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Biosorption of Cr(VI) using a novel microalga *Rhizoclonium hookeri*: equilibrium, kinetics and thermodynamic studies

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ABSTRACT

Heavy metal pollution is a major environmental concern in many countries. Among heavy metals, chromium is one of the widely used despite being one of the most toxic metal ions. The present study deals with the evaluation of Cr(VI) biosorption using a novel fresh water alga *Rhizoclonium hookeri*. Batch experiments were conducted and the maximum adsorption capacity was evaluated as 67.3 mg/g at pH 2 at a biomass dosage of 1 g/L and 1,000 mg/L initial Cr(VI) concentration. Fourier transform infrared spectroscopy analysis of alga before and after biosorption revealed a shift in the carboxylic O–H stretching vibration from 3,401 to 3,373 cm^{-1}, which confirmed its involvement in biosorption of Cr(VI) by *R. hookeri*. Surface morphology of alga was examined using the scanning electron microscopy, which indicated the highly porous nature of biomass. Non-linear regression analyses of isotherm models revealed that the three-parameter model isotherms (Redlich–Peterson and Sips) better described the experimental data compared with two-parameter model isotherms (Langmuir and Freundlich). An analysis of the kinetic models (pseudo-first-order, pseudo-second-order and Elovich models) indicated that the experimental data followed pseudo-second-order kinetics. The thermodynamic parameters such as free energy, enthalpy and entropy were calculated and Cr(VI) biosorption was found to be a spontaneous and endothermic process.

Keywords: Biosorption; Isotherm; Kinetics; Thermodynamics; Wastewater treatment

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1. Introduction

In recent years, industrial pollution, soil erosion, deforestation, urbanization and land degradation are putting a great strain on the environment. Among the different pollutants, the role of heavy metals in the deterioration of the environment is noteworthy. Chromium is one of the most widely used heavy metals and has widespread application in the making of alloys, chrome plating, leather tanning, batteries, dyes, paints, welding, catalysis and wood preservatives. Of the different forms of chromium, the hexavalent chromium usually occurs as a highly soluble and toxic chromate anion, which is suspected carcinogen and

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mutagen. Potable waters containing more than 0.05 mg/L Cr(VI) are considered toxic [1]. Many diseases such as epigastric pain, haemorrhage, severe diarrhoea, vomiting, nausea, dermatitis by skin contact, ulcer, lung cancer and tissue neurosis have been reported to be associated with occupational Cr(VI) exposure. Therefore, the removal of Cr(VI) from industrial wastewaters has been an area of interest in the recent years.

Ion exchange, chemical precipitation, electrochemical methods and membrane technology are some of the most widely used methods to remove Cr(VI) from contaminated solutions. However, these methods have been found to be inefficient and expensive when heavy metals are present in low concentrations, and these methods may also generate secondary wastes which are difficult to treat [2]. One of the recently emerging techniques to decontaminate metal bearing wastewaters is biosorption. Biosorption is due to a number of metabolism-independent processes, which essentially take place in the cell wall where the mechanisms responsible for the pollutant uptake will differ according to the biomass type. The mechanism of binding depends upon the type of biomass, chemical nature of the pollutant and environmental conditions such as pH, temperature and ionic strength [3]. Abundant and inexpensive materials, such as algae, moss, fungi, bacteria and chitosans have proved to have a reasonably high metal sequestering capacity and may be used as biomass. Biosorption has distinct advantages over conventional treatment methods, which include the process being very cheap, environment friendly, absence of final chemical sludge and easily operable [4].

In the present study, a freshwater alga *Rhizoclonium hookeri* was used as a biosorbent for the removal of Cr(VI) from an aqueous solution. Alga *R. hookeri* belongs to the family of Cladophoraceae. The alga appears as a wood, fibre-like filament and consisting of tubular end-to-end connections of individual cells. In recent years, there is interest in the use of different marine algae to remove Cr(VI), but microalgae are seldom studied for the removal of Cr(VI). Thus, the present study explored the effect of protonation, biosorbent dosage, initial pH, contact time, initial metal ion concentration and temperature on Cr(VI) biosorption by *R. hookeri*. The kinetics, equilibrium and the thermodynamics of biosorption were also been studied.

2. Materials and methods

2.1. Chemicals

Rankem Fine Chemicals Ltd, India, supplied all the chemicals used in the study, which were of analytical grade. Cr(VI) stock solution was prepared using $K_2Cr_2O_7$ in double distilled water. Standard acid (0.1 M HCl) and base (0.1 M NaOH) solutions were used for pH adjustments.

