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Biosorption of total chromium from aqueous solution by red algae (*Ceramium virgatum*): Equilibrium, kinetic and thermodynamic studies

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ABSTRACT

This study focused on the biosorption of total chromium onto red algae (*Ceramium virgatum*) biomass from aqueous solution. Experimental parameters affecting biosorption process such as pH, contact time, biomass dosage and temperature were studied. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherms. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The biosorption capacity of *C. virgatum* biomass for total chromium was found to be 26.5 mg/g at pH 1.5 and 10 g/L biomass dosage, 90 min equilibrium time and 20 °C. From the D–R isotherm model, the mean free energy was calculated as 9.7 kJ/mol, indicating that the biosorption of total chromium was taken place by chemisorption. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the biosorption of total chromium onto *C. virgatum* biomass was feasible, spontaneous and exothermic at 20–50 °C. Kinetic evaluation of experimental data showed that the biosorption processes of total chromium followed well pseudo-second-order kinetics.

1. Introduction

The presence of toxic heavy metals contaminated in aqueous streams, arising from the discharge of untreated metal containing effluent into water bodies, is one of the most important environmental issues [1]. Their presence in aquatic ecosystem causes harmful effect to living organisms [2].

Chromium(VI) is one such metal known to be carcinogenic and has an adverse potential to modify the DNA transcription process. It is also reported to cause epigastric pain, nausea, vomiting, severe diarrhea and hemorrhage [3]. It is reported that, chromate (CrO_4^{-2}) is the prevalent species of Cr (VI) in natural aqueous environments, and is the major pollutant from chromium related industries such as mining, iron sheet cleaning, chrome plating, leather tanning and wood preservation [4–6]. Therefore, the reduction of amount of this metal from such effluents to a permissible limit before discharging them into streams and rivers is very important for human health and environment. In this regard, several conventional wastewater treatment technologies such as ion exchange, chemical precipitation, evaporation, membrane filtration, reverse osmosis, electrodialysis and adsorption were developed and are used successfully [7–10]. Application of such traditional treatment techniques needs enormous cost and continuous input of chemicals which becomes impracticable and uneconomical and causes further environment damage [11]. On the other hand, biosorption is an emerging technology for removal of heavy metals from industrial wastewater [12]. The major advantages of this technique are the reusability of biomaterial, low operating cost, improved selectivity for specific 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 [13,14].

Marine algae otherwise known as seaweeds are extremely efficient biosorbents with the ability to bind various metals from aqueous effluents because of their cheap availability both in fresh and saltwater, relatively high surface area and high binding affinity [15–17]. Numerous chemical groups may be responsible for metal biosorption by seaweeds, e.g. carboxyl, sulphonate, hydroxyl and amino [18–20].

Ceramium virgatum as known red algae colonizes rock and algal habitats from the midshore in rockpools to the open shore near to low water level and in the shallow subtidal. *C. virgatum* is widespread along the shores of Turkey, grows well along the Black Sea coasts [21]. Different species of algal biomasses (brown, green and red) have been used for the removal of heavy metals from aqueous solution [22–27]. However, according to authors' survey, there is no extensive study on the biosorption of total chromium using *C. virgatum* in literature. In addition, this new material was chosen as biosorbent in this study due to being of its natural, renewable and thus cost-effective biomass.

The present work aims to investigate the biosorption potential of *C. virgatum* for removal of total chromium from aqueous solution. Experimental parameters affecting biosorption process such

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as pH, contact time, biomass dosage and temperature were studied. The equilibrium biosorption data were evaluated by Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models. The biosorption mechanism was also investigated in terms of thermodynamics and kinetics.

2. Experimental procedures

2.1. Biomass preparation

The red alga (*C. virgatum*) was used as biosorbent for the biosorption of total chromium. Samples of the biomass were collected from the East Black Sea coast of Turkey. Samples were washed several times using deionized water to remove extraneous and salts. They were then dried in an oven at 60 °C for 48 h. The dried algae biomass was chopped, sieved and the particles with an average size of 0.5 mm were used for biosorption experiments.

