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

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Abstract

The biosorption characteristics of Cd(II) ions using the red alga (*Ceramium virgatum*) were investigated. Experimental parameters affecting the 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. The biosorption capacity of *C. virgatum* biomass for Cd(II) ions was found to be 39.7 mg/g. From the D–R isotherm model, the mean free energy was calculated as 12.7 kJ/mol, indicating that the biosorption of Cd(II) the metal ions was taken place by chemisorption. The calculated thermodynamic parameters (ΔG°, ΔH° and ΔS°) showed that the biosorption of Cd(II) ions onto *C. virgatum* was feasible, spontaneous and exothermic at 293–323 K. Evaluation of experimental data in terms of biosorption kinetics showed that the biosorption of Cd(II) *C. virgatum* followed well pseudo-second-order kinetics.
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Keywords: *Ceramium virgatum*; Cadmium(II); Biosorption; Thermodynamics; Kinetics

1. Introduction

Heavy metal pollution has become a major issue throughout many countries because the heavy metal content in drinking waters and wastewaters often exceed the permissible standards. Many industrial activities such as metal plating, fertilizer industry, mining operations, and textile reveal heavy metals to environment via their waste effluents [1,2]. Cadmium toxicity may be observed by a variety of syndromes and effects including renal dysfunction, hypertension, hepatic injury, lung damage and teratogenic effects [3–5]. Therefore, cadmium level in wastewater, drinking water, and water used for agriculture should be reduced to the maximum permissible concentration (0.01 mg/L) [6]. Several methods have been applied over the years on the elimination of Cd(II) present in industrial wastewaters and soils. The usual methods for removal of heavy metal ions from aqueous solutions can be ordered as chemical precipitation, ion exchange, solvent extraction, phytoextraction, ultrafiltration, reverse osmosis, electrodialysis, and adsorption [7,8]. However,

technical or economic factors limit sometimes the feasibility of such processes.

Biosorption is an emerging technology for the removal heavy metals from industrial wastewater. The major advantages of the biosorption technology are its effectiveness in reducing the concentration of heavy metal ions to very low levels and the use of inexpensive biosorbent materials such as naturally abundant algae or by products of fermentation industries as biosorbents [9–11].

Marine algae otherwise known as seaweeds have been found to be potentially suitable biosorbents because of their cheap availability both in fresh and saltwater, relatively high surface area and high-binding affinity [12]. Biosorption in algae has mainly been attributed the cell wall structure containing functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals via both electrostatic attraction and complexation [13,14].

Ceramium virgatum is both epilithic and epiphytic, often growing on the stipes and fronds of *Fucus* spp., *C. virgatum* 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 [15].

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Different species of algal biomasses (brown, green and red) have been used for the removal of heavy metals from aqueous solution [2,16–20]. However, according to authors' survey, there is no extensive study on the biosorption of Cd(II) using *C. virgatum* as red algae 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 focused on the investigation of potential of *C. virgatum* biomass for removal of Cd(II) ions from aqueous solution. Experimental parameters affecting the biosorption process such 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 Cd(II) ions. 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 333 K 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. All measurements were carried out in an air/acetylene flame.

2.3. Batch biosorption procedure

Biosorption experiments were carried out at the desired pH value, contact time and biomass dosage level using the necessary biomass in a 100 mL stoppered conical flask containing 25 mL of test solution. Initial solutions with different concentration of Cd(II) were prepared by proper dilution from stock 1000 mg/L Cd(II) standards. Sodium phosphate buffer (0.1 mol/L) was prepared by adding an appropriate amount of phosphoric acid to sodium dihydrogen phosphate solution to result in a solution of pH 2. Ammonium acetate buffers (0.1 mol/L) were prepared by adding an appropriate amount of acetic acid to ammonium acetate solutions to result in 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 result in 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 293, 303, 313, and 323 K. The time required for reaching the equilibrium condition 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 using flame AAS. The percent biosorption of metal ion was calculated as follows