2.2. Analytical procedure

UV spectrophotometer (Z-7000, Elico Ltd) was used to analyse the concentration of Cr(VI) in the aqueous solution. pH meter (Elico LI-120, India) was used to measure solution pH. Fourier transform infrared spectroscopy (Perkin Elmer FTIR, spectrophotometer model-1600, USA) and scanning electron microscopy (SEM-Hitachi 5-3400N) with a coating unit ion sputter coater with gold target were used for biomass characterization.

2.3. Preparation of biomass

R. hookeri, a freshwater alga, was procured locally from ponds and other water pools near Dharmapuri, Tamilnadu, India. To remove sand and other debris material the algal biomass was washed with distilled water. For 3 d, the cleaned fresh water alga was dried in sunlight and then finally ground. Protonated biomass was used in biosorption experiments was prepared using the procedure explained below. The ground particles (raw biomass) were treated with 0.1 M HC1 for 5 h in orbital shaker at a speed of 150 rpm followed by washing it with distilled water. Finally, it was dried in the oven overnight at 60°C.

2.4. Batch biosorption studies

To evaluate the effects of biomass dosage, pH, contact time, initial metal ion concentration and temperature on removal of Cr(VI) ions by *R. hookeri* batch biosorption experiments were conducted. All the biosorption experiments were conducted in 250 mL Erlenmeyer flask on a rotary shaker containing 100 mL of different metal concentrations at 150 rpm. After the desired contact period with 0.1 g *R. hookeri,* the flasks were removed and the solution was filtered through 0.45 μm Whatman filter paper. The filtrate was analysed for Cr(VI) concentration using a spectrophotometer at a wavelength of 540 nm using the diphenylcarbazide method [5].

The amount of metal sorbed by biomass was calculated from the differences between the metal quantity added to the biomass and the metal content of the supernatant using the following equation:

$$Q = (C_o - C_f) * V/M \qquad (1)$$

where Q is the metal uptake (mg/g); C_0 and C_f are the initial and final (equilibrium) metal concentrations in the solution (mg/L), respectively; V is the solution volume (L); and M is the mass of biomass (g).

2.5. Isotherm and kinetic modelling

To describe Cr(VI) isotherm data, two-parameter and three-parameter equilibrium models were used as follows:
Langmuir model [6]:

$$Q = \frac{Q_{\max} b_L C_f}{1 + b_L C_f} \tag{2}$$

Freundlich model [7]:

$$Q = K_F C_f^{1/n} \tag{3}$$

Redlich–Peterson model [8]:

$$Q = \frac{K_{RP} C_f}{1 + a_{RP} C_f^{\beta_{RP}}} \tag{4}$$

Sips model [9]:

$$Q = \frac{K_S C_f^{\beta_s}}{1 + a_S C_f^{1/\beta_s}} \tag{5}$$

where $Q_{\max}$ is the maximum metal uptake (mg/g), b_L is the Langmuir equilibrium constant (L/mg), K_F is the Freundlich constant $(g/L)^{1/n}$, n is the Freundlich exponent, K_{RP} is the Redlich–Peterson isotherm constant (L/g), a_{RP} is the Redlich–Peterson isotherm constant $(L/mg)^{1/\beta_{RP}}$, β_{RP} is the Redlich–Peterson model exponent equilibrium constant, K_S is the Sips model isotherm constant $(L/g)^{\beta_S}$, a_S is the Sips model constant $(L/mg)^{\beta_S}$ and β_S is the Sips model exponent. The experimental biosorption kinetic data were modelled using the pseudo-first-order, pseudo-second-order and Elovich models which can be expressed in their non-linear forms, as follows:

Pseudo-first-order model [10]:

$$Q_t = Q_e(1 - \exp(-k_1 t)) \tag{6}$$

Pseudo-second-order model [11]:

$$Q_t = \frac{Q_e^2 K_2 t}{1 + Q_e k_2 t} \tag{7}$$

Elovich model [12]:

$$Q_t = (1 + \beta_E) \ln(1 + \alpha_E \beta_E t) \tag{8}$$

where Q_t is the amount of metal sorbed at time t (mg/g), Q_e is the amount of metal sorbed at equilibrium (mg/g), k_1 is the pseudo-first-order rate constant (1/min), k_2 is the pseudo-second-order rate constant (g/mg min), α_E is the initial adsorption rate (mg/(g min)) and β_E is the desorption constant (g/mg). All the model parameters were evaluated by non-linear regression using SIGMA plot (version 4.0, SPSS, USA) software. The fitness of data was measured according to the coefficient of determination (R^2) and % error (ε). All experiments were done in duplicates and the data presented are the average of two experiments.