2.2. Reagents and equipments

All chemicals used in this work, were of analytical reagent grade and were used without further purification. A PerkinElmer AAnalyst 700 flame atomic absorption spectrometer with deuterium background corrector was used.

2.3. Batch biosorption procedure

Biosorption experiments were carried out at the optimum pH value, contact time and adsorbent dosage level using the necessary adsorbent in a 100 mL stoppered conical flask containing 25 mL of test solution. Total chromium stock solutions were prepared from $K_2Cr_2O_7$. 0.1 and 0.03 mol/L HCl were used for pH 1 and 1.5, respectively. Sodium phosphate buffers (0.1 mol/L) were prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to obtain solutions of pH 2–3. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to obtain solutions of pH 4–6. Ammonium chloride buffer solutions (0.1 mol/L) were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions to obtain solutions of pH 8.

Necessary amount of the biomass was then added and contents in the flask were shaken for the desired contact time in an electrically thermostatic reciprocating shaker at 100 rpm. The experiments were repeated at 20, 30, 40 and 50 °C. The time required for reaching the equilibrium condition was estimated by drawing samples at regular intervals of time till equilibrium was reached. The contents of the flask were filtered through filter paper and the filtrate was analyzed for metal concentration by flame AAS. The percent biosorption of metal ion was calculated as follows:

$$\text{Biosorption}\,(\%) = \left[\frac{C_i - C_f}{C_i}\right] \times 100 \quad (1)$$

where C_i and C_f are the initial and final metal ion concentrations, respectively. Biosorption experiments for investigating the effect of pH were conducted by using a solution having 10 mg/L of total chromium concentration with a biomass dosage of 10 g/L. Throughout the study, the contact time was varied from 10 to 150 min, the pH from 1 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 0.4 to 40 g/L.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectra of unloaded biomass, total chromium loaded biomass were taken to obtain information on the nature of possible interactions between the functional groups of *C. virgatum* biomass and the metal ions and is presented in Fig. 1. The broad and strong band at 3367 cm^{-1} may be due to the overlapping of O–H and N–H stretching vibration. The band at 2921 cm^{-1} is assigned to the –CH stretch. The bands peaks at 1639 and 1471 cm^{-1} may be attributed to asymmetric and symmetric stretching vibration of C=O groups. The bands at 1251 and 1079 cm^{-1} assign to stretching of C–O groups on the biomass surface. Some bands in the fingerprint region could be attributed to the phosphate groups. After total chromium biosorption, the bands observed at 1471, 1251 and 1079 cm^{-1} were shifted to 1468, 1241 and 1025 cm^{-1}. The significant changes in the wave numbers of these specific peaks suggested that amido, hydroxy, C=O and C–O groups could be involved in the biosorption of total chromium onto *C. virgatum*. The similar results were reported for the biosorption of different heavy metals on various algae species [22,26,28].

3.2. Effect of pH

One of the important factors affecting adsorption of metal ions is acidity of solution. Solution pH affects the cell wall metal binding sites and the metal ion chemistry in water. Various authors [29,30] have shown that solution pH greatly influences metal biosorption by algae biomass. The effect of pH on the removal efficiency of total chromium onto *C. virgatum* was studied by changing pH values in the range of 1–8 and the results were presented in Fig. 2. From this figure it is clear that the percent removal of total chromium is maximum for all the concentrations at pH 1.5 and thereafter decreases with further increase in pH.

Generally, metal biosorption involves complex mechanisms of ion exchange, chelation, adsorption by physical forces and ion entrapment in inter- and intra-fibrillar capillaries and spaces of the cell structural network of a biosorbent [31,32]. The FT-IR spectroscopic analysis showed that the moss biomass has a variety of functional groups, such as carboxyl, hydroxyl and amine and these groups are involved in almost all potential binding mechanisms. Moreover, depending on the pH value of the aqueous solution, these functional groups participate in metal ion bindings.