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

where C_i and C_f are the initial and final metal ion concentrations, respectively. Biosorption experiments for the effect of pH were conducted by using a solution having 10 mg/L of Cd(II) concentration with a biomass dosage of 10 g/L. Throughout the study, the contact time was varied from 2.5 to 120 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 1 to 40 g/L.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectra of unloaded biomass, Cd(II)-loaded biomass were taken to obtain information on the nature of possible interactions between the functional groups of *C. virgatum* 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 2924 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 Cd(II) biosorption, the bands observed at 3367, 1639, 1471, 1251, and 1079 cm^{-1} were shifted to 3376, 1629,
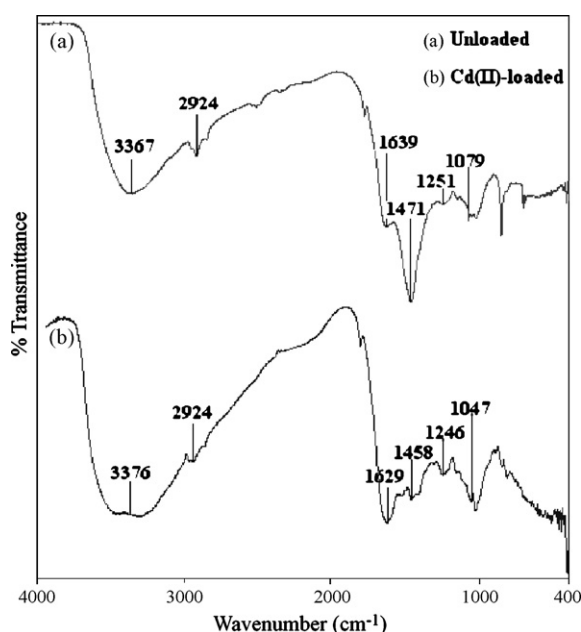

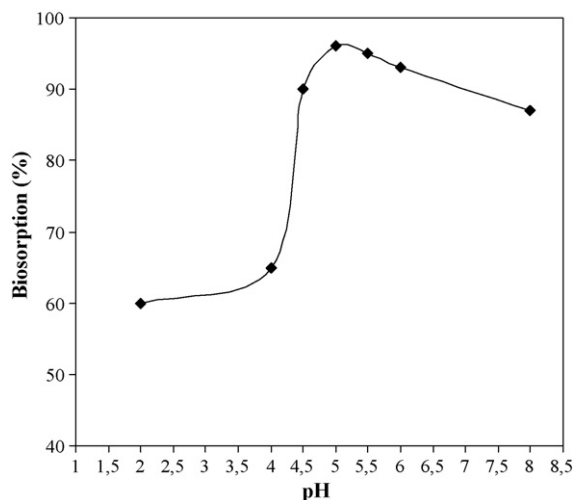Fig. 1. FT-IR spectrum of unloaded and Cd(II)-loaded biomass.

Fig. 2. Effect of pH (metal concentration 10 mg/L; temperature 293 K).

Fig. 3. Effect of biomass dosage (metal concentration 10 mg/L; pH 5; temperature 293 K).

1458, 1246 and 1047 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 Cd(II) onto *C. virgatum*. The similar results was reported for the biosorption of different heavy metals on various species of algae [4,16,21].

3.2. Effect of pH

The pH parameter plays an important role for the biosorption process of heavy metal ions from aqueous solution. Algal biomasses contain high content of carboxyl groups from mannuronic and gururonic acids on the cell wall polysaccharides, which suggests that the biosorption process could be affected by changes in the solution pH [22]. To examine the effect of pH on the cadmium ions removal efficiency, several experiments were performed at different pH ranges from 2 to 8 as shown in Fig. 2. The high biosorption efficiency was obtained as 90, 96, and 94% at pH 4.5, 5, and 5.5. All the biosorption experiments were carried out at pH 5 because the maximum efficiency was obtained as 96% at this pH value. At higher pH values, the biosorption yield for Cd(II) was dramatically decreased. At pH range 2–4, the poor biosorption of Cd(II) in the low pH range could be due to competition with the H$^+$ ions for metal binding sites on the algal cell. While increase in pH, the biosorption of the Cd(II) with positive charge was reached maximum. The decrease in the biosorption efficiency at higher pH (6–8) values may be attributed to the formation of anionic hydroxide complexes and their competition with the active sites [23,24].

