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Removal of cadmium(II) from aqueous solutions by biosorption onto the brown macroalga (*Dictyota dichotoma*)

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ABSTRACT

This paper presents the characteristics of Cd(II) biosorption from aqueous solution using the brown alga (*Dictyota dichotoma*) as a function of pH, biomass dosage, contact time and temperature. Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were applied to describe the biosorption isotherms of Cd(II) by *D. dichotoma* biomass. The monolayer biosorption capacity of *D. dichotoma* biomass for Cd(II) ions was found to be 75 mg/g. The mean free energy calculated from D–R isotherm indicated that the biosorption of Cd(II) onto *D. dichotoma* macroalga took place by chemisorption. Kinetic evaluation of the experimental data showed that the biosorption process followed pseudo-second-order model.The calculated thermodynamic parameters ΔG°, ΔH° and ΔS°, showed that the biosorption of Cd(II) onto *D. dichotoma* biomass was feasible, spontaneous and exothermic under examined conditions. X-ray photoelectron spectroscopy (XPS) and FT-IR analysis of *D. dichotoma* revealed the chelating character of the ion coordination to carboxyl groups. It was confirmed that carboxyl, ether, alcoholic and amino groups are responsible for the binding of the metal ions.

Keywords: *Dictyota dichotoma;* Biosorption; Langmuir and Freundlich models; Kinetic; XPS; FT-IR

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1. Introduction

Rapid industrialization and urbanization have resulted in the discharge of various toxic pollutants into the water bodies. The discharge of metal ions in industrial effluents is of great concern because their presence and accumulation have a toxic or carcinogenic effect on living species. Cadmium for instance, which is widely used and extremely toxic in relatively low dosages, is one of the principle heavy metals responsible for causing kidney damage, renal disorder, high blood pressure, bone fraction and destruction of red blood cells [1]. Because of the toxicity and bioaccumulation, Cd(II) is considered as a priority pollutant by the US Environmental Protection Agency. The permissible limit for cadmium as described by WHO is 0.01 mg/dm^3 [2].

The main anthropogenic pathway through which Cd(II) enters the water bodies is via wastes from industrial processes such as electroplating, plastic manufacturing, metallurgical processes and industries of pigments and Cd/Ni batteries [3]. Therefore, the

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removal of this toxic metal ion from water prior to supplying water for drinking, bathing, etc. is very important and urgent.

Conventional methods for removing cadmium from aqueous solutions include chemical precipitation, chemical oxidation or reduction, ion exchange, filtration, electrochemical treatment, solvent extraction, reverse osmosis, membrane technologies and evaporation recovery [4].

These processes may be ineffective or extremely expensive especially when the metals in solution are in the range of 1–100 mg L^{-1}. Another major disadvantage with conventional treatment methods is the production of a toxic chemical sludge and its disposal/treatment which becomes a costly affair and is not eco-friendly. Therefore, removal of cadmium to an environmentally safe level in a cost effective and environment-friendly manner assumes great importance [5].

Biosorption, a property of certain types of inactive, dead microbial biomass to bind and concentrate heavy metals from even very dilute aqueous solutions, is one of the most promising methods used in the removal of toxic metals from industrial waste streams and natural waters. The major advantages of the biosorption technology are its effectiveness in quickly reducing the concentration of heavy metal ions to very low levels with high efficiency and the use of inexpensive biosorbent materials. These characteristics make biosorption an ideal alternative for treating high volumes of low concentration complex wastewaters. Biosorption can be considered a collective term for a number of passive, metabolism independent, accumulation processes and may include physical and/or chemical adsorption, ion exchange, coordination, complexation, chelation and microprécipitation [6].

Among biosorbent materials, algae have proved to be both economic and eco-friendly, as they are abundantly available, have regeneration and metal recovery potentiality, lesser volume of chemical and/or biological sludge to be disposed off, high efficiency in dilute effluents and high surface area-to-volume ratio. It provides a cost-effective solution for industrial wastewater management [7]. The cell walls of brown algae generally contain three components: cellulose, the structural support; alginic acid, a polymer of mannuronic and guluronic acids and the corresponding salts of sodium, potassium, magnesium and calcium; and sulphated polysaccharides. These compounds contain several functional groups (amino, carboxyl, sulphate and hydroxyl) which could play an important role in the biosorption process [8]. The mechanism of binding metal ions by inactivated algal biomass may depend on the species and ionic charges of the metal ions, the algal organisms, the chemical compositions of the metal ion solution and other external environmental factors such as pH and temperature [9]. *Dictyota dichotoma* is very abundant in the coast of Sochi (southwest part of Russia) and information about biosorption with it, is still scanty.

