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Biosorption of hexavalent chromium by raw and acid-treated green alga *Oedogonium hatei* from aqueous solutions

V.K. Gupta*, A. Rastogi

Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee 247 667, India

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ABSTRACT

The hexavalent chromium, Cr(VI), biosorption by raw and acid-treated *Oedogonium hatei* were studied from aqueous solutions. Batch experiments were conducted to determine the biosorption properties of the biomass. The optimum conditions of biosorption were found to be: a biomass dose of 0.8 g/L, contact time of 110 min, pH and temperature 2.0 and 318 K respectively. Both Langmuir and Freundlich isotherm equations could fit the equilibrium data. Under the optimal conditions, the biosorption capacities of the raw and acid-treated algae were 31 and 35.2 mg Cr(VI) per g of dry adsorbent, respectively. Thermodynamic parameters showed that the adsorption of Cr(VI) onto algal biomass was feasible, spontaneous and endothermic under studied conditions. The pseudo-first-order kinetic model adequately describe the kinetic data in comparison to second-order model and the process involving rate-controlling step is much complex involving both boundary layer and intra-particle diffusion processes. The physical and chemical properties of the biosorbent were determined and the nature of biomass–metal ions interactions were evaluated by FTIR analysis, which showed the participation of —COOH, —OH and —NH_2 groups in the biosorption process. Biosorbents could be regenerated using 0.1 M NaOH solution, with up to 75% recovery. Thus, the biomass used in this work proved to be effective materials for the treatment of chromium bearing aqueous solutions.

1. Introduction

Widespread contamination of aqueous environment by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain. Chromium has been considered as one of the top 16th toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern [1]. Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production [2]. Extensive use of chromium results in large quantities of chromium-containing effluents which need an exigent treatment. Though chromium exists in nine valency states ranging from −2 to +6, Cr(III) and Cr(VI) are of major environmental significance. Cr(VI) is more mobile and toxic than Cr(III). Hence, Cr(VI) is more important than Cr(III) in water pollution control. According to the World Health Organization (WHO) drinking water guidelines, the maximum allowable limit for hexavalent chromium and total chromium (including Cr(III), Cr(VI) and other forms) are 0.05 and 2 mg/L, respectively [3]. It is therefore essential to remove Cr(VI) from wastewater before disposal.

Traditional chromium treatment technologies include ion-exchange, chemical reduction/precipitation, membrane separation, and adsorption. Since these methods are often very costly, requiring high energy input or large quantities of chemical reagents, biosorption or biosorption to materials of biological origin has been proposed as a potential alternative. Biosorption has gained important credibility during recent years because of its ecofriendly nature, excellent performance, and low cost domestic technique for remediating even, heavily metal loaded wastewater. New approaches of developing various microbial sources, seaweed, aquatic plants and leaf based adsorbents as cost effective and efficient biosorbents have been reported by various investigators [4–13]. Among them, algae have proved to possess high metal binding capacities [8], 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]. Industrial applications of biosorption often make use of dead biomass, which does not require nutrients and can be exposed to environments of high toxicity.

Recent investigations by various researchers have shown that a number of marine and freshwater algae possess impressive sorption capacities or removal efficiencies for the biosorption of the

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

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hexavalent chromium from aqueous solutions [15–19]. Thus, in the present communication an abundantly available green filamentous alga, *Oedogonium hatei* (a chlorophyta, Family Oedogoniacae), living in freshwater of ponds and pools, was economically used as a biosorbent for chromium removal from aqueous solutions. Earlier, we have reported excellent biosorption capacity of this alga for the removal of lead and cadmium [20,21]. The alga was acid pretreated in order to enhance the sorption performance and also to strengthen it for sorption process applications. To enhance the removal efficiency of metal ions by the biomass, various pretreatments can be used. Pretreatments can be either heat treatment [15], or increasing the negative charge on the cell surface by NaOH treatment [22], or opening of the available sites for the adsorption by acid treatment [23]. However, the studies on the use of pretreated alga for hexavalent chromium removal from wastewater are very limited.

The aim of the present investigation is to detect the performance of raw and acid pretreated alga *O. hatei* on chromium removal from aqueous solution and to evaluate the effect of various parameters including pH, contact time, temperature and adsorbent dose. Adsorption isotherms and kinetic models were applied to fit the experimental data. The effectiveness of desorbing agent (NaOH) in stripping adsorbed metal ions from biomass was also investigated.

2. Experimental procedures

2.1. Algal biomass preparations

O. hatei was sampled locally 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 followed by Milli-Q water 4–5 times, for removing from its surface interfering ions and other undesired materials, such as, sand particles and debris. The biomass was 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 and subsequently referred as raw biomass. The acid-treated alga was prepared by transferring the raw biomass into 0.1 M HCl and then stirring the mixture at 200 rpm for 8.0 h at room temperature. The algal biomass was then centrifuged (Eppendorf Centrifuge model HM-150 IV, Korea), washed with the physiological saline solution and dried in an oven at 60 °C. Subsequently, it was ground on an agate stone pestle mortar and sieved, to select the particles between 150 and 250 mesh sizes for use.