3. Results and discussion

3.1. Effect of protonation

Protonation is the addition of a proton (H^+) to an atom, molecule or ion. The process removes the ions blocking the binding sites and increases the overall positive charge of the biomass. For the present system, protonation improved the uptake capacity in comparison with raw biomass. The uptake capacity increased from 55 mg Cr(VI)/g to 60 mg Cr(VI)/g upon protonation at pH 2 and 1 g/L biomass dosage with 0.7 mm algal biomass size and 40 min contact time.

3.2. Effect of biomass dosage

Experiments were also performed to study the influence of biomass dosage on Cr(VI) removal efficiency of *R. hookeri*. It was observed that the amount of Cr(VI) adsorbed decreases from 60 to 41 mg/g with an increase in the quantity of dosage from 1 to 5 g/L. This behaviour could be explained by the formation of aggregates of the biomass at higher doses, which decreases the effective surface area for biosorption [13]. Another important factor being that at high biomass dosages, the available Cr(VI) molecules are insufficient to cover all the exchangeable sites on the biomass, usually resulting in low Cr(VI) uptake.

Furthermore, the high concentration of biomass resulted in screen effect of the dense outer layer of cells and blocking the binding site from metal ions, resulting in lower metal removal per unit of biomass [14]. Therefore, 1 g/L dose was selected as the optimum biomass dosage for the present study.

3.3. Effect of pH on Cr(VI) biosorption and isotherm studies

The metal removal efficiency of biomass is usually strongly influenced by the pH of the reaction mixture. For the present system, increasing the pH from 2 resulted in decreased Cr(VI) uptake by *R. hookeri* (Fig. 1). High biosorptional uptake of Cr(VI) in strong acidic conditions suggest that the negatively charged chromium species (chromate/dichromate) exhibited electrostatic attraction towards positively charged nitrogen containing functional groups on the surface of algal cell wall [15]. At these pH ranges, functional groups will be protonated due to excess H^+ ions. The lowest sorption occurred at pH 3.5 with an uptake of 56 mg/g and the greatest sorption occurred at pH 2 with 64 mg/g. Many published literatures on chromium biosorption observed maximum uptake at pH 2. Bermúdez et al. [16] studied biosorption of hexavalent chromium onto *Sargassum muticum* (brown alga). The authors observed that biosorption of chromium(VI) by algal biomass is highly pH dependent and maximum Cr(VI) uptake capacity was observed at pH 2. Similarly, Gupta et al. [17] studied biosorption of hexavalent chromium by green algae *Spirogyra* species and observed that maximum removal of Cr(VI) was around 14.7×10^3 mg metal/kg of dry weight biomass at a pH of 2.0 in 120 min with 5 mg/L of initial concentration. In the examined pH range of 2–3.5, no precipitation of Cr(VI) was observed in the control experiments.

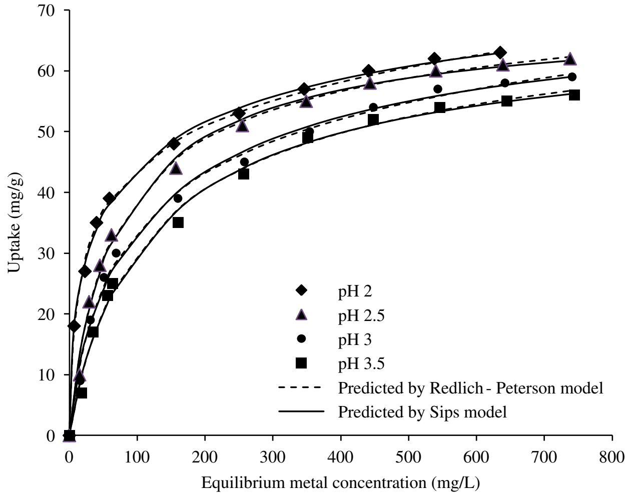


Fig. 1. Biosorption isotherms at different pH conditions.