The objective of the present work is to investigate the biosorption potential of *D. dichotoma* biomass in the removal of cadmium from aqueous solution. Optimum biosorption conditions were determined as a function of pH, biomass dosage, contact time and temperature. The Langmuir, Freundlich and Dubinin–Radushkevich (D–R) models were used to describe equilibrium isotherms. Biosorption mechanism of Cd (II) onto *D. dichotoma* biomass was also evaluated in terms of thermodynamics and kinetics. The functional groups involved in metal biosorption were identified using X-ray photoelectron spectroscopy (XPS) and FT-IR analysis.

2. Materials and methods

2.1. Materials

The raw biomass of *D. dichotoma* was harvested from the Sochi beach (southwest coast of Russia). The samples were washed with copious quantities of deionized water to remove extraneous materials as well as release common ions (e.g. Na^+ and Ca^{2+}) present in seawater. The washed biomass was dried at 70˚C for 48 h. The dried algae biomass was chopped, sieved and the particles with an average size 0.5 mm were used for biosorption experiments.

2.2. Reagents and equipments

Stock metal solution at various concentrations was prepared by dissolving cadmium nitrate (analytical reagent grade, Sigma–Aldrich (Ireland)). The pH of the solution was monitored in a 5500 EUTECH pH Meter using FET solid electrode calibrated with standard buffer solutions by addition of 0.1 mol/L HNO_3 and 0.1 mol/L NaOH solutions as per the required pH value. The metal concentration was measured using an atomic absorption spectrophotometer (SHIMADZU AA-680, Japan). FT-IR spectroscopy was used to detect vibration frequency changes in the algal sorbent. The spectra were collected by an FTS-135 (Bio-Rad) spectrometer within the range 400–4,000 cm^{-1} using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. XPS (Kratos XPS System-AXIS Nova) was applied to determine the interactions between the organic functional groups in the biomass and the metals adsorbed. The functional groups were characterized by the binding energy (BE) of C. In addition, the metal ions adsorbed on these functional groups were also analysed.

2.3. Batch biosorption experiments

Biosorption experiments were optimized at the desired pH value, contact time and biomass dosage level using the necessary biomass in a 250 mL stoppered conical flask containing 25 mL of test solution.

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 120 rpm. The experiments were repeated at 20, 30, 40 and 50°C. 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 analysed for metal concentration by using AAS. The percent biosorption of metal ion was calculated as follows:

$$\text{Biosorption }(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \tag{1}$$

where C_i and C_f are the initial and final (or equilibrium) metal concentrations, respectively.

The effect of pH on biosorption was conducted by using a solution having 10 mg/L of Cd(II) concentration with a biomass dosage of 4 g/L. Throughout the study, the contact time was selected in the range of 5–90 min, pH 2–8, initial metal concentration from10 to 400 mg/L and the biosorbent dosage from 1 to 20 g/L were investigated.

3. Results and discussion

3.1. Effect of pH solution

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction [10]. The biosorption of Cd(II) onto *D. dichotoma* was studied over a pH range of 2–8 and the results are given in Fig. 1.

It can be seen from Fig. 1 that the biosorption yield of cadmium increases as the pH increases, and reaches the maximum at pH 5, and then decreases as the pH continues to increase. Because H^+ vies with metal ion in lower pH, the sorbent surface takes up more H^+, consequently reducing metal ions' bind on the sorbent surface. At higher pH levels, the sorbent surface takes more negative charges, thus attracting greater metal ions. But with further increase in pH level, the formation of anionic hydroxide complexes decreases the concentration of free metal ions, thereby decreasing the adsorption capacity of the metal ions. According to the results of this initial experiment, further biosorption investigations were performed at pH value of 5 as an optimal value.

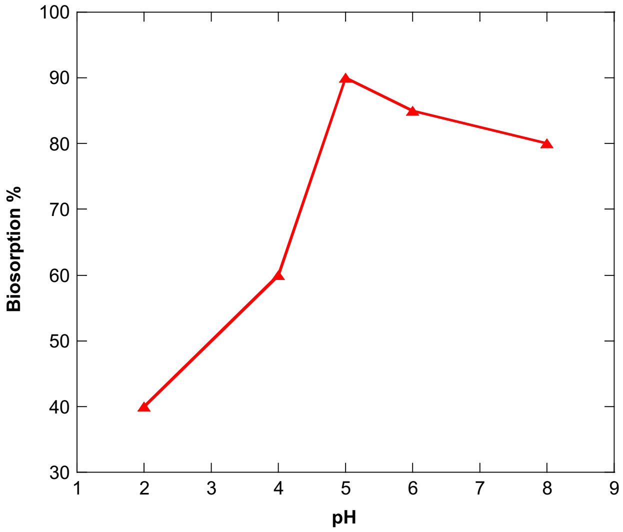

Fig. 1. Effect of pH on biosorption of Cd(II) onto *D. dichotoma* (metal concentration: 10 mg/L; temperature: 20°C).