Biosorption of total chromium varies as a function of pH, with H_2CrO_4, $HCrO_4^-$, $Cr_2O_7^{2-}$, CrO_4^{2-} and Cr^{3+} ions present as dominant species. At pH 1–2, $HCrO_4^-$ was the dominant species [33].

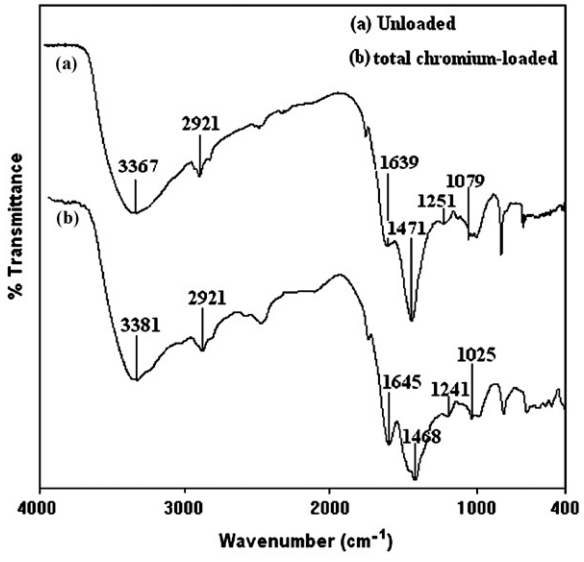

Fig. 1. FT-IR spectrum of unloaded and total chromium-loaded biomass.

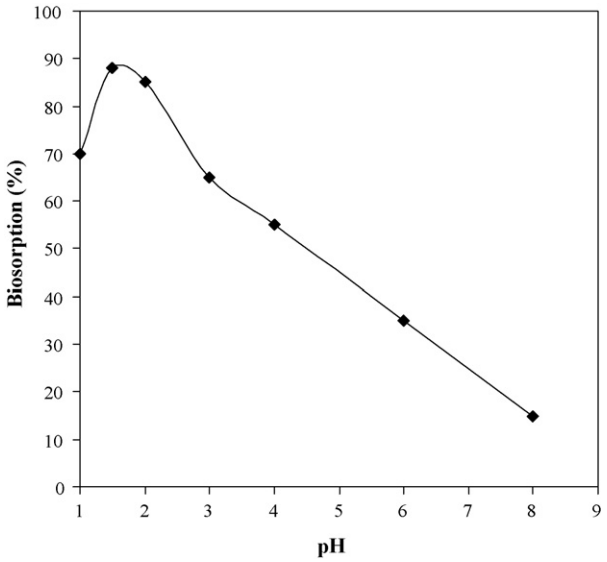

Fig. 2. Effect of pH (metal concentration:10 mg/L; temperature: 20 °C).

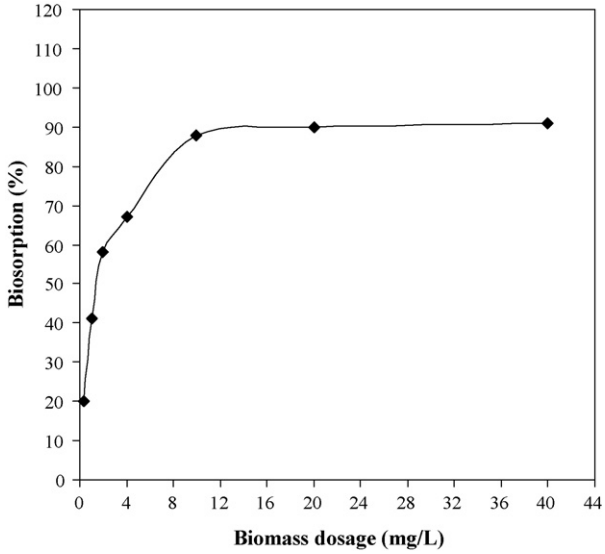

Fig. 3. Effect of biomass dosage (metal concentration, 10 mg/L; pH, 1.5; temperature, 20 °C).