2.2. Physical and chemical properties of algal biomass

The physical and chemical properties of the raw and acid treated algal biomass were determined by the routine methods. Bruanauer, Emmett and Teller method (BET method) was used to determine the surface area of the biosorbents and zeta potential measurement was obtained by the application of a constant electric potential across the suspension and by determining the rate at which particles migrate into the cell (electrophoretic mobility). The zeta potential was measured using a zeta potential analyzer (model 1200 Micromeritics) (T = 20 °C; sample density 1 g/cm^3; test duration 150 s; conductivity cell constant 0.750 cm^{-1}; intensity I = 0.007 A; pH 5.0 for the raw biomass; pH 2 for the acid treated biomass).

To give a qualitative and preliminary analysis of the main chemical groups present on the cell wall of biomass, an IR analysis in solid phase was carried out. For the FTIR study, 0.1 g of finely sized particle of the biomass was encapsulated in 1 g of KBr keeping the ratio 1:10, in order to prepare the translucent sample disks. Infrared spectra were obtained with the help of PerkinElmer FTIR-1600 spectrophotometer, USA.

2.3. Preparation and analysis of metal solution

A stock solution of Cr(VI) (1000 mg/L) was prepared in milli-Q water with potassium dichromate ($K_2Cr_2O_7$). It was then diluted to prepare solutions of the desired concentrations. All the chemicals used throughout this study were of analytical grade either from Merck, Germany or SD Fine Chem. Ltd., India. Biosorption studies were conducted in a routine manner by the batch technique 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 298 ± 2 K, 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. The filtrate was collected in polythene tubes and diluted before analysis. The concentration of remaining Cr(VI) ions in the biosorption medium was determined spectrophotometrically at 540 nm using a double beam UV/vis spectrophotometer (Shimadzu, Japan, Model SPECORD 200) after complexation with 1,5 diphenyl carbazide in acidic medium [24]. Before determination of the total quantity of chromium Cr(VI) in the adsorption medium, Cr^{3+} and Cr^{2+} were converted to Cr(VI) using $KMnO_4$. The adsorption capacities were then 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 ±1.6%. Further, the error bars for the figures were even smaller than the symbols used to plot the graphs and, hence, not shown.

2.4. Batch adsorption studies

The biosorption of Cr(VI) on the algal biomass *O. hatei* was investigated in batch mode. The effect of solution pH (range 1.0–4.0), biosorbent dose (0.1–1.0 g/L), contact time (10–160 min) and temperature (298, 308 and 318 K) on the biosorption rate and capacity were studied. The adsorption procedure was the same as described earlier. To obtain adsorption isotherms, the biosorbent (0.8 g/L) was suspended in chromium solutions (concentration range 10–100 mg/L) at three different temperatures i.e. 298, 308 and 318 K. Kinetic studies of adsorption by alga under study was also carried out at two initial chromium concentrations (50 and 100 mg/L) at 318 K wherein the extent of adsorption was analyzed at regular time interval.

2.5. Desorption studies

In order to determine the reusability of the biosorbent, consecutive biosorption–desorption cycles were repeated five times. For this, 0.1 M NaOH, was used as the desorbing agent. The algal biomass loaded with heavy metal ions was placed in the desorbing medium and was constantly stirred on a rotatory shaker at 100 rpm for 1 h at 318 K. After each cycle of adsorption and desorption, the algal biomass was washed with milli-Q water and reconditioned for adsorption in the succeeding cycle.

3. Results and discussion

On comparing biosorption method with other conventional methods for the removal of Cr(VI) from aqueous solution indicates or the major advantages of this technique are the reusability of the biomaterial, low operating cost, improved selectivity for specific

Table 1
IR absorption bands and corresponding possible groups observed on raw and acid-treated green alga *Oedogonium hatei*

Raw alga wavenumber (cm^{-1})	Raw alga with Cr(VI) (cm^{-1})	Acid-treated alga with Cr(VI) (cm^{-1})	Functional groups
3404	3412	3388	Carboxylic/OH stretch and N—H stretch
2917	2914	2914	Phenolic/carboxylic
–	2358	–	—CH Stretch
1646	1652	1650	C=O chelate stretching, amide I band
1540	1537	1539	Amide II band, OH bonds,
1426	1425	–	Symmetric bending of CH_3 of the acetyl moiety
1243	1249	1249	=C—C=, P=O
1168	1171	1171	≡C—N<
1058	1059	1060	—CN stretching, plane deformation

metals of interest, removal of heavy metals from effluent irrespective of toxicity, short operation time and no production of secondary compounds which might be toxic.

3.1. Characterization of the biosorbent

The physical and chemical properties of the raw and acid treated algal biomass were determined by the standard methods. The surface area of both the algal biomass, as determined by Quantasorb surface area analyzer, was 1.3 m^2/g and the elemental analysis depicted the composition of biosorbents as C, 24.4%; N, 3.08%; S, 1.79%. The humidity and the zeta potential were calculated to be 1.2, 3.5% and −0.065, −0.081 V for the raw and acid treated alga respectively. The apparent density of the biosorbent was determined to be 1.1 g/cm^3.