3.2. Effect of biomass dosage

The biomass concentration is another important variable during metal uptake. At a given equilibrium concentration, the biomass takes up more metal ions at lower than at higher cell densities [11]. The effect of biomass dosage on the biosorption of Cd(II) ions was studied using different biomass dosage in the range 1–20 g/L (Fig. 2).

The percentage of the metal biosorption steeply increases with the biomass loading up to 4 g/L. The maximum biosorption of the metal ions was attained at about 4 g/L biomass dosage, and it was almost same at higher dosages, 10, 16 and 20 g/L. This trend can be explained as a consequence of a partial aggregation, which occurs at higher biomass dosages giving rise to a decrease in the active sites on the biomass [12]. Therefore, the optimum biomass dosage was selected as 4 g/L for further experiments.

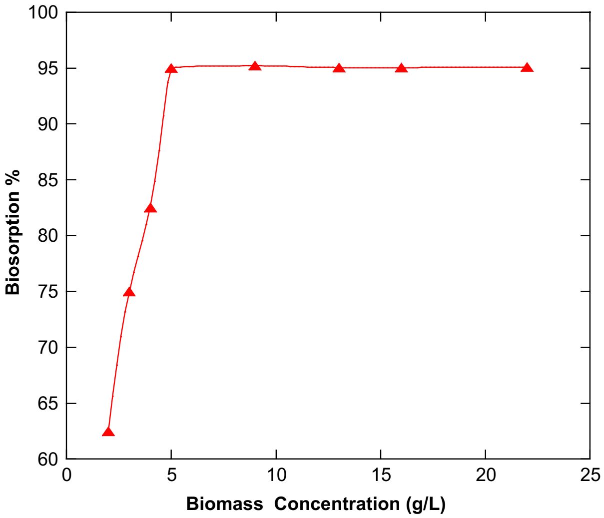

Fig. 2. Effect of biomass dosage on biosorption of Cd(II) by *D. dichotoma* (metal concentration: 10 mg/L; pH: 5; temperature: 20˚C).

3.3. Effects of contact time and temperature

The sorption of heavy metal ions by algae followed a two-step mechanism where the metal ion was physically/chemically taken up onto the surface of the algae before being taken up biologically into the cell [13]. The first step, known as a passive transport, took place quite rapidly, i.e. within 20–30 min whilst the second biological step or active transport, could take much longer time to complete. In this case, since the alga was dried and biological functions were no longer in process, the sorption could only take place on the surface of the cell. Therefore, the sorption equilibrium took place quickly within 20 min and no further sorption was observed thereafter. Fig. 3 shows the biosorption efficiency of Cd(II) ions by *D. dichotoma* as a function of contact time and temperature. According to this figure, the biosorption yield of Cd (II) increases with rise in contact time up to 30 min at 20–50˚C. After this time there was no considerable increase. Therefore, the optimum contact time was selected as 30 min for further experiments. On the other hand, the biosorption percentage decreased from 96 to 82% as temperature was increased from 20 to 50˚C for the equilibrium time, 30 min.

This result indicated the exothermic nature of Cd (II) biosorption onto *D. dichotoma* biomass. A decrease in the biosorption of Cd(II) ions with the rise in temperature may be due to either the damage of active-binding sites in the biomass or increasing tendency to desorb metal ions from the interface to the solution [14]. The optimum temperature was selected as 20˚C for further biosorption experiments.

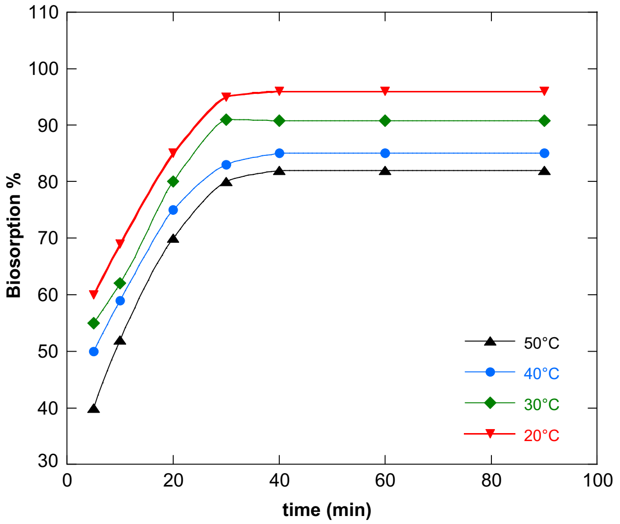

Fig. 3. Effect of contact time and temperature on biosorption of Cd(II) by *D. dichotoma* (metal concentration: 10 mg/L; biomass dosage: 4 g/L; pH: 5).