The surface charge of *C. virgatum* should be positive at low pH, and this should promote the binding of the negatively charged $HCrO_4^-$ ions. The $HCrO_4^-$ species are most easily exchanged with OH^- ions at active surfaces under acidic conditions. In the pH 3–5 range the sorption capacity decreased with increasing pH, because the coordination bonds between metal ions and phenolic hydroxyl functional groups and other ion exchangeable moieties on the biomass surface are rather weak in the slightly acidic solution (i.e. pH 3.5–5.0) [34]. Moreover, decrease in biosorption at higher pH (pH > 5) is not only related the formation of soluble hydroxilated complexes of the metal ions but also to the ionized nature of the cell wall surface of the biomass under the studied pH.

3.3. Effect of biomass dosage

The effect of biomass dosage on the biosorption of total chromium was studied using different biomass dosage in the range, 0.4–40 g/L (Fig. 3). Results showed that the biosorption efficiency is highly dependent on the increase in biomass dosage of the solution. This is expected because the higher dose of adsorbent in the solution, the greater availability of exchangeable sites for the ions. The maximum biosorption yield (90%) was attained at about biomass dosage, 10 g/L and was almost same at higher dosages. The decrease in biosorption efficiency at higher biomass concentration could be explained as a consequence of a partial aggregation of biomass, which results in a decrease in effective surface area for the biosorption [35]. Therefore, the optimum biomass dosage was selected as 10 g/L for further experiments.

3.4. Effects of contact time and temperature

The contact time was evaluated as one of the most important factors affecting the biosorption efficiency. Fig. 4 shows the biosorption efficiency as a function of contact time and temperature. The biosorption efficiency increases with rise in contact time up to 90 min at 20–50 °C and after then it is almost constant. Therefore, the optimum contact time was selected as 90 min for further experiments.

On the other hand, the biosorption yield decreased from 90 to 78% for total chromium with increasing temperature from 20 to 50 °C during a 90-min contact time. This result indicated the exothermic nature of total chromium biosorption onto *C. virgatum*. This decreasing in biosorption efficiency may be attributed to many parameters: the relative increase in the escaping tendency of the chromium ions from the solid phase to the bulk phase; deactivating the biosorbent surface or destructing some active sites on the biosorbent surface due to bond ruptures [36,37] or due to the weakness of biosorptive forces between the active sites of the sorbents and the sorbate species and also between the adjacent molecules of sorbed phase [38]. The results are in agreement with the thermodynamics point of view.

3.5. Biosorption isotherm models

The capacity of a biomass can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the biomass [39]. In this study, three important sorption isotherm models were selected to fit experimental data, which are namely Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models.

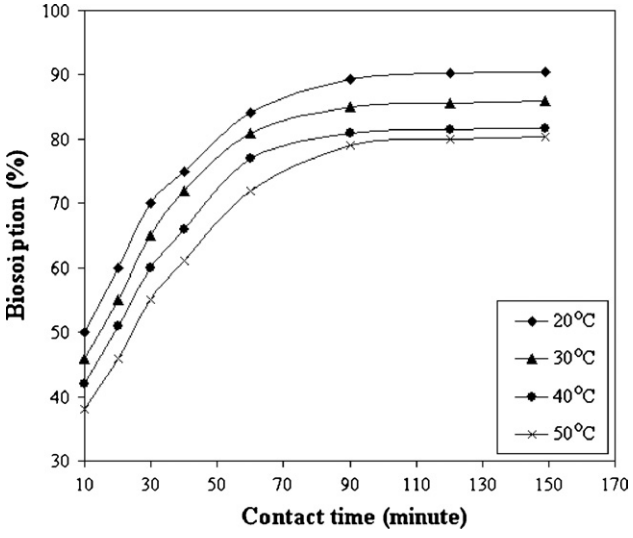

Fig. 4. Effect of contact time and temperature (metal concentration, 10 mg/L; biomass dosage, 10 g/L; pH 1.5).