The pH dependence of metal sorption can largely be related to the type and ionic state of these functional groups and also on the metal chemistry of the solution. At pH above 3, the biomass possesses more functional groups carrying a net negative charge, which tends to repulse the anions. However, it should be noted that Cr(VI) removal still occurred above pH 3, but the extent of removal had considerably reduced. Moreover, at very low pH values (acidic), the surface of biomass is surrounded by the hydronium ions which enhanced Cr(VI) interaction with the binding sites of *R. hookeri* through greater attractive force. The experimental isotherms followed a general trend i.e. Cr(VI) uptake increased with increasing Cr(VI) concentration and reached saturation at higher equilibrium concentrations. The isotherms obtained at all pH conditions can be classified as "L" shaped i.e. the ratio between the concentration of Cr(VI) remaining in the solution and sorbed onto *R. hookeri* decreases when the solute concentration increases, providing a concave curve.

In the present study, two-parameter isotherm models (Langmuir and Freundlich) and three-parameter isotherm models (Redlich–Peterson and Sips) were used to describe the equilibrium between the Cr(VI) sorbed onto the biomass of *R. hookeri* and Cr(VI) in the solution. The isotherm constants, along with % error and R^2 are presented in Table 1. The Langmuir model was found to exhibit better fit than the Freundlich model with high R^2 values and low % error values (Table 1). The Langmuir isotherm is often used to describe sorption of a solute from a liquid solution [18]. The Langmuir constant "$Q_{\max}$" is often used to compare the performance of biomass; while "b_L" characterizes the initial slope of the isotherm. Thus, for good biosorbents, in general, a high $Q_{\max}$ and steep initial isotherm slope (i.e. high b_L) are desirable. The Freundlich isotherm equation describes the sorption of solute from liquid to solid surface and assumes that the stronger binding sites are occupied first and the binding strength decreases with an increase in the degree of site occupation. The model constant, K_F, can be defined as the adsorption or distribution coefficient and represents the quantity of metal adsorbed onto biomass for unit equilibrium concentration. The other constant, $1/n$, is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. Its value indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value of n is equal to unity, the adsorption is linear; if the value is below unity, this implies that adsorption process is chemical; and if the value is

Table 1
Isotherm constants of two-parameter and three-parameter models for removal of Cr(VI)

Two-parameters model constants

	Langmuir				Freundlich			
pH	$Q_{\max}$ (mg/g)	b_L (L/mg)	R^2	ε (%)	K_F $(g/L)^{1/n}$	n	R^2	ε (%)
2.0	67.3	0.025	0.969	2.65	13.9	4.21	0.990	1.57
2.5	66.6	0.015	0.995	1.02	8.08	3.14	0.969	6.87
3.0	64.2	0.012	0.991	0.04	6.23	2.86	0.979	6.19
3.5	64.1	0.009	0.995	1.18	4.77	2.61	0.973	8.65

Three-parameters model constants

pH	Redlich–Peterson					Sips				
	K_{RP} (L/g)	$a_{RP} \times 10^{-3}$ $(L/mg)^{\beta_{RP}}$	β_{RP}	R^2	ε (%)	K_S $(L/g)^{\beta_S}$	$a_S \times 10^{-3}$ $(L/g)^{\beta_S}$	β_S	R^2	ε (%)
2.0	5.42	0.241	0.837	0.999	0.18	8.41	0.0967	0.511	0.999	0.05
2.5	1.17	0.027	0.932	0.997	2.02	1.44	0.0206	0.894	0.996	1.88
3.0	1.06	0.040	0.867	0.996	1.95	1.671	0.0225	0.780	0.995	2.19
3.5	0.672	0.018	0.922	0.996	2.59	0.858	0.0126	0.897	0.995	2.29

above unity, adsorption is a favourable physical process [19]. However, the results of the present study indicated that the Freundlich model provided relatively less R^2 values and high % error as shown in Table 1.

Table 1 also shows the parameters obtained using the non-linear regression of three-parameter models. Due to the presence of an additional parameter and complexity nature, three-parameter models describe biosorption isotherms better compared with the two-parameter models. Among the tested models, the Sips model (Fig. 1) gives a better fit. The Redlich–Peterson model exponent (β_{RP}) values were found to be closer to unity, which indicate that the data obey the Langmuir model. In the present study, the Sips model exhibited relatively low error values and high correlation coefficients. The Sips model exponent, β_S values were found to be significantly closer to unity which indicates that the present data support the Langmuir form [20]. The successful description of experimental data by the Sips model indicates that Cr(VI) sorption process followed heterogeneous mode of adsorption. A comparison of the maximum Cr(VI) uptake of *R. hookeri* with those of other biosorbents reported in the literature is given in Table 2.