3.4. Biosorption isotherms

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. The biosorption isotherms were investigated using three equilibrium models, which are namely the Langmuir, Freundlich and D–R isotherm models. The Langmuir isotherm model [15] is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface. This model can be written in linear form:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} b} + \frac{C_e}{q_{\max}} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the biosorbent (mg/g), C_e is the equilibrium metal ion concentration in the solution (mg/L), $q_{\max}$ is the monolayer biosorption capacity of the biosorbent (mg/g) and b is the Langmuir biosorption constant (L/mg) relating the free energy of adsorption. The values of Langmuir constants $q_{\max}$ and b were calculated from the slope and intercept of the linear plot of C_e/q_e vs. C_e (Fig. 4).

Fig. 4 indicates the linear relationship between the amount (mg) of Cd(II) ions sorbed per unit mass (g) of *D. dichotoma* biomass against the concentration of

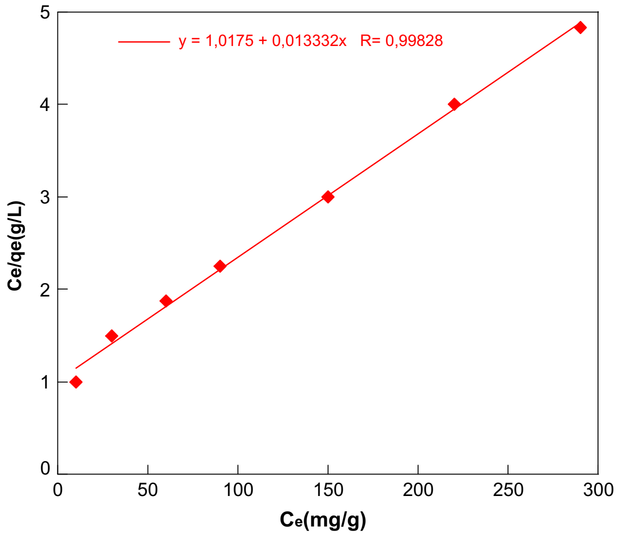

Fig. 4. Langmuir isotherm plots for biosorption of Cd(II) onto *D. dichotoma* (biomass dosage: 4 g/L; contact time: 30 min; pH: 5; temperature: 20°C).

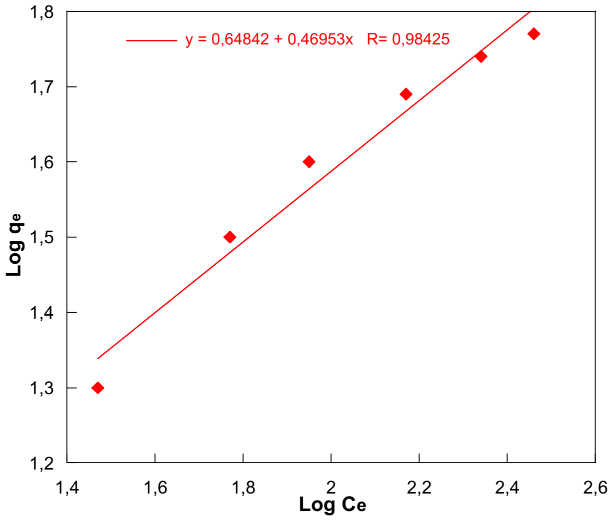

Fig. 5. Freundlich isotherm plots for biosorption of Cd(II) *D. dichotoma* (biomass dosage: 4 g/L; contact time: 30 min; pH: 5; temperature: 20°C).

cadmium ions remaining in solution (mg/L). The correlation coefficient (R^2) was found to be 0.998. These results indicate that the biosorption of the metal ions onto *D. dichotoma* biomass fitted well the Langmuir model. In other words, the sorption of cadmium using *D. dichotoma* took place at the functional groups/binding sites on the surface of the biomass which is regarded as monolayer biosorption. The maximum biosorption capacity (q_m) of *D. dichotoma* biomass was found to be 75 mg/g. Moreover, the b value was found as 1.31×10^{-2} L/mg.

The Freundlich isotherm model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between the sorbed molecules.

The linear form of the Freundlich adsorption isotherm can be defined by the following equation [16]:

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \tag{3}$$

where k_f a constant is related to the biosorption capacity and $1/n$ is an empirical parameter related to the biosorption intensity of the adsorbent. The Freundlich isotherm constants k_f and $1/n$ were calculated from the slopes and intercepts of the linear plot of log q_e vs. log C_e.

Fig. 5 shows the Freundlich isotherms obtained for the adsorption of Cd(II) ions onto *D. dichotoma* biomass using Eq. (3). The values of k_f and $1/n$ were found to be 4.45 and 0.46, respectively. The $1/n$ values were between 0 and 1, indicating that the biosorption of Cd(II) using *D. dichotoma* biomass was favourable at studied conditions. However, compared to the R^2 values, 0.984 with that obtained from the Langmuir model, it can be remarkably noted that the Langmuir isotherm model better fitted the equilibrium data.