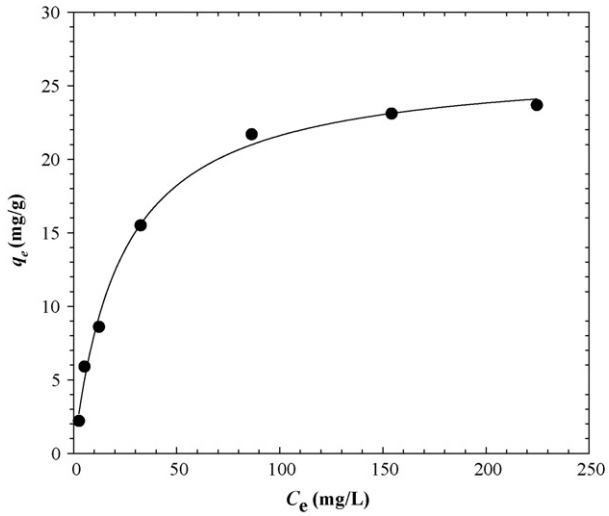

Fig. 5. Langmuir isotherm plots for biosorption of total chromium onto *Ceramium virgatum* (biomass dosage, 10 g/L; contact time, 90 min; pH 1.5; temperature, 20 °C).

The Langmuir model assumes that the uptake of metal ions on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. Langmuir isotherm can be defined according to the following formula [40]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), q_m is the monolayer biosorption capacity of the adsorbent (mg/g) and K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption.

Fig. 5 indicates the non-linear relationship between the amount (mg) of total chromium sorbed per unit mass (g) of *C. virgatum* biomass against the concentration of total chromium remaining in solution (mg/L). The coefficients of determination (R^2) were found to be 0.995 for total chromium biosorption, indicating that the biosorption of the metal ions onto *C. virgatum* fitted well the Langmuir model. In other words, the sorption of metal ions onto *C. virgatum* was taken place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption.

The K_L value was found as 4.4×10^{-2} L/mg and the maximum biosorption capacity (q_m) was found to be 26.5 mg/g. As also seen in Table 1, in order to indicate the biosorption potential of *C. virgatum* for total chromium, q_m value is compared with other biosorbents reported in the literature [7,41–47]. The biosorption capacity of *C. virgatum* biomass for total chromium is higher than that of the majority of the biomasses. Therefore, it can be noteworthy that the *C. virgatum* has considerable potential for the removal of total chromium from aqueous solution.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained as follows [48]:

$$q_e = K_f C_e^{1/n} \quad (3)$$

where K_f is a constant relating the biosorption capacity and $1/n$ is an empirical parameter relating the biosorption intensity, which varies with the heterogeneity of the material.

Fig. 6 shows the Freundlich isotherms obtained by fitting equilibrium data to Eq. (3). The values of K_f and $1/n$ were found to be 3.8 and 0.4, respectively. The $1/n$ values were between 0 and 1, indicating that the biosorption of total chromium onto *C. virgatum* was favorable at studied conditions. However, compared to the R^2 values, 0.931 with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir isotherm model is better fitted the equilibrium data.

Table 1
Comparison of biosorption capacity of *Ceramium virgatum* for total chromium with that of various sorbents

Sorbent	pH	q_m (mg/g)	Reference
Neurospora crassa (acetic acid pretreated)	1	15.8	[7]
Brown coal	3	50.9	[41]
Pseudomonas sp.	1	95.0	[42]
Staphylococcus xylosus	1	143.0	[42]
Activated bentonite	5	91.7	[43]
Hazelnut shell ash (1 mm)	3	195.2	[43]
Olive oil industry waste	2	13.9	[44]
Fucus vesiculosus (brown algae)	2	42.7	[45]
Fucus spiralis (brown algae)	2	5.4	[45]
Ulva lactuca (green algae)	2	27.6	[45]
Ulva spp. (green algae)	2	30.2	[45]
Palmaria palmate (red algae)	2	33.8	[45]
Polysiphonia lanosa (red algae)	2	45.8	[45]
Saccharomyces cerevisiae	1	32.6	[46]
Alternanthera philoxeroides	2	17.7	[47]
C. virgatum (red algae)	1.5	26.5	Present study

The equilibrium data were also applied to the D–R isotherm model to determine the nature of biosorption processes as physical or chemical. The linear form of the D–R isotherm equation [49] shown in the following equation:

$$\ln\ q_e = \ln\ q_m - \beta\varepsilon^2 \quad (4)$$

where q_e is the amount of metal ions adsorbed on per unit weight of biomass (mol/L), q_m is the maximum biosorption capacity (mol/g), β is the activity coefficient related to mean biosorption energy (mol^2/J^2) and ε is the Polanyi potential ($\varepsilon = RT\ln(1 + 1/C_e)$).