3.3. Effect of biomass dosage

The effect of biomass dosage on the biosorption of Cd(II) ions was studied using different biomass dosage in the range, 1–40 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
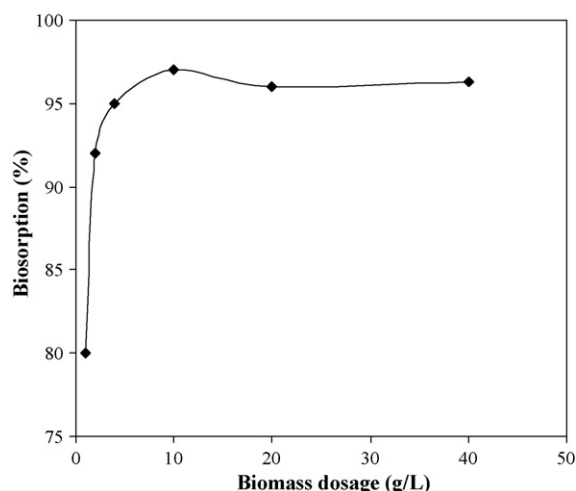
for the ions. The maximum biosorption of the metal ions was attained at about biomass dosage, 10 g/L and was almost same at higher dosages. The decrease in biosorption efficiency at higher biomass concentration could be explained as a consequence of a partial aggregation of biomass, which results in a decrease in effective surface area for the biosorption [11]. 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 also evaluated as one of the most important factors affecting the biosorption efficiency. Fig. 4 shows the biosorption efficiency of Cd(II) ions by *C. virgatum* as a function of contact time and temperature. The biosorption efficiency increases with rise in contact time up to 60 min at 293–323 K and after then it is almost constant. Therefore, the optimum contact time was selected as 60 min for further experiments.

On the other hand, the biosorption yield decreased from 97 to 87% for Cd(II) ion with increasing temperature from 293
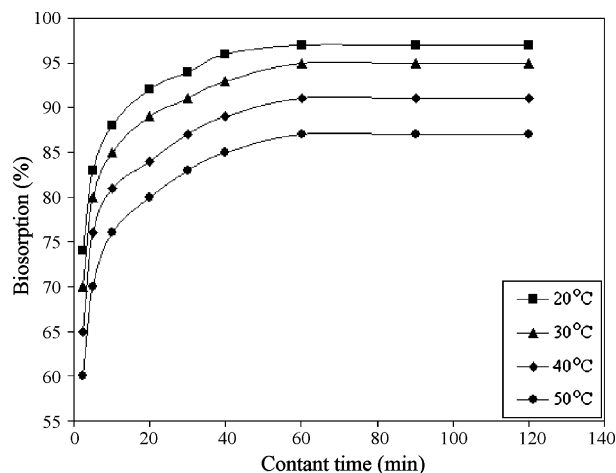

Fig. 4. Effect of contact time and temperature (metal concentration 10 mg/L; biomass dosage 10 g/L; pH 5).

to 323 K during a 60-min contact time. This result indicated the exothermic nature of Cd(II) biosorption onto *C. virgatum*. This decreasing in biosorption efficiency may be attributed to many parameters: the relative increase in the escaping tendency of the cadmium 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 [25]; 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 [26]. Our results are in agreement with the thermodynamics point of view.

3.5. Biosorption isotherm models

A biosorption isotherm is characterized by certain constant values, which express the surface properties and affinity of the biosorbent and can also be used to compare the biosorptive capacities of the biosorbent for different pollutants [27]. 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. Langmuir isotherm models the single coating layer on sorption surface. This model supposes that the sorption process takes place at a specific sorption surface. The attraction between molecules decreases as getting further from the sorption surface. Langmuir isotherm can be defined according to the following equation [28]:

$$\frac{C_e}{q_e} = \left(\frac{C_e}{q_m}\right) + \left(\frac{1}{K_L q_m}\right) \qquad (2)$$

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 linear relationship between the amount (mg) of Cd(II) ions sorbed per unit mass (g) of *C. virgatum* against the concentration of Cd(II) ions remaining in solution