The equilibrium data were also subjected to the DR isotherm model to determine the nature of biosorption processes as physical or chemical. The D–R sorption isotherm is more general than Langmuir isotherm, as its derivation is not based on ideal assumptions such as equipotent of the sorption sites, absence of steric hindrance between sorbed and incoming particles and surface homogeneity on microscopic level [17] The linear presentation of the D–R isotherm equation [18] is expressed by:

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{4}$$

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 biosorption mean free energy (mol^2/J^2) and is the Polanyi potential [$\varepsilon = RT$ ln $(1 + \frac{1}{C_e})$].

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.997 (Fig. 6). From the intercept of the plots, the q_m value was found to be 19.8×10^{-4} mol/g. The biosorption mean free energy (E, kJ/mol) is as follows:

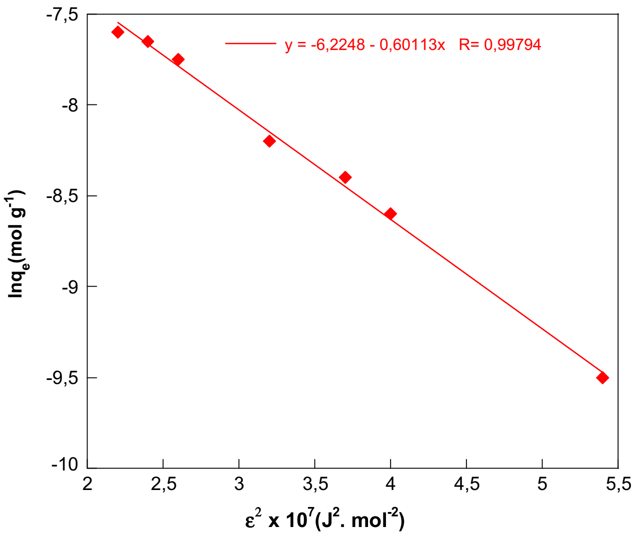

Fig. 6. D–R isotherm plots for biosorption of Cd(II) onto *D. dichotoma* biomass (pH: 5; biosorbent dosage: 4 g/L; contact time: 30 min; temperature: 20˚C).

$$E = \frac{1}{\sqrt{-2\beta}} \tag{5}$$

The *E* (kJ/mol) value gives information about adsorption mechanism, physical or chemical. If it lies between 8 and 16 kJ/mol, the adsorption process takes place chemically and when $E < 8$ kJ/mol, the adsorption process proceeds physically [19]. The mean biosorption energy was calculated as 9.17 kJ/mol for the biosorption of Cd(II) ions. These results indicated that the biosorption processes of cadmium onto *D. dichotoma* biomass may be carried out via chemisorption involving valence forces through sharing or exchange of electrons between the sorbent and the sorbate [20].

3.5. Adsorption kinetics study

The biosorption kinetics involves the search for a best model that well represents the experimental data. Several kinetic models are available to understand the behaviour of the biosorbent and also to examine the controlling mechanism of the biosorption process and to test the experimental data. In this study, the biosorption equilibrium data were analysed using two simplest kinetic models, pseudo-first-order and pseudo-second-order model.

The linearized form of the pseudo-first-order rate equation by Lagergren [21] 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 biosorbed at equilibrium (mg/g) and t (min), respectively and k_1 is the rate constant of the equation (min^{-1}).

Results obtained by applying the first-order Lagergren model to the experimental data were given in Table 1.

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \tag{7}$$

where k_2 (g/mg/min) is the rate constant of adsorption, q_2 is maximum adsorption capacity (mg/g) [22] . The values of k$_1$, q_e and k_2, q_2 were obtained from the slopes and intercepts of plots of log $(q_e - q_t)$ vs. t and t/q_t vs. t at different temperatures.

The linear plots of t/q_t vs. t for the pseudo-second-order model for the biosorption of Cd(II) ions onto the alga biomass at 20–50˚C were shown in Fig. 7.

The Pseudo-first-order and pseudo-second-order parameters for the biosorption of Cd(II) onto *D. dichotoma* at different temperatures were given in Table 1.

As seen from Table 1, the R^2 values are in range of 0.996–0.998 and the theoretical $q_{e2,\text{cal}}$ values were closer to the experimental $q_{e,\text{exp}}$ values. Based on these results, it can be concluded that the pseudo-second-order kinetic model provided a good correlation for the biosorption of Cd(II) by *D. dichotoma* in contrast to the pseudo-first-order model.

3.6. Thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy change ΔG°, standard enthalpy change ΔH° and standard entropy change ΔS° were also found out to give more information about the nature of sorption process. The thermodynamic parameters were calculated by the following equations:

$$\ln K_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT} (van't\,Hoff\ equation) \tag{8}$$

$$\Delta G^\circ = -RT \ln K_c \tag{9}$$

where $K_c = (q_e\ /C_e)$ is the adsorption equilibrium constant, T is absolute temperature (K) and R is the gas constant. When ln K_c vs. $1/T$ is plotted (Fig. 8), ΔH° and ΔS° values can be computed from slope and intercept of the van't Hoff equation. The calculated parameters were given in Table 2.