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to 0.990 (Fig. 7). From the intercept of the plots, the q_m value was found to be 1.4×10^{-3} mol/g. The mean biosorption energy (E; kJ/mol) is as follows:

$$E = \frac{1}{\sqrt{-2\beta}} \quad (5)$$

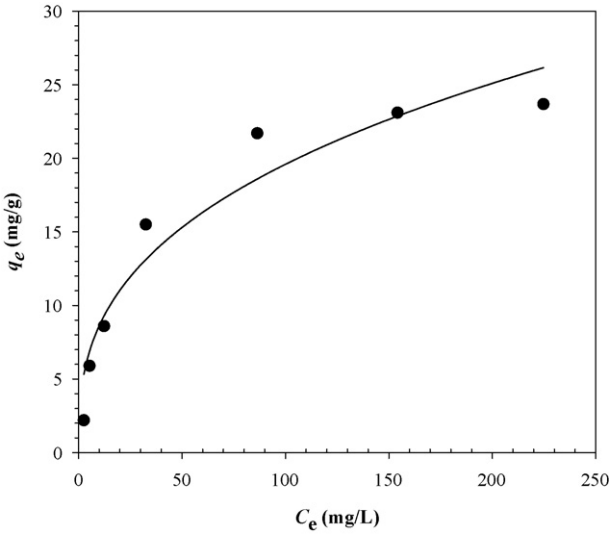

Fig. 6. Freundlich isotherm plots for biosorption of total chromium onto *C. virgatum* (biomass dosage, 10 g/L; contact time, 90 min; pH 1.5; temperature, 20 °C).

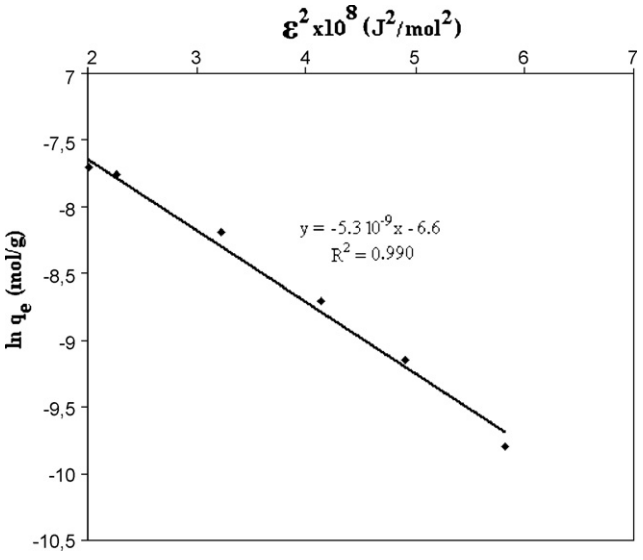

Fig. 7. D–R isotherm plots for biosorption of total chromium onto *C. virgatum* (pH 1.5; biomass dosage, 10 g/L; contact time, 90 min; temperature, 20 °C).