3.4. Kinetic studies

The extent of biosorption is dependent only on the initial and final equilibrium state, whereas the rate of biosorption is dependent on the way that leads from the initial to the final step. Sorption solid–liquid kinetics may be controlled by several independent processes, which normally act in conjunction, and involve transport phenomenon and chemical reactions [21]. Fig. 2 shows the results of kinetic experiments at different initial Cr(VI) concentrations. On changing the initial Cr(VI) concentration from 250 to 1,000 mg/L, the amount sorbed increased from 48.1 to 70.4 mg/g. Biosorption of Cr(VI) by *R. hookeri* exhibited a general trend such that the biosorptional uptake was a rapid process in the initial stages (time <30 min) followed by equilibrium attainment. A close examination of curves revealed that more than 80% of sorption process was completed within 30 min. This initial quick phase was followed by slow attainment of equilibrium. The high sorption rate at the initial period (30 min) may be due to an increased number of vacant sites available at the early stage, which results in an increased concentration gradient between sorbate in the solution and sorbate on the biomass surface. As time progressed, this concentration gradient was reduced due to the sorption of Cr(VI) onto the vacant sites, leading to decreased sorption rate in the later stages [22]. The increase in Cr(VI) removal with an increased initial Cr(VI) concentration is due to higher availability of Cr(VI) ions in the solution. The initial Cr(VI) concentration in the solution provides an important driving force to overcome mass transfer resistance of metal ions between the aqueous and solid phases [23].

In order to investigate the rate of biosorption and controlling mechanisms, the experimental kinetic data

Table 2
Comparison of Cr(VI) biosorption by different biomasses on the basis of maximum uptake capacity (Q_{max})

Biomass	Q_{max} (mg/g)	Refs.
Rhizoclonium hookeri	67.3	This study
Algal bloom residue-derived activated carbon	152.52	[30]
Nannochloris oculata	37.7	[31]
Acid treated *Oedogonium hatei*	35.2	[32]
Raw *Oedogonium hatei*	31.0	[32]
Prawn pong algae	29.8	[33]
Cystoseira indica—chemically modified by cross-linking with epichlorohydrin	22.7	[34]
Cystoseira indica—oxidized by potassium permanganate	20.1	[34]
Cystoseira indica—washed by distilled water	17.8	[34]

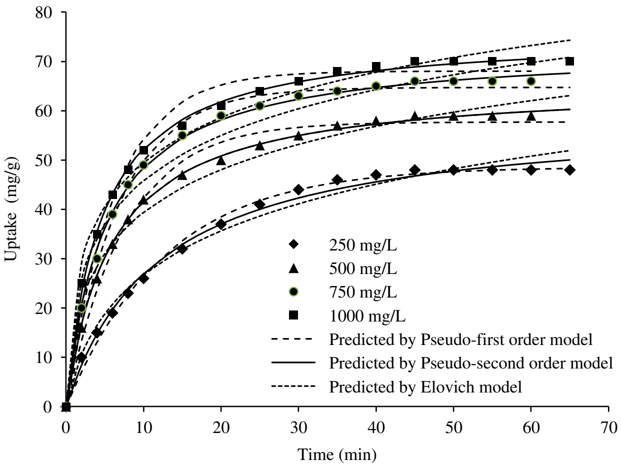


Fig. 2. Biosorption kinetics during Cr(VI) removal by *R. hookeri*.

were modelled using pseudo-first-order, pseudo-second-order and Elovich models. Table 3 represents the values of kinetic constants during sorption of Cr(VI) by *R. hookeri*. The results demonstrated that pseudo-second-order model showed the best fit among all the models (Fig. 2) with high correlation coefficients and low % error values as shown in Table 3. Even though Q_e values agrees well with the pseudo-first-order model, based on R^2 and % error values it was confirmed that pseudo-second-order model best fits the biosorption data, an indication of chemisorption mechanism.

3.5. Effect of temperature

The biosorption process of metal ions can be represented by the following reversible process which represents a heterogeneous equilibrium:

$$\text{Metal ion in solution} \leftrightarrow \text{Metal ion} - \text{Biomass}$$

The equilibrium constant (K_c) of the biosorption can be defined as:

$$K_c = Q_e/C_e \tag{9}$$

The Gibbs free energy ΔG° was determined by the following equation:

$$\Delta G^\circ = RT \ln K_c \tag{10}$$

The relationship between the equilibrium constant and the temperature is given by Van't Hoff's equation.

$$\ln K_c = \Delta S^\circ/R - \Delta H^\circ/RT \tag{11}$$

where R is the universal gas constant (8.314 J/mol/K), T the solution temperature (K), ΔS° is change in entropy (kJ/mol K) and ΔH° is change in enthalpy (kJ/mol).