(mg/L). The correlation coefficient (R^2) were found to be 0.992 for Cd(II) biosorption. The high R^2 values indicated that the equilibrium data well fitted to 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 5.4×10^{-3} L/mg for Cd(II) ion. The maximum biosorption capacity (q_m) was found to be 39.7 mg/g for Cd(II) ion. Our experimental data of values q_m are compared with other biosorbents in order to validate *C. virgatum* as a suitable adsorbent for Cd(II) ions biosorption. Table 1 shows the q_m value for the biosorption of Cd(II) ions on different algae species and other biomasses in the literature. The biosorption capacity of *C. virgatum* biomass for Cd(II) is higher than that of the majority of the biomasses given in this table. Therefore, it can be noteworthy that the *C. virgatum* has considerable potential for the removal of Cd(II) ions from aqueous solution.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. This isotherm can be explained as follows [29]:

$$\log q_e = \log K_F + \left(\frac{1}{n}\right) \log C \qquad (3)$$

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 for the biosorption of Cd(II) ions onto *C. virgatum* biomass using Eq. (3). The values of K_F and $1/n$ were found to be 4.4 and 0.3, respectively. The $1/n$ values were between 0 and 1, indicating that the biosorption of Cd(II) onto *C. virgatum* biomass was favourable at studied conditions. However, compared to the R^2 values, 0.978 with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir isotherm model is better fitted the equilibrium data.

The equilibrium data were also applied to the D–R isotherm model to determine the nature of biosorption process as physical
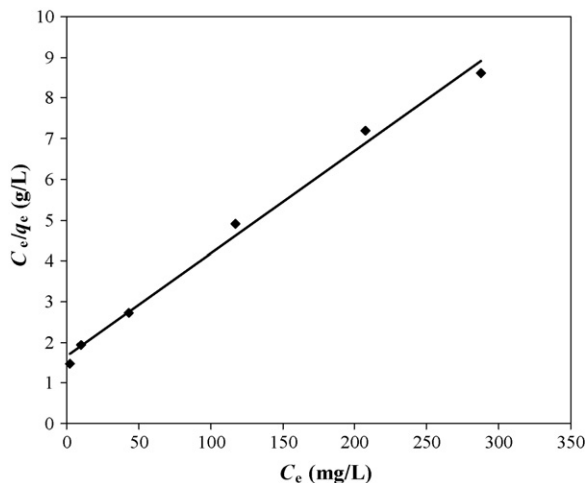

Fig. 5. Langmuir isotherm plots for biosorption of Cd(II) onto *C. virgatum* biomass (biomass dosage 10 g/L; contact time 60 min; pH 5; temperature 293 K).

Table 1
Comparison of biosorption capacity (q_m) of *C. virgatum* for Cd(II) ions with that of different algae species and other biomasses

| Biomass	pH	q_m (mg/g)	Reference
Ulva sp. (green algae)	5.5	65.2	[16]
Gracillaria sp. (red algae)	5.5	33.7	[16]
Pre-treated *Padina* sp. (brown algae)	5	59.6	[5]
Padina tetrastomatica (brown algae)	5	53.6	[17]
Gracilaria edulis (red algae)	5	27.0	[17]
Gracilaria changii (red algae)	5	25.9	[17]
Gracilaria salicornia (red algae)	5	18.0	[17]
Scenedesmus subspicatus (green algae)	6	7.3	[18]
Porphyridium purpureum (red algae)	6	0.42	[18]
Pinus sylvesteris	5	19.1	[36]
Mucor rouxii	4–5	8.5	[37]
Caulerpa lentillifera	5	4.7	[38]
Chlorella minutissima	–	11.1	[39]
Rhizopus arrhizus	–	27.0	[40]
C. virgatum (red algae)	5	39.7	Present study
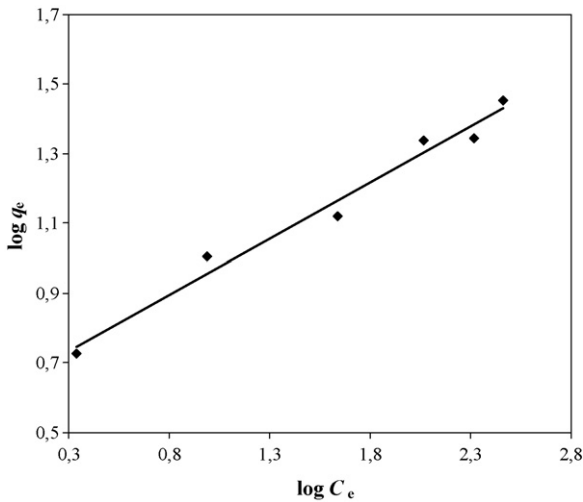
Fig. 6. Freundlich isotherm plots for biosorption of Cd(II) onto *C. virgatum* biomass (biomass dosage 10 g/L; contact time 60 min; pH 5; temperature 293 K).
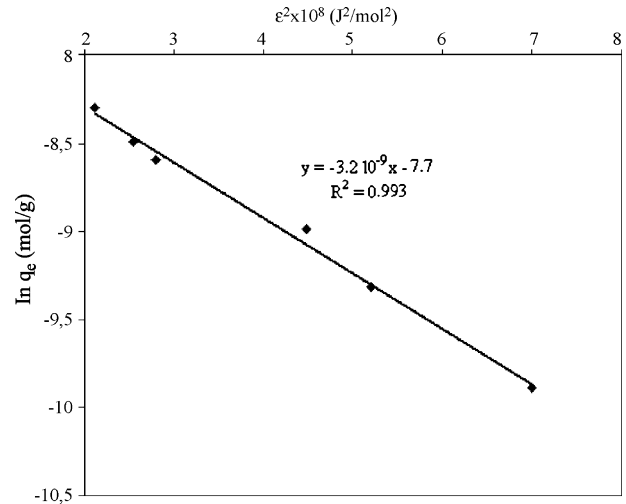