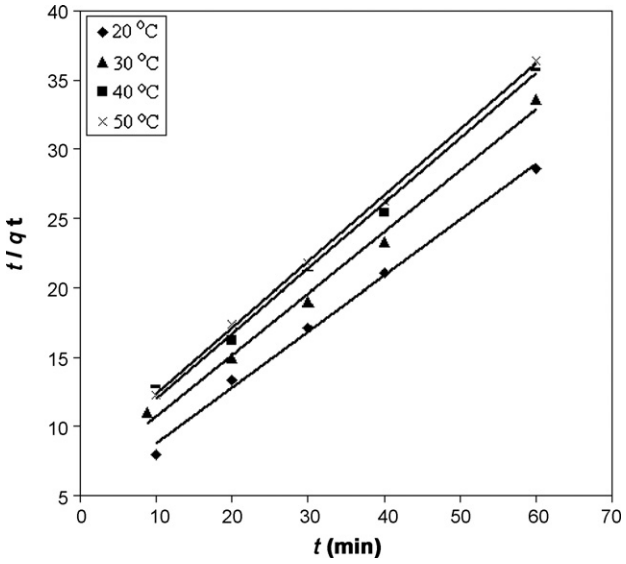

Fig. 8. Pseudo-second-order kinetic plots at different temperatures.

The mean free energy of biosorption gives information about biosorption mechanism, physical or chemical. If E value lies between 8 and 16 kJ/mol, the biosorption process takes place chemically and while $E < 8$ kJ/mol the biosorption process is physically [28]. The mean biosorption energy was calculated as 9.7 kJ/mol and indicated that the biosorption of total chromium onto *C. virgatum* may be proceeded by binding surface functional groups. This result is also confirmed by FT-IR spectroscopy and thermodynamic results.

3.6. Biosorption kinetics

Kinetics is one of the major parameters to evaluate biosorption dynamics and the kinetic constants can be used to optimize the residence time of a biosorption process. In order to examine the controlling mechanism of the biosorption process, kinetic models are used to test the experimental data. In this study, the equilibrium data were analyzed using two simplest kinetic models, pseudo-first-order and pseudo-second-order model.

The linear form of the pseudo-first-order rate equation [50] is given as

$$\ln(q_e - q_t) = \ln\ q_e - k_1 t \tag{6}$$

where q_t and q_e (mg/g) are the amounts of the metal ions sorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}). The biosorption rate constants (k_1) can be determined experimentally by plotting of $\ln(q_e - q_t)$ versus t.

The plots of $\ln(q_e - q_t)$ versus t for the pseudo-first-order model were not shown as figure because the R^2 values are found to be low (R^2 = 0.932–0.981, as seen in Table 2). Based on these results it can be concluded that the biosorption of total chromium onto *C. virgatum* does not fit a pseudo-first-order kinetic model. Moreover, from Table 2, it can be seen that the experimental values of $q_{e,exp}$ are not in good agreement with the theoretical values calculated ($q_{e1,cal}$) from Eq. (6). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of total chromium onto *C. virgatum*. Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [51]:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{t}{q_e}\right) \tag{7}$$

where k_2 (g/mg min) is the rate constant of the second-order equation, q_t (mg/g) is the amount of biosorption time t (min) and q_e is the amount of biosorption equilibrium (mg/g).

This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step [51]. The linear plots of t/qt versus t for the pseudo-second-order model at 20–50 °C were shown in Fig. 8. The R^2 values are very high (0.993–0.999) as seen in Table 2. In addition, the theoretical $q_{e2,cal}$ values are closer to the experimental $q_{e,exp}$ values. In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the biosorption of total chromium onto *C. virgatum* in contrast to the pseudo-first-order model. This conclusion is in agreement with literature [52,53].

3.7. Biosorption thermodynamics

Thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were used to describe thermodynamic behaviour of the biosorption of total chromium onto *C. virgatum*. These parameters were calculated from following

Table 2
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order for total chromium bisorption onto *C. virgatum* at different temperatures

Temperature (°C)	Pseudo-first-order				Pseudo-second-order		
	$q_{e,exp}$ (mg/g)	k_1 (min^{-1})	$q_{e1,cal}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{e2,cal}$ (mg/g)	R^2
20	2.2	3.5×10^{-2}	1.4	0.981	2.4	3.5	0.995
30	2.1	3.2×10^{-2}	1.1	0.962	2.2	3.2	0.998
40	2.0	2.0×10^{-2}	1.0	0.932	2.1	3.0	0.997
50	1.9	1.8×10^{-2}	0.9	0.954	2.0	2.9	0.998