Table 1
Pseudo-first-order and pseudo-second-order parameters for the biosorption of Cd(II) onto *D. dichotoma* at different temperatures

		Pseudo-first-order			Pseudo-second-order		
Temperature (°C)	$q_{e,exp}$ (mg/g)	k_1 (min^{-1})	$q_{e,cal}$ (mg/g)	r_2	k_2 (g/mg/min)	$q_{e,cal}$ (mg/g)	r_2
20	2.37	6.8×10^{-2}	0.98	0.978	1.91	3.12	0.997
30	2.27	6.4×10^{-2}	0.95	0.972	1.13	2.97	0.998
40	2.07	5.9×10^{-2}	0.87	0.976	0.97	2.84	0.997
50	2	5.6×10^{-2}	0.82	0.981	0.65	2.65	0.998

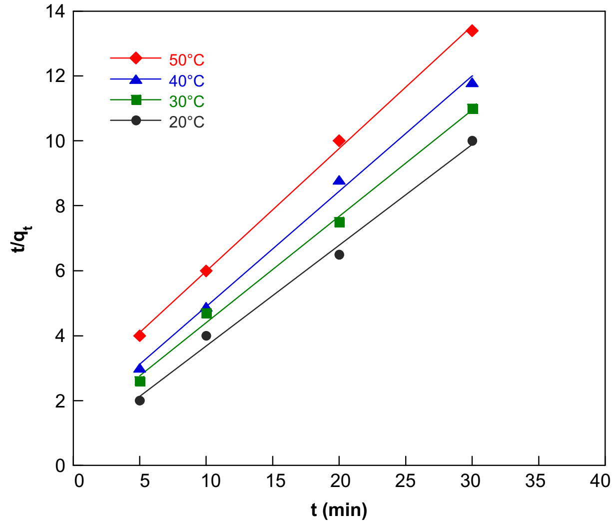

Fig. 7. Pseudo-second-order kinetic plots at different temperatures (pH: 5; biosorbent dosage: 4 g/L; contact time: 30 min; temperature: 20°C).

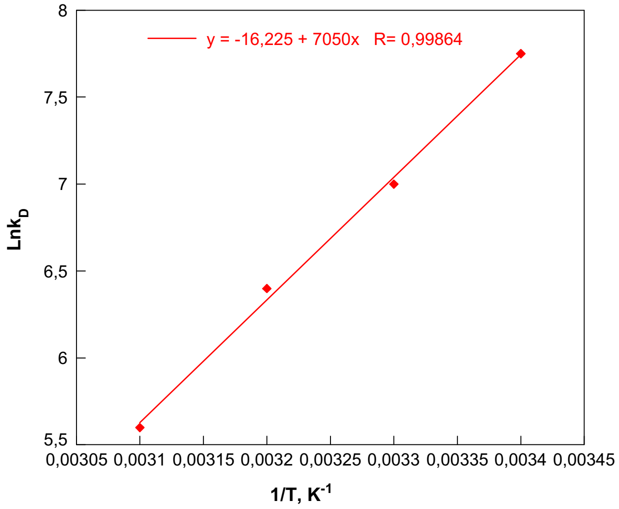

Fig. 8. Determination of thermodynamic parameters for biosorption of Cd(II) onto *D. dichotoma* biomass.

Table 2
Thermodynamic parameters for Cd(II) biosorption onto *D. dichotoma*

T (k)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/k)
Cd(II)			
293	−19.3	−58.61	−134.85
303	−18.1		
313	−16.6		
323	−15.3		

The negative ΔG° values indicated thermodynamically feasible and spontaneous nature of the biosorption. The decrease in ΔG° value with increase in temperature shows a decrease in feasibility of biosorption at higher temperatures.

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. Therefore, the ΔH° values showed that the biosorption processes of Cd(II) ions onto *D. dichotoma* biomass took place via chemisorption. The negative ΔS° value (−134.85 J/mol K) suggests a decrease in the randomness at the solid/solution interface during the biosorption process [23].

3.7. X-ray photoelectron spectroscopy

XPS was employed to study the changes of BE of the coordination carbon atom (C1*s*) in the biomass of *D. dichotoma* before and after metal adsorption. The results are summarized in Table 3 and the spectra for *D. dichotoma* are also presented in Fig. 9. It is clear that the C1*s* spectra comprised three peaks with BE of 285.72, 287.45 and 289.45 eV, identified via deconvolution. These peaks can be assigned by following the above sequence to ether, alcoholic and carboxylate groups [24,25], because carbon atoms in the three respective chemical functional groups (mainly in alginate) of the biomass possess slightly different electron densities.