The equilibrium biosorption capacity of Cr(VI) onto *R. hookeri* was favoured at higher temperatures. An increase in the temperature from 25 to 40°C leads to an increase in the biosorption capacity from 61 to 75 mg/g at an equilibrium time of 45 min. After equilibrium was attained, the uptake increased with increasing temperature. This effect may be explained by availability of more active sites of biosorbent, which is due to bond rupture at higher temperatures [24]. This suggests that biosorption between *R. hookeri* and Cr(VI) could involve a combination of chemical interaction and physical adsorption. With the increase in temperature, pores in the biomass enlarge, resulting in increased surface available for the sorption, diffusion and penetration of Cr(VI) ions within the pore of alga causing increased sorption. Also, increasing the temperature is known to increase the diffusion rate of

Table 3
Predicted kinetic parameters for removal of Cr(VI) by *R. hookeri*

		Pseudo-first-order				Pseudo-second-order				Elovich			
C_0 (mg/L)	Experimental Q_e (mg/g)	k_1 (L/min)	Q_e (mg/g)	R^2	ε (%)	$K_2 \times 10^{-3}$ (g/(mg min))	Q_e (mg/g)	R^2	ε (%)	α_E (mg/(g min))	β_E (g/mg)	R^2	ε (%)
250	48.1	0.079	48.6	0.995	2.43	1.4	59.3	0.994	0.720	7.66	0.069	0.985	1.22
500	59.0	0.132	57.7	0.989	1.36	2.6	65.7	0.996	0.603	25.8	0.077	0.981	1.49
750	66.3	0.147	64.8	0.993	1.1	2.7	72.9	0.998	0.543	38.1	0.074	0.974	1.43
1,000	70.4	0.159	68.0	0.979	1.57	2.9	75.9	0.998	0.216	52.3	0.075	0.985	0.735

adsorbate molecules within pores as a result of decreasing solution viscosity and will also modify the equilibrium capacity of the biomass for a particular adsorbate [25].

The thermodynamic parameters were evaluated and the values of ΔG° were obtained as −17.5, −22.5, −28.1 and −34.4 kJ/mol at 25, 30, 35 and 40°C, respectively. This indicates that the magnitude of ΔG° increased with an increase in temperature. The negative value of ΔG° confirmed the feasibility of the process and the spontaneous nature of sorption of Cr(VI) ions onto alga. The change in entropy and the change in enthalpy can be obtained from the slope and intercept of a Van't Hoff plot of ln (K_c) versus. $1/T$. The value of ΔH° was positive (31.28 kJ/mol), indicating that the binding of Cr(VI) ions to *R. hookeri* was endothermic. Also, the ΔS° was observed to be positive (11.25 kJ/mol K), indicating the increasing randomness at the solid/liquid interface during biosorption [26].

3.6. Characterization of the biosorbent

3.6.1. FTIR analysis

FTIR technique is an important tool to identify functional groups such as carboxyl, hydroxyl and amine which are capable of adsorbing metal ions. In order to determine the functional groups responsible for metal uptake, *R. hookeri* samples before and after adsorption of Cr(VI) were analysed using FTIR in the spectral region of 400–4,000 cm^{-1}. In Fig. 3(a), the intense broad band peak at 3,401 cm^{-1} is due to O–H carboxylic acid stretching vibration of water and alcohol [27]. Presence of water in *R. hookeri* was confirmed by its N–H amine bending vibration at 1,651 cm^{-1}. The peak at 2,924 cm^{-1} shows the presence of alkyl groups in *R. hookeri*. The peak near 1,141 cm^{-1} can be assigned to the C–H_2 bending vibrations of alkane's functional group on biomass. The alcoholic C–O stretching vibration gave peaks at 1,113 and 1,059 cm^{-1}. The peak at 712 cm^{-1} is due to alkane C–H_2 rocking vibration. The FTIR spectrum of Cr(VI) adsorbed algal biomass is shown in Fig. 3(b). The spectrum displayed similar features as that of Fig. 3(a). However, the carboxylic O–H stretching vibration at 3,401 cm^{-1} shifted to 3,373 cm^{-1} indicating that it was one of the main functional groups for biosorption. The above changes after Cr(VI) adsorption illustrate that the carboxylate, amino, alkane, alcoholic and hydroxyl groups on biosorbent are involved in the Cr(VI) binding. The analysis of the FTIR spectra showed the presence of ionizable functional groups (i.e. carboxyl, amino and