Changes in the functional groups and surface properties of the biosorbent were confirmed by FTIR spectra. The spectra revealed biosorbent heterogeneity, evidenced by different characteristic peaks with the possible presence of amino, carboxylic, hydroxyl and carbonyl groups. The IR absorption bands and corresponding possible groups able to interact with protons or metal ions are presented in Table 1. It was observed from the table that after adsorbing chromium in raw and acid treated alga there were slight changes in the absorption peak frequencies, which suggested that there was a metal binding process taking place on the surface of the biomass. The above results obtained give an idea about the presence of functional groups on the algal cell surfaces and also the mechanism of adsorption, which is dependent on functional groups especially carboxyl and amino groups.

3.2. Adsorption studies

Adsorption of Cr(VI) by raw and acid-treated algal biomass *O. hatei* was studied as a function of contact time and concentration, biosorbent dose, pH, and temperature. The adsorption data were fitted to different isotherms.

3.2.1. Effect of contact time and concentration

Fig. 1 shows the comparative data of the effect of contact time on the extent of biosorption of Cr(VI) on the biomass at 50 and 100 mg/L initial chromium concentration at pH 2.0 and temperature 318 K for the raw and acid treated alga *O. hatei*. It has been observed that the metal adsorption rate is high at the beginning for both the algal biomasses and then decreases slowly till saturation levels were completely reached at equilibration point (110 min). The initial rapid phase may involve physical adsorption or ion exchange at cell surface and the subsequent slower phase may involve other mechanisms such as complexation, micro-precipitation or saturation of binding sites. An increase in adsorption was observed from 12.7 to 26.8 mg/g for raw alga and from 14.5 to 30.0 mg/g for acid treated alga with 50 and 100 mg/L initial concentration of Cr(VI). Note that there are several parameters, which determine the adsorption rate such as structural properties of both sorbate and biosorbent (e.g. protein and carbohydrate composition and surface charge density, topography and surface area). The amount of biosorbent, initial concentration of metal ions and existence of other ions (which may compete with the ions of interest for the active biosorption sites) also affect the adsorption rate.

3.2.2. Effect of biosorbent dose

To assess the effect of biosorbent dose, different amounts (0.1–1.0 g/L) of biosorbent (*O. hatei*) was suspended in 50 mL Cr(VI) solution (100 mg/L) under optimized conditions of pH and contact time. The effect of adsorbent dose on the amount of Cr(VI) adsorbed in mg/g and extent of removal of metal for the raw and acid-treated algal preparation is shown in Fig. 2. The amount of adsorbent significantly influenced the extent of Cr(VI) adsorption i.e. the biosorption of metal ions increased with increasing biomass dosage and almost constant at dose higher than 0.8 g/L. This trend could be explained as a consequence of partial aggregation of biomass at higher biomass concentration, which results in the decrease in effective surface area for the biosorption [25]. Therefore, the optimum algal biomass dose selected was 0.8 g/L for the rest of the experimental studies. The experimental data also showed that the acid treated algal form had a higher level of performance for removal of Cr(VI) from aqueous medium than that of the raw alga.

3.2.3. Effect of solution pH

The effect of pH on chromium (concentration 50 and 100 mg/L) adsorption on raw and acid-treated forms of *O. hatei* algal biomasses were studied by varying the pH of chromium solution–algae sus-

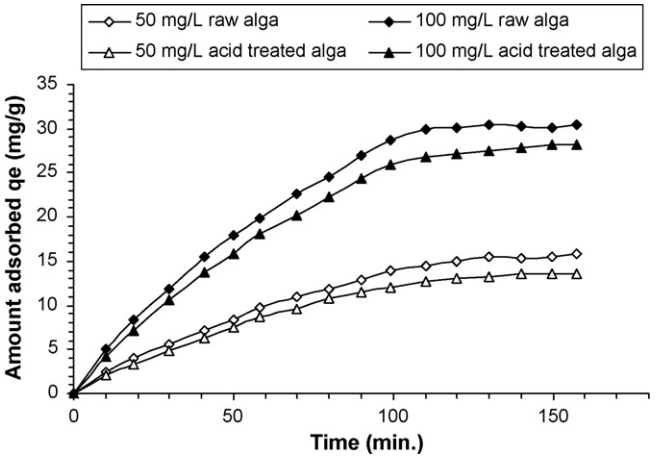

Fig. 1. Effect of contact time on the uptake of Cr(VI) onto raw and acid-treated *Oedogonium hatei* algal biomass at different concentrations (temperature: 45 °C, pH 2.0, initial Cr(VI) concentration 50 and 100 mg/L).

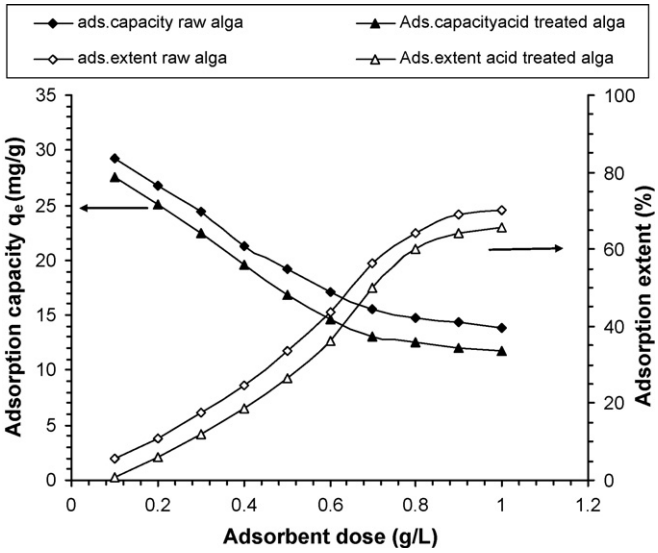

Fig. 2. Effect of biosorbent dosage on the uptake of Cr(VI) onto raw and acid-treated *Oedogonium hatei* algal biomass (temperature: 45 °C, pH 2.0, initial Cr(VI) concentration 100 mg/L).