Table 3
Peak numbers and area ratios of C1s spectra

		Peak area ratio (%)	
Biomass	Peak (eV)	Virgin	Cd-loaded
D. dichotoma	285.72	57.64	47.65
	287.45	29.42	37.53
	289.45	13.76	15.80

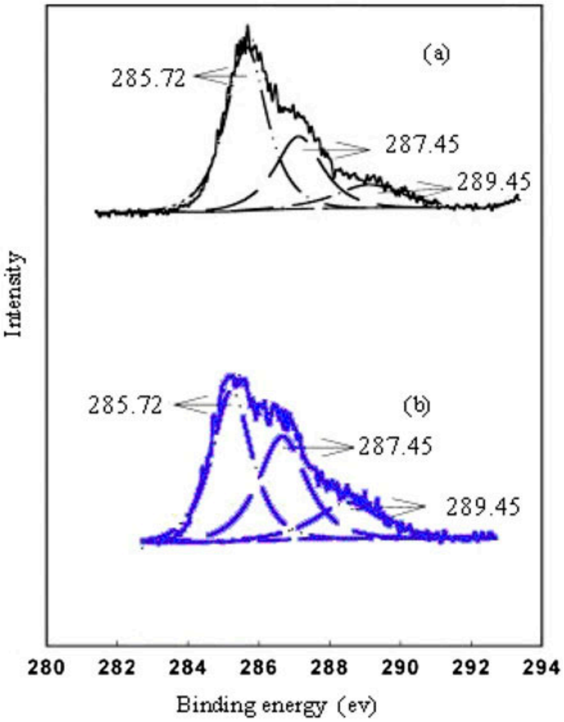

Fig. 9. XPS (C1*s*) spectra of *D. dichotoma*. (a) Pristine; (b) Cd-loaded.

The area distribution of the three peaks implied that ether and alcoholic carbons are dominant in the brown alga.

Furthermore, it can be observed in Fig. 9 that the area ratios of ether carbon decreased dramatically after metal adsorption. This is indicative of the formation of ether–metal complex species, in which the ether oxygen donates electrons to metal ions and, therefore, the electron density at the adjacent two carbon atoms decreases. Consequently, the BE of the carbons is lifted up and becomes indistinguishable from that of the carbons of the alcoholic and carboxylate groups. Although the sorption of heavy metal ions on the biomass resulted in a change of peak area distribution of the three functional groups, there is no clear correlation between the uptake capacities of the metal ions and the corresponding changes of the peak area. The metal ions adsorbed on *D. dichotoma* were also analysed (Fig. 10). The peak of Cd $3d_{5/2}$ at 404.57 eV was due to the formation of (–COO)$_2$Cd sorption species. The Cd^{2+} ions could be adsorbed through ionic bonding due to their possessing full *d* subshells.

3.8. FT-IR analysis of biomass

Numerous chemical groups have been proposed to be responsible for the biosorption of metals by macroalgae. These include carboxyl, sulphonate, hydroxyl and amino [25]. Their relative importance in metal sorption may depend on factors such as the quantity of sites, their accessibility, chemical state and affinity between the site and metal.

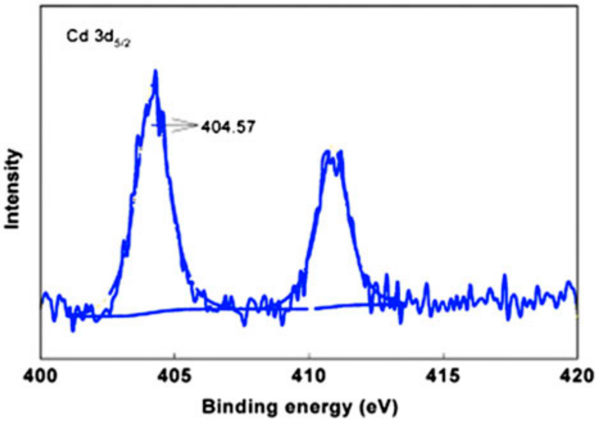

Fig. 10. XPS spectra of *D. dichotoma* loaded with Cd(II).

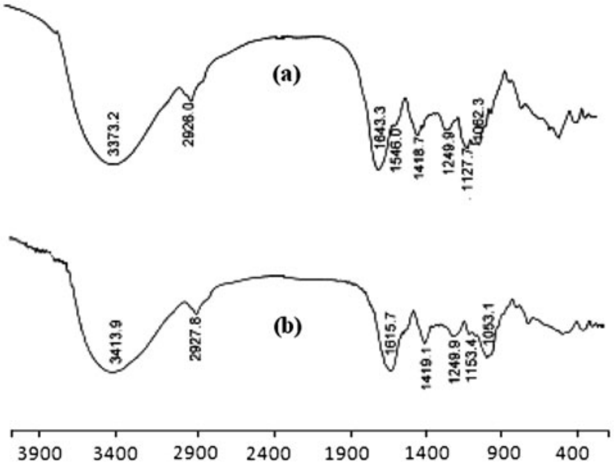

Fig. 11. FT-IR spectra of *D. dichotoma* (a) Virgin; (b) Cd-loaded.