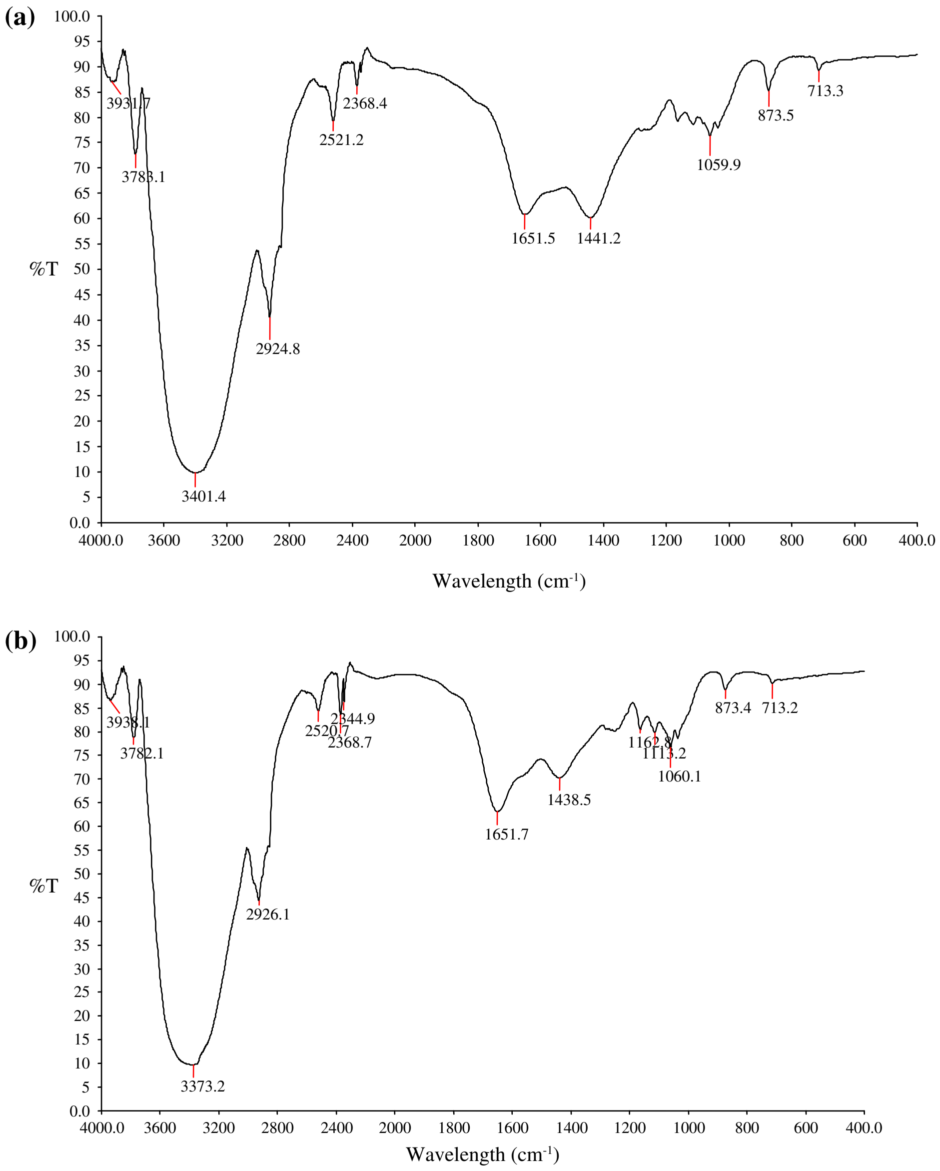
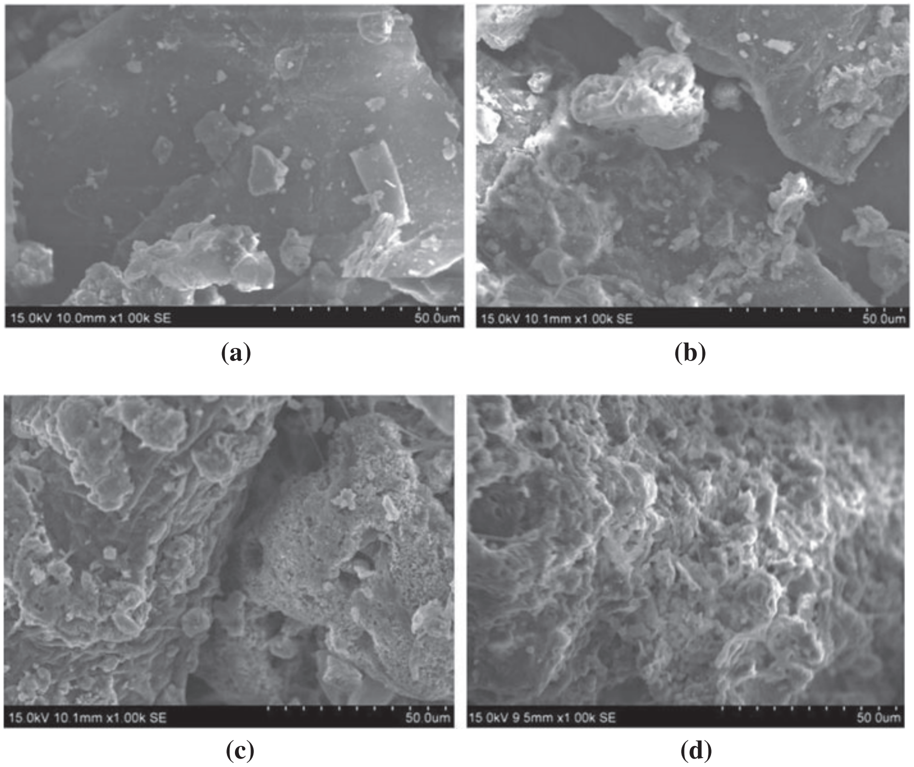