pension from 1 to 4.0. The plot of metal adsorption capacity (mg/g) versus pH is shown in Fig. 3. It is observed from the graph that the equilibrium chromium sorption was favored by acidic pH range of 1–2.0 and maximum adsorption by the algal biomass was observed at pH 2.0. Increase in pH decreased the adsorption of chromium by the algae. Maximum metal adsorption at pH 2 seems to be due to a net positive charge on algal surface at low pH. Earlier similar results have reported that the optimal pH for Cr(VI) adsorption was around 2–3 [17,18]. Chromium, which may exist as $HCrO^{4-}$, $Cr_2O_7^{2-}$, etc. in solution at optimum sorption pH [26] has a tendency to bind the protonated active sites of the biosorbent. But as pH of the solution increases, algal cell wall becomes more and more negatively charged due to functional groups, which repulse the negatively charged chromate ions thereby affecting Cr(VI) adsorption on the algal surface.

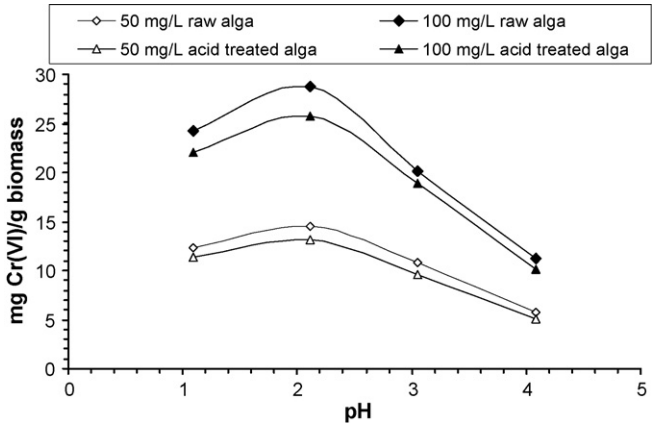

Fig. 3. Effect of pH on the uptake of Cr(VI) onto raw and acid-treated *Oedogonium hatei* algal biomass (temperature: 45 °C, dosage: 800 mg/L, initial Cr(VI) concentration 50 and 100 mg/L).

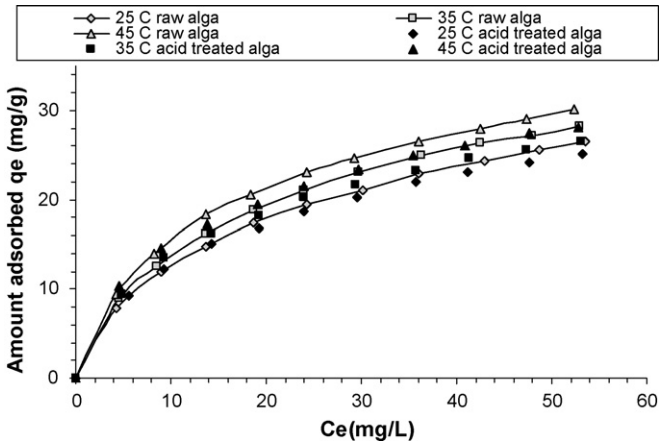

Fig. 4. Effect of temperature (25, 35 and 45 °C) on the adsorption of Cr(VI) onto raw and acid-treated *Oedogonium hatei* algal biomass at pH 2.0.

3.2.4. Effect of temperature

The effect of temperature on the adsorption of Cr(VI) on the biomass is investigated at three different temperatures (298, 308 and 318 K) as given in Fig. 4. The temperature of the adsorption medium could be important for energy dependent mechanisms in metal adsorption by microbial cells. For an increase in temperature from 298 to 318 K, the adsorption capacities of the raw and acid-treated algal biomass for Cr(VI) showed an increase. The increase in adsorption with increasing temperature indicated endothermic nature of the adsorption process. Similar endothermic nature of the adsorption process has been reported for other adsorbent systems [26,27]. The increase in sorption with temperature may be attributed to either increase in the number of active surface sites available for sorption on the adsorbent or due to the decrease in the boundary layer thickness surrounding the sorbent, so that the mass transfer resistance of adsorbate in the boundary layer decreased [28].