Fig. 7. D–R isotherm plots for biosorption of Cd(II) onto *C. virgatum* biomass (pH 5; biomass dosage 10 g/L; contact time 60 min; temperature 293 K).

or chemical. The linear form of the D–R isotherm equation [30]:

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

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 0.993 (Fig. 7). From the intercept of the plots, the q_m value was found to be 4.7×10^{-4} mol/g. The mean biosorption energy (E, kJ/mol) is as follows

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

The mean free energy of biosorption gives information about biosorption mechanism, physical or chemical. If E value is between 8 and 16 kJ/mol, the biosorption process follows chemically and if E < 8 kJ/mol, the biosorption process is of a physically [4]. The mean biosorption energy was calculated as 12.7 kJ/mol for the biosorption of Cd(II) ions. These results indicated that the biosorption process Cd(II) onto *C. virgatum* may be carried out chemically via involving valence forces through sharing or exchange of electrons between sorbent and sorbate [31].

3.6. Biosorption kinetics

In order to examine the controlling mechanism of the biosorption process, kinetic models are used to test the experimental data. 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 by Lagergren [32] is given as

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

where q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the first-order 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 coefficients of determination for this model at studied temperatures is low ($R^2 = 0.967$–0.979, as seen in Table 2). It can be concluded from the R^2 values that the biosorption of Cd(II) ions onto *C. virgatum* does not fit a pseudo-first-order kinetic model.
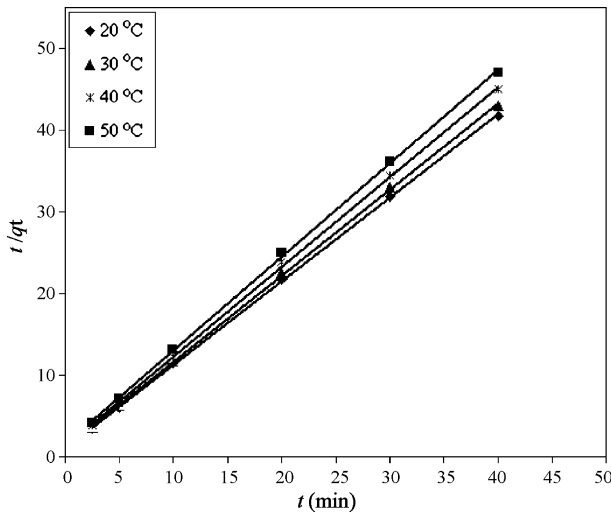
Table 2
Pseudo-first-order and pseudo-second-order parameters for the biosorption of Cd(II) onto *C. virgatum* biomass at different temperatures (k_1: rate constant of first-order equation; k_2: rate constant of second-order equation; q_t: the amounts of the metal ions biosorbed at equilibrium q_e: the amounts of the metal ions biosorbed at t time; R^2: correlation coefficient)

