] K. Naddafi, R. Nabizadeh, R. Saeedi, A.H. Mahvi, F. Vaezi, K. Yaghmaeiian, A. Ghasri, S. Nazmara, Biosorption of lead (II) and cadmium(II) by protonated Sargassum glaucescens biomass in a continuous packed bed column, J. Hazard. Mater. 147 (2007) 785–791.

[16] R.J.E. Martinsa, R. Pardob, R.A.R. Boaventurab, Cadmium(II) and zinc(II) adsorption by the aquatic moss *Fontinalis antipyretica*: effect of temperature, pH and water hardness, Water Res. 38 (2004) 693–699.

[17] C.W. Cheung, J.F. Porter, G. Mckay, Sorption kinetic analysis for the removal of Cadmium ions from effluents using bone char, Water Res. 35 (2001) 605–612.

[18] S. Bunluesin, M. Kruatrachue, P. Pokethitiyook, S. Upatham, G.R. Lanza, Batch and continuous packed column studies of cadmium biosorption by *Hydrilla verticillata* biomass, J. Biosci. Bioeng. 103 (2007) 509–513.

[19] S.K. Mehta, J.P. Gaur, Use of algae for removing heavy metal ions from wastewater: progress and prospects, Crit. Rev. Biotechnol. 25 (2005) 113–152.

[20] S. Karthikeyan, R. Balasubramanian, C.S.P. Iyer, Evaluation of the marine algae *Ulva fasciata* and *Sargassum* sp. for the biosorption of Cu(II) from aqueous solutions, Biores. Technol. 98 (2007) 452–455.

[21] G.C. D̎onmez, Z. Aksu, A. Ozturk, T. Kutsal, A comparative study on heavy metal biosorption characteristics of some algae, Process Biochem. 34 (1999) 885–892.

[22] Z. Aksu, Equilibrium and kinetic modelling of cadmium (II) biosorption by *C. vulgaris* in a batch system: effect of temperature, Sep. Purif. Technol. 21 (2001) 285–294.

[23] M. Ajmal, R.A.K. Rao, S. Anwar, J. Ahmad, R. Ahmad, Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater, Biores. Technol. 86 (2003) 147–149.

[24] Z. Aksu, T. Kutsal, A comparative study for biosorption characteristics of heavy metal ions with *C. vulgaris*, Environ. Technol. 11 (1990) 979–987.

[25] P. Lodeiro, J.L. Barriada, R. Herrero, M.E. Sastre de Vicente, The marine macroalga *Cystoseira baccata* as biosorbent for cadmium(II) and lead(II) removal: kinetic and equilibrium studies, Environ. Pollut. 142 (2006) 264–273.

[26] I. Tuzun, G. Bayramoglu, Y.E. alcin, G. Basaran, G. Celik, M.Y. Arica, Equilibrium and kinetic studies on biosorption of Hg (II), Cd(II) and Pb(II) ions onto microalgae *Chlamydomonas reinhardtii*, J. Environ. Man. 77 (2005) 85–92.

[27] C.C.V. Cruz, A.C.A. Costa, C.A. Henriques, A.S. Luna, Kinetic modelling and equilibrium studies during cadmium biosorption by dead *Sargassum* sp. biomass, Biores. Technol. 91 (2004) 249–257.

[28] B. Benguella, H. Benaissa, Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.

[29] V.J.P. Vilar, C.M.S. Botelho, R.A.R. Boaventura, Equilibrium and kinetic modelling of Cd(II) biosorption by algae *Gelidium* and agar extraction algal waste, Water Res. 40 (2006) 291–302.

[30] P.X. Sheng, Y.P. Ting, J.P. Chen, L. Hong, Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms, J. Coll. Int. Sci. 275 (2004) 131–141.

[31] Y.S. Ho, G. McKay, The sorption of lead(II) ions on peat response to comment, Water Res. 33 (1999) 578–584.

[32] G. McKay, Y.S. Ho, Pseudo-second-order model for sorption processes, Process Biochem. 34 (1999) 451–465.

[33] S. Al-Asheh, Z. Duvnjak, Binary metal sorption by pine barks: study of equilibria and mechanisms, Sep. Sci. Technol. 33 (1998) 1303–1329.

[34] T.W. Tee, A.R.M. Khan, Removal of lead, cadmium and zinc by waste tea leaves, Environ. Technol. Lett. 9 (1988) 1223–1232.

[35] G. Cimino, A. Passerini, G. Toscano, Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell, Water Res. 34 (2000) 2955–2962.

[36] T. Gosset, J.L. Transcart, D.R. Thevenot, Batch metal removal by peat: kinetics and thermodynamics, Water Res. 20 (1986) 21–26.

[37] N. Rangsayatorn, E.S. Upatham, M. Kruatrachue, P. Pokethitiyook, G.R. Lanza, Phytoremediation potential of *Spirulina platensis*: biosorption and toxicity studies of cadmium, Environ. Pollut. 119 (2002) 45–53.

[38] S.K. Mehta, B.N. Tripathi, J.P. Gaur, Enhanced sorption of Cu^{2+} and Ni^{2+} by acid-pretreated *Chlorella vulgaris* from single and binary metal solutions, J. Appl. Phycol. 14 (2002) 267–273.

[39] J.L. Zhou, P.L. Huang, R.G. Lin, Sorption and desorption of Cu and Cd by macroalgae and microalgae, Environ. Pollut. 101 (1998) 67–75.

[40] S. Al-Asheh, Z. Duvnjak, Sorption of heavy metals from synthetic metal solutions and industrial wastewater using plant materials, Water Qual. Res. J. Canada 34 (1999) 481–503.

[41] S.B. Bortnikova, B.S. Smolyakov, N.B. Sidenko, G.R. Kolonin, E.P. Bessonova, N.V. Androsova, Geochemical consequences of acid mine drainage into a natural reservoir: inorganic precipitation and effects on plankton activity, J. Geochem. Explor. 74 (2001) 127–139.

[42] R.R. Karna, L. Uma, G. Subramanian, P.M. Mohan, Biosorption of toxic metal ions by alkali-extracted biomass of a marine cyanobacterium *Phormidium valderianum* BDU 30501, World J. Microbiol. Biotechnol. 15 (1999) 729–732.