3.3. Modeling of adsorption isotherms

The results obtained from adsorption isotherms were analyzed with Langmuir and Freundlich models as discussed earlier [29]. The Langmuir and Freundlich adsorption constants and the regression correlation coefficient are given in Table 2. The values of regression coefficients obtained from these models were used as the fitting criteria to find out these isotherms. It was observed that the

Table 2
Langmuir and Freundlich isotherm constants for the adsorption of Cr(VI) onto raw and acid-treated green alga *Oedogonium hatei* at different temperatures

Biomass	Temperature (K)	Langmuir constant			Freundlich constant		
		b (L mg^{-1})	Q_0 (mg g^{-1})	R^2	n	K_F (mg g^{-1})	R^2
Raw alga	298	0.082	28.985	0.990	2.304	1.941	0.995
	308	0.090	30.120	0.992	2.345	2.022	0.991
	318	0.105	30.959	0.986	2.471	2.150	0.993
Acid-treated alga	298	0.078	30.395	0.991	2.096	1.849	0.993
	308	0.080	32.679	0.990	2.149	1.948	0.992
	318	0.083	35.211	0.997	2.215	2.060	0.985

Table 3
Thermodynamic parameters for the adsorption of chromium onto raw and acid-treated green alga *Oedogonium hatei* at different temperatures

Biomass	Temperature (K)	ΔG° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔH° [a] (kJ mol^{-1})
Raw alga	298	−19.880	0.075	
	308	−21.345	0.078	2.639
	318	−22.138	0.078	
Acid-treated alga	298	−20.704	0.102	
	308	−21.645	0.102	9.744
	318	−22.748	0.102	

[a] Measured between 298 and 318 K.

experimental data fits well to both Langmuir (R^2 = 0.99) and the Freundlich adsorption isotherm (R^2 = 0.99) indicating both monolayer biosorption and heterogeneous surface conditions. From the Langmuir adsorption constant Q_o value, it was observed that acid-treated *O. hatei* (Q_o = 35.2 mg/g) has slightly better adsorbing capacity for Cr(VI) than raw *O. hatei* (Q_o = 31.0 mg/g) biomass at 318 K.

3.4. Thermodynamic study

To study the thermodynamics of adsorption of Cr(VI) on raw and acid treated *O. hatei* alga, thermodynamic constants such as enthalpy change ΔH°, free energy change ΔG° and entropy change ΔS° were calculated using equations described in our earlier work [29]. The values of these parameters are given in Table 3. A perusal of Table 4 indicated that the enthalpy change ΔH° is positive (endothermic) due to increase in adsorption on successive increase in temperature. The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the biosorption. The positive value of ΔS° reveals the increased randomness at the solid–solution interface during the fixation of the chromium ion on the active sites of the biosorbent.

3.5. Dynamic modeling

In the present study, 'anionic adsorption' is the removal mechanism of chromium, as it is reported by various other researchers also [5,30–33]. Thus, various kinetic models applied to the kinetic data were, viz. the intraparticle diffusion model, Lagergren pseudo-first-order and Ho's pseudo-second-order model [34–36].

3.5.1. Intraparticle diffusion model

According to the intraparticle diffusion model proposed by Weber and Morris [34], the initial rate of intraparticle diffusion is calculated by linearization of the curve $q = f(t^{0.5})$:

$$q = K_W t^{0.5} \quad (1)$$

where q is the amount of adsorbed metal ion on the biomass (mg/g), K_W (mg/g min$^{-0.5}$) represents intraparticle diffusion rate constant and t denotes contact time (min). The plot between fraction of metal ion removal and square root of contact time (Fig. 5) was initially curved with a final linear portion. The initial curved portions might be attributed to the boundary layer diffusion effect [37], while the final linear portion might be due to intraparticle diffusion effects [38]. This further indicated that the intraparticle diffusion was not only the rate-controlling step rather the process is much complex involving both boundary layer and intraparticle diffusion. The slope of the linear portion was defined as a rate parameter (K_W) and characteristic of the rate of adsorption in this region where intraparticle diffusion was rate limiting is given in Table 4.

3.5.2. Lagergren pseudo-first-order and second-order kinetic models

The mathematical representations of models are given in Eqs. (2) and (3).

$$\log(q_e - q_t) = \log q_e - \frac{k_{1,ads}}{2.303} t \quad (2)$$

$$\frac{t}{q} = \frac{1}{k_{2,ads} q_e^2} + \frac{1}{q_e} t \quad (3)$$

where q_e the equilibrium sorption uptake at time t = infinity and q_t (mg/g) is the amount of adsorbed chromium on the algal biomass at time t and $k_{1,ads}$ (/min) and $k_{2,ads}$ (g/mg/min) are the rate constant of first-order and second-order adsorption. The adsorption rate constant (k_1) for chromium sorption was calculated from the slope of the linear plot of $\ln(q_e - q_t)$ versus time. In the latter case, kinetic data were plotted between t/q_t against t. The kinetic rate constants obtained from first-order and second-order pseudo kinetic model are given in Table 4. Though, both first-order and pseudo-second-order kinetics possess high correlation coefficient values of 0.97–0.98 for both the algal biomasses, but the Table 4 data indicates that the $q_{e,cal}$. values for the first-order model are more close to $q_{e,exp}$ values in comparison to second-order values. So, it can be concluded that chromium sorption on to the biosorbent seems to be more pseudo-first-order.