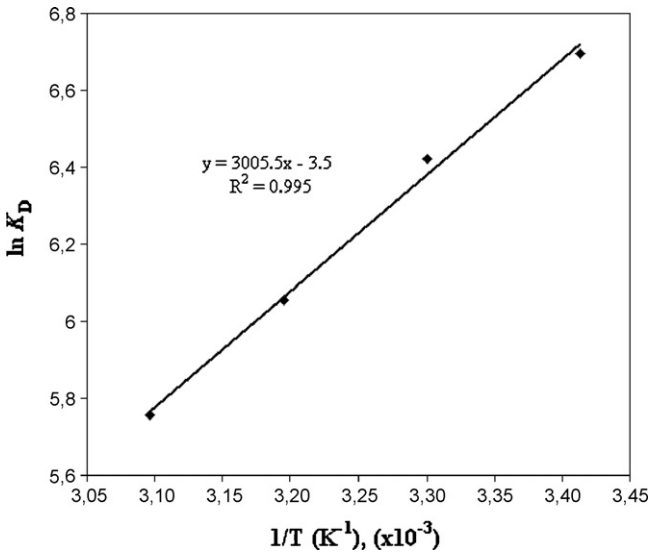

Fig. 9. Plot of ln K_D vs. 1/T for the estimation of thermodynamic parameters for biosorption of total chromium onto *C. virgatum*.

equations:

$$\Delta G^\circ = -RT \ \ln \ K_D \tag{8}$$

where R is the universal gas constant (8.314 J/mol K), T is temperature (K) and K_D (q_e/C_e) is the distribution coefficient.

By considering Eq. (9), the enthalpy (ΔH°) and entropy (ΔS°) of biosorption were estimated from the slope and intercept of the plot of ln K_D versus $1/T$ yields, respectively (Fig. 9).

$$\ln \ K_D = \left(\frac{\Delta S^\circ}{T}\right) - \left(\frac{\Delta H^\circ}{RT}\right) \tag{9}$$

The free energy change (ΔG°) was calculated to be −16.3, −16.1, −15.8 and −15.5 kJ/mol for the biosorption of total chromium at 20, 30, 40 and 50 °C, respectively. The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG° values with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures. The enthalpy of biosorption (ΔH°) was found to be −24.9 kJ/mol. The negative ΔH° is indicator of exothermic nature of the biosorption and also its magnitude gives information on the type of biosorption, which can be either physical or chemical. The enthalpy or heat of biosorption, ranging from 0.5 to 5 kcal/mol (2.1–20.9 kJ/mol) corresponds a physical sorption as it ranges from 20.9 to 418.4 kJ/mol in case of a chemical sorption [54]. The biosorption heat falls into the heat range of chemisorption. Therefore, the ΔH° values showed that the biosorption process of total chromium onto *C. virgatum* were taken place via chemisorption. The energy value obtained from the D–R model also confirms this result. The ΔS° parameter was found to be −29.4 J/mol K for total chromium biosorption. The negative ΔS° value suggests a decrease in the randomness at the solid/solution interface during the biosorption of total chromium onto *C. virgatum*.

4. Conclusions

This study focused on the biosorption of total chromium onto *C. virgatum* algal biomass from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time and temperature, were effective on the biosorption efficiency of total chromium. Biosorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The biosorption capacity of *C. virgatum* for total chromium was found to be 26.5 mg/g at pH 1.5 and 10 g/L biomass dosage, 90 min equilibrium time and 20 °C. From the D–R model, the mean energy was determined as 9.7 kJ/mol, indicating that the biosorption of total chromium onto *C. virgatum* may be carried out by chemisorption. Kinetic examination of the equilibrium data showed that the biosorption of total chromium ions onto *C. virgatum* followed well the pseudo-second-order kinetic model. The thermodynamic calculations indicated the feasibility, exothermic and spontaneous nature of the biosorption process at 20–50 °C. Based on all results, it can be also concluded that the *C. virgatum* is an effective and alternative biomass for the removal of total chromium from an aqueous solution because of its considerable biosorption capacity, being of its natural, renewable and thus cost-effective biomass.

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