Temperature (°C)	Pseudo-first-order			Pseudo-second-order		
	k_1 (1/(min)$^{-1}$)	q_e (mg/g)	R^2	k_2 (g/(mg min))	q_e (mg/g)	R^2
293	7.5×10^{-2}	0.23	0.976	0.29	1.04	0.999
303	6.1×10^{-2}	0.22	0.967	0.24	0.99	0.998
313	5.9×10^{-2}	0.21	0.979	0.22	0.91	0.999
323	5.3×10^{-2}	0.20	0.976	0.16	0.87	0.999

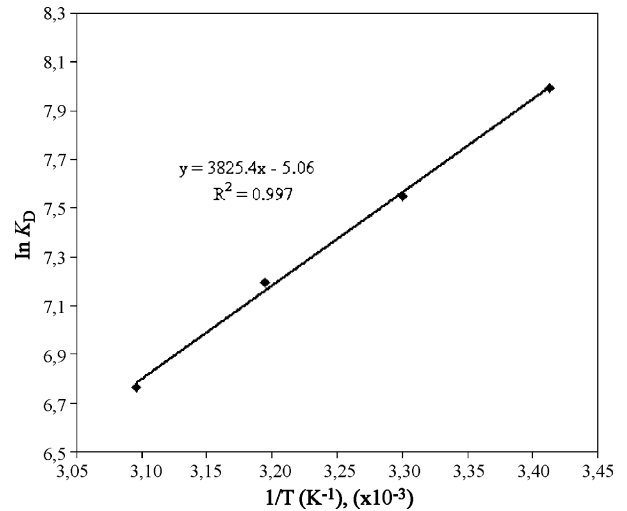Fig. 8. Pseudo-second-order kinetic plots at different temperatures.

Fig. 9. Plot of $\ln K_D$ vs. $1/T$ for the estimation of thermodynamic parameters for biosorption of Cd(II) onto *C. virgatum* biomass.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [33]:

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

where k_2(g/mg min) is the rate constant of the second-order equation, q_t and q_e (mg/g) are the amounts of the metal ions biosorbed at equilibrium (mg/g) and t (min), respectively. This model is more likely to predict kinetic behavior of biosorption with chemical sorption being the rate-controlling step [33]. The linear plots of t/q_t versus t for the pseudo-second-order model for the biosorption of Cd(II) ions onto the alga biomass at 293–323 K were shown in Fig. 8. The rate constants (k_2), the R^2 and the q_e values are given in Table 2. It is clear from these results that the R^2 values are very high (0.998–0.999). These results suggest that this model successfully describes the kinetics of the biosorption of Cd(II) ions onto *C. virgatum*. This conclusion is in agreement with those obtained by other authors [2,24,34].

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 Cd(II) ions onto *C. virgatum*. These parameters were calculated from the following 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 [35].

By considering the following equation, 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):

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

The free energy change (ΔG°) was calculated to be -19.5, -19.0, -18.7, and -18.2 kJ/mol for the biosorption of Cd(II) at 293, 303, 313, and 323 °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 -31.8 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 value (-31.8 kJ/mol) indicated that the biosorption process of Cd(II) ions onto *C. virgatum* biomass proceeded chemically because it falls into the 20.9–418.4 kJ/mol [34]. The ΔS° parameter was found to be -42.4 J/mol K for Cd(II) biosorption. The negative ΔS° value suggests a decrease in the randomness at the solid/solution interface during the biosorption process.

4. Conclusions

This study focused on the biosorption of Cd(II) ions onto algal biomass (*C. virgatum*) from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time, and temperature, were effective on the biosorption efficiency of Cd(II). Biosorption equilibrium was better described by the Langmuir isotherm model than the Freundlich model. The monolayer biosorption capacity of *C. virgatum* for Cd(II) was found to be 39.7 mg/g ions. From the D–R model, the mean energy was determined as 12.7 kJ/mol, indicating that the biosorption of Cd(II) onto *C. virgatum* biomass may be carried out chemically. Kinetic examination of the equilibrium data showed that the biosorption of Cd(II) 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 293–323 °C. Based on all results, it can be also concluded that the *C. virgatum* is an effective and alternative biomass for the removal of Cd(II) ions from aqueous solution because of its considerable biosorption capacity, being of natural, renewable and thus cost-effective biomass.

Acknowledgements

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