3.6. Diffusion processes

In order to assess the nature of the diffusion process responsible for the adsorption of chromium on biosorbent, attempts were made to calculate the coefficients of the process as explained by Chabani et al. [39]. Assuming spherical geometry for the biosorbent, the overall rate constant of the process can be correlated with the pore diffusion coefficient (D_p) and the film diffusion coefficient (D_f) independently according to reference [40] as described below.

$$D_p = 0.03 \left[\frac{R_p^2}{t_{1/2}} \right] \quad (4)$$

$$D_f = 0.23 \left[\left(\frac{R_p \varepsilon}{t_{1/2}} \right) \times \left(\frac{q_e}{C_0} \right) \right] \quad (5)$$

where R_p (~0.05 cm) is the radius of the biosorbent, ε the film thickness (10^{-3} cm) [34] q_e the amount of metal sorbed (mg/l), C_0 the initial concentration and $t_{1/2}$ is the time for half sorption (min). If film diffusion was to be the rate-determining step in the adsorption of nitrates on the surface of the resin, the value of the film diffusion

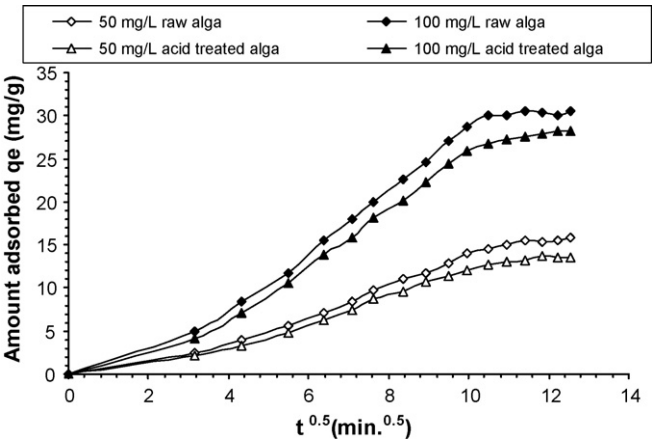

Fig. 5. Intraparticle diffusion model plot of Cr(VI) adsorption on *Oedogonium hatei* algal biomass.

Table 4
Summary of sorption data evaluated by different kinetic models for the raw and acid-treated green alga *Oedogonium hatei* (pH 2.0)

Biomass	Initial Cr concentration (mg/L)	$q_{e\,exp}$ (mg g^{-1})	First-order model			Second-order model			Intraparticle model	
			$k_1 \times 10^{-3}$ (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	K_W (mg/g min$^{0.5}$)	R^2
Raw alga	50	14.6	21.648	16.323	0.983	0.321	28.011	0.976	1.439	0.978
	100	28.2	23.721	33.335	0.981	0.220	50.761	0.968	2.810	0.968
Acid-treated alga	50	13.3	23.030	15.191	0.968	0.368	24.450	0.972	1.255	0.976
	100	26.2	25.333	31.060	0.972	0.194	49.505	0.971	2.602	0.973

coefficient (D_f) should be in the range 10^{-6} to 10^{-8} cm^2/s. If pore diffusion was to be rate limiting, the pore diffusion coefficient (D_p) should be in the range 10^{-11} to 10^{-13} cm^2/s [37]. By considering the appropriate data and the respective overall rate constants, pore and film diffusion coefficients were determined. It clearly appeared that chromium removal on algal biosorbent was controlled by film diffusion process since coefficient values were around 10^{-6} cm^2/s.

3.7. Comparison with other adsorbents

Table 5 compares maximum adsorption capacities obtained in this study with some other values reported in the literature. The adsorption capacity for chromium using the raw and acid-treated algal biomass *O. hatei* is of the same order of magnitude or greater than that has been found using similar biosorbents [5,15,18,41].

3.8. Desorption and reuse

Regeneration of biosorbent for repeated reuse is of crucial importance in industrial practice for metal removal from wastewater. Experiments were conducted for regenerating raw and acid-treated algal biomass *O. hatei* using 0.1 M NaOH. More than 75% of the adsorbed chromium was desorbed from the algal biomass. In order to show the reusability of the biosorbent, adsorption-desorption cycle of chromium was repeated five times using the same preparations. The adsorption capacities for all the tested algal preparations did not noticeably change (only a maximum 20–25% change was observed) during the repeated adsorption–desorption operations (figure not shown). Thus, the reuse of the biomass and desorbent is an important feature for its possible utilization in continuous systems in industrial processes.

3.9. Effect of cations on biosorption

Actual industrial wastewaters contain different kinds of impurities, which may significantly affect metal biosorption. Among such impurities, cations such as Na^+, K^+, Mg^{2+} and Ca^{2+}, may be present which may interfere with the uptake of heavy metal ions by biomass. So, in the present investigation, the effect of different concentrations (0, i.e. control, 1, 5, 10 mmol/L) of these cations on chromium uptake by the raw and acid-treated algal biomass *O. hatei* was studied. It was found that the effect of Na^+, K^+ and Mg^{2+} on adsorption of Cr(VI) was very small (maximum 5–8%), though Ca^{2+} caused removal percentage to drop by 15% at 10 mmol/L concentration (figure not shown). The effect of Ca^{2+} on uptake is due to the competition with Cr(VI) for the binding sites.