Fig. 3. FTIR spectra of (a) *R. hookeri* and (b) Cr(VI)-loaded *R. hookeri*.

hydroxyl) able to interact with protons or metal ions.

3.6.2. SEM analysis

The SEM images of *R. hookeri* examined at 100X are shown in Fig. 4. Images of raw algal biomass reveal that pores are dominant after biosorption (Fig. 4(b)) than before biosorption (Fig. 4(a)). Due to the irregular surface of the alga, the sorption of metal is possible on different parts of the surface. Fig. 4(c) indicates pores of different sizes and shapes in protonated algal biomass. This increases the surface area of biosorption. The presence of excessive pores indicates that intra particle diffusion could also be the mechanism of biosorption [28]. Fig. 4(d) shows the SEM images of Cr(VI)-loaded *R. hookeri* biomass. Surface protuberances and microstructures were observed more here compared with protonated biomass before biosorption. Increase in pores increases sorption capacity of biomass. After completion of the metal binding, obvious morphological changes were seen in the cell wall matrix, such as shrinking and sticking of layers [29].



(a) **(b)**

(c) **(d)**

Fig. 4. SEM images of *R. hookeri* (a) raw biomass before biosorption, (b) raw biomass after biosorption, (c) protonated biomass before biosorption and (d) protonated biomass after biosorption.

4. Conclusion

The present study examined a novel alga, *R. hookeri*, for biosorption of Cr(VI) from aqueous solutions. Based on the experimental results of this work, the following conclusions can be drawn.

- It was found that the maximum biosorption capacity of 67.3 mg/g was observed at pH 2 with contact time of 45 min and 0.7 mm particle size.
- The pseudo-second-order model best describes the kinetics and the Sips model best fits the equilibrium data for the biosorption of Cr(VI) ions.
- Observed negative values of ΔG° and positive value of ΔH° indicate the spontaneous and endothermic nature of Cr(VI) biosorption onto *R. hookeri.*
- The FTIR carboxylic O–H stretching vibration shift in 3,401–3,373 cm^{-1} show that it was one of the main functional groups for biosorption. SEM analysis shows that the mechanism of biosorption may be due to intra particle diffusion.
- The proposed biosorption process is economically cheaper, easy to operate, efficient, environment-friendly and can reduce the huge amount of indiscriminate chromium effluent discharges from the industries. One common concern about the practical application of the biosorption technology is the ultimate fate of used biosorbents. Considering that *R. hookeri* is abundantly available causing nuisance to the local community, regeneration of biomass may not be economically feasible. Thus, chromium-loaded algal biomass can be incinerated and disposed in secured landfills. The combustion process usually yields ash with a high concentration of the desired metal.

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