Table 5
Comparison of biosorption capacity of *Oedogonium hatei* for chromium with that of various algal biomasses

Algal biomass	q_m[a] (mg/g)	pH	Literature
Spirogyra sp.	14.7	2.0	[18]
Chlamydomonas reinhardetti (heat inactivated)	25.6	2.0	[15]
Chlamydomonas reinhardetti (acid treated)	21.2	2.0	[15]
Lyngbya putealis	113.6	3.0	[5]
Ulva lactuca (green algae)	27.6	2.0	[41]
Ulva spp. (green algae)	30.2	2.0	[41]
Fucus vesiculosus (brown algae)	42.7	2.0	[41]
Fucus spiralis (brown algae)	5.4	2.0	[41]
Polysiphonia lanosa (red algae)	45.8	2.0	[41]
Palmaria palmate (red algae)	33.8	2.0	[41]
Oedogonium hatei (raw)	31.0	2.0	This study
Oedogonium hatei (acid treated)	35.2	2.0	This study

[a] The adsorption capacity of various adsorbents.

4. Conclusion

This study identified raw and acid-treated algal biomass *O. hatei* as a suitable biosorbent for Cr(VI) removal in batch experiments. The experimental evidence showed the strong effect of the operating variables (pH, temperature, contact time and dosage) on biosorption performance of *O. hatei* biomass. The biosorption capacity of acid-treated algal biomass is found to be greater than the raw biomass. Equilibrium is well described by both Langmuir and Freundlich adsorption isotherms. Thermodynamic parameters showed that the biosorption of Cr(VI) ions onto algal biomass was feasible, spontaneous and endothermic under studied conditions. Biosorption kinetics is fast and is well represented by pseudo-first-order models. The kinetic evaluation data suggests that the rate limiting step is predominantly film diffusion, although intraparticle diffusion also appears to be rate limiting. The interactions between the metal ion and the functional groups on the cell wall surface of the biomass were confirmed by FTIR analysis, which indicated the participation of —COOH, —OH and —NH_2 groups in the chromium adsorption. This study demonstrated that the raw and acid-treated algal biomass *O. hatei* could be used as efficient biomasses for the treatment of Cr (VI) containing aqueous solutions.

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References

[1] Z.J. Kowalski, Treatment of chromic tannery wastes, J. Hazard. Mater. 37 (1994) 137–144.
[2] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of Cr(VI) in industrial waste water using low-cost abundantly available adsorbents, Adv. Environ. Res. 6 (2002) 533–540.
[3] A. Baral, R.D. Engelken, Chromium-based regulation and greening in metal finishing industries in the USA, Environ. Sci. Pollut. 5 (2002) 121–133.
[4] G. Donmez, Z. Aksu, Selective adsorption of Cr(VI) in industrial waste water using low-cost abundantly available adsorbents, Process Biochem. 38 (2002) 751–762.
[5] B. Kiran, A. Kaushik, C.P. Kaushik, Biosorption of Cr(VI) by native isolate of *Lyngbya putealis* (HH-15) in the presence of salts, J. Hazard. Mater. 141 (2007) 662–667.
[6] W.C. Leung, Biosorption of heavy metals by bacterial isolated from activated sludge, Appl. Biochem. Biotechnol. 91 (2001) 171–184.

[7] D. Park, Y.S. Yun, J.H. Jo, J.M. Park, Mechanism of hexavalent chromium removal by dead fungal biomass of *Aspergillus niger*, Water Res. 39 (2005) 533–540.
[8] S.K. Das, A.K. Guha, Biosorption of chromium by *Termitomyces clypeatus*, Colloids Surf. B: Biointerfaces 60 (2007) 46–54.
[9] D. Park, Y.S. Yun, J.M. Park, Studies on hexavalent chromium biosorption by chemically-treated biomass of *Ecklonia* sp, Chemosphere 60 (2005) 1356–1364.
[10] D. Kratochvil, P. Pimentel, B. Volesky, Removal of trivalent and hexavalent chromium by seaweed biosorbent, Environ. Sci. Technol. 32 (1998) 2693–2698.
[11] S. Basha, Z.V.P. Murthy, B. Jha, Biosorption of hexavalent chromium by chemically modified seaweed, *Cystoseira indica*, Chem. Eng. J. 137 (2008) 480–488.
[12] P. Suksabye, P. Thiravetyan, W. Nakbanpote, S. Chayabutra, Chromium removal from electroplating wastewater by coir pith, J. Hazard. Mater. 141 (2007) 637–644.
[13] H. Gao, Y. Liu, G. Zeng, W. Xu, T. Li, W. Xia, Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste, Rice Straw 150 (2008) 446–452.
[14] H.R. Crist, K. Oberholser, N. Shank, M. Nguyen, Nature of bonding between metallic ions and algal cell walls, Environ. Sci. Technol. 15 (1981) 1212–1217.
[15] M.Y. Arica, I. Tuzun, E. Yalcin, O. Ince, G. Bayramoglu, Utilization of native, heat and acid-treated microalgae *Chlamydomonas reinhardtii* preparations for biosorption of Cr(VI) ions, Process Biochem. 40 (2005) 2351–2358.
[16] A.E. Sikaily, A.E. Nemr, A. Khaled, O. Abdelwehab, Removal of toxic chromium from waste water using green alga *Ulva lactuca* and its activated carbon, J. Hazard. Mater. 148 (2007) 216–228.
[17] X. Han, Y.S. Wong, M.H. Wong, N.F.Y. Tam, Biosorption and bioreduction of Cr(VI) by a microalgal isolate, *Chlorella miniata*, J. Hazard. Mater. 146 (2007) 65–72.
[18] V.K. Gupta, A.K. Shrivastava, N. Jain, Biosorption of chromium(VI) from aqueous solutions by green algae *Spirogyra* species, Water Res. 35 (2001) 4079–4085.
[19] S.V. Gokhale, K.K. Jyoti, S.S. Lele, Kinetic and equilibrium modeling of chromium(VI) biosorption on fresh and spent *Spirulina platensis*/*Chlorella vulgaris* biomass, Bioresour. Technol. 99 (2008) 3949–3964.
[20] V.K. Gupta, A. Rastogi, Biosorption of lead(II) from aqueous solutions by nonliving algal biomass *Oedogonium* sp. and *Nostoc* sp.—A comparative study, Colloids Surf. B: Biointerfaces 64 (2008) 170–178.
[21] V.K. Gupta, A. Rastogi, Equilibrium and kinetic modeling of cadmium(II) biosorption by nonliving algal biomass *Oedogonium* sp. from aqueous phase, J. Hazard. Mater. 153 (2008) 759–766.
[22] E. Gurisik, M.Y. Arica, S. Bektas, O. Genc, Comparison of the heavy metal biosorption capacity of active, heat-inactivated and NaOH-treated *Phanerochaete chrysosporium* biosorbents, Eng. Life Sci. 4 (2004) 86–89.
[23] J. Yang, B. Volesky, Modeling uranium—proton ion exchange in biosorption, Environ. Sci. Technol. 33 (1999) 4079–4085.
[24] L.S. Clesceri, A.E. Greenberg, A.D. Eaton, Standard Methods for the Examination of Water and Wastewater, 20th ed., American Public Health Association, American Water Work Association, and Water Environment Federation, Washington, DC, 1998.
[25] 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, Bioresour. Technol. 98 (2007) 452–455.
[26] Z. Aksu, U. Acikel, E. Kabasakal, S. Tezer, Equilibrium modelling of individual and simultaneous biosorption of chromium(VI) and nickel(II) onto dried activated sludge, Water Res. 36 (2002) 3063–3073.
[27] R.S. Prakashan, J.S. Merrie, R. Sheela, N. Saswathi, S.V. Ramakrishna, Biosorption of chromium(VI) by free and immobilized *Rhizopus arrhizus*, Environ. Pollut. 104 (1999) 421–427.
[28] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal, P.N. Nagar, Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent, J. Hazard. Mater. 122 (2005) 161–170.
[29] V.K. Gupta, A. Rastogi, Biosorption of lead from aqueous solutions by green algae *Spirogyra species*: kinetics and equilibrium studies, J. Hazard. Mater. 152 (2008) 407–414.
[30] G.S. Agarwal, H.K. Bhuptawat, S. Chaudhari, Biosorption of aqueous chromium(VI) by *Tamarindus indica* seeds, Bioresour. Technol. 97 (2006) 949–956.
[31] K.K. Deepa, M. Sathishkumar, A.R. Binupriya, G.S. Murugesan, K. Swaminathan, S.E. Yun, Sorption of Cr(VI) from dilute solutions and wastewater by live and pretreated biomass of *Aspergillus flavus*, Chemosphere 62 (2006) 833–840.
[32] V. Sarin, K.K. Pant, Removal of chromium from industrial waste by using eucalyptus bark, Bioresour. Technol. 97 (2006) 15–20.
[33] 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, Bioresour. Technol. 98 (2007) 2859–2865.
[34] W.J. Weber, J.C. Morris, Advances in water pollution research: removal of biologically-resistant pollutants from waste waters by adsorption, in: Proceedings of International Conference on Water Pollution Symposium, vol. 2, Pergamon Press, Oxford, 1962, pp. 231–266.
[35] Y.S. Ho, G. McKay, The sorption of lead(II) ions on peat response to comment, Water Res. 33 (1999) 578–584.
[36] G. McKay, Y.S. Ho, Pseudo-second-order model for sorption processes, Process Biochem. 34 (1999) 451–465.
[37] C.Y. Chang, W.T.T. Sai, C.H. Ing, C.H. Chang, Adsorption of polyethylene glycol (PEG) from aqueous solution onto hydrophobic zeolite, J. Colloid Interface Sci. 260 (2003) 273–279.
[38] C.L. Brierley, in: H.L. Ehrlic, C.L. Brierly (Eds.), Microbial Mineral Recovery, McGraw-Hill, New York, 1990, pp. 303–324.
[39] M. Chabani, A. Amraneb, A. Bensmaili, Kinetic modelling of the adsorption of nitrates by ion exchange resin, Chem. Eng. J. 125 (2006) 111–117.
[40] S.V. Mohan, S.V. Ramanaiah, P.N. Sharma, Biosorption of direct azo dye from aqueous phase onto *Spirogyra* sp I02: evaluation of kinetics and mechanistic aspects, Biochem. Eng. J. 38 (2008) 61–69.
[41] V. Murphy, H. Hughes, P. McLoughlin, Comparative study of chromium biosorption by red, green and brown seaweed biomass, Chemosphere 70 (2008) 1128–1134.