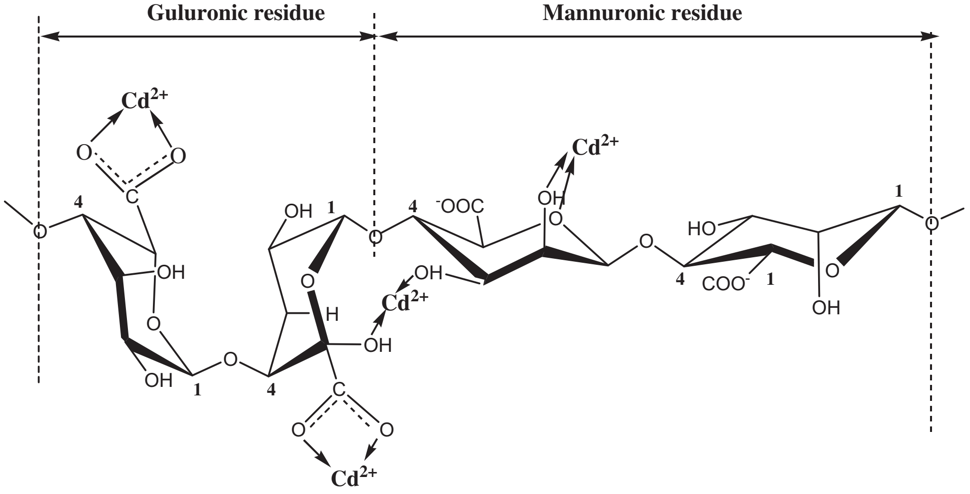

Fig. 12. Mechanism of Cd^{2+} biosorption onto the brown alga *D. dichotoma*.

The FT-IR spectra of the virgin and metal-loaded brown marine algae *D. dichotoma* are shown in Fig. 11.

For the pristine *D. dichotoma* biosorbent (sample1), it was clear that the carboxylate ions gave rise to two bands: a strong asymmetrical stretching band at 1,643 and a weaker symmetrical stretching band at 1,418. The double bands of the carboxylate ion were identical with the observations made on Ca–alginate-based resin [24,25]. Although both bands exhibited shifts to different extents after contact with metal solutions, the differences between these two peaks (Δ) was 225 cm^{-1}.

The peak values suggested the chelating (bidentate) character of the metal biosorption onto carboxyl groups.

The bands at 1,127 cm^{-1} (sample 1) was due to the –C–O stretching of ether groups; the bands at 1,062 cm^{-1} (sample 1) was assigned to the –C–O stretching of alcoholic groups. An interesting phenomenon was the sharp decrease in the band intensity of the ether groups after metal binding. From the changes of band areas, it was reasonable to assume that most of the ester groups had been converted to carboxylic and alcoholic groups. When the algal biomass was loaded with metal ions, the bands of alcoholic groups shifted to lower frequency; the shift was equal to 9 cm^{-1}.

The FT-IR spectroscopic analysis indicated broad bands at 3,373–3,413 cm^{-1}, representing bonded –OH and –NH groups. The bands observed at about 2,926 cm^{-1} could be assigned to the –CH stretch. The spectral analysis before and after metal binding indicated that the –NH was also involved in metal biosorption. There were clear band shifts and intensity decrease of the –NH band at 1,546–1,556 cm^{-1}. The change in the intensity of the bands at 3,373–3,413 cm^{-1} also suggested changes in the amino groups present in the biomass.

The bands at about 1,249 cm^{-1} represented $–SO_3$ stretching. Since these peaks presented approximately the same frequency before and after metal binding, it is likely that $–SO_{3,}$ mainly present in sulphonic acids of polysaccharides, such as Fucoidan, was not involved in metal complexation by *D. dichotoma*. Binding mechanism of the brown alga with Cd^{2+} is shown in Fig. 12.

3.9. Comparison of Cd(II) removal with different adsorbents reported in literature

The sorption capacity of *D. dichotoma* biomass for the removal of Cd(II) has been compared with that of different adsorbents reported in literature and the values of sorption capacities have been presented in Table 4.

Table 4
Comparison of adsorption capacity of *D. dichotoma* biomass for Cd(II) with that of other adsorbent

Adsorbents	Biosorption capacity (mg/g) Cd(II)	Reference
Calcite	18.52	[29]
Grape stalk wastes	33.12	[27]
Wheat bran	21	[26]
Hibiscus dye waste	103.09	[28]
D. dichotoma	75	Present study

The biosorption capacity of *D. dichotoma* biomass for Cd(II) is higher than that of the majority of other adsorbents mentioned [26–29]. The sorption capacity varies and it depends on the characteristics of the individual adsorbent, the extent of surface/surface modification and the initial concentration of the adsorbate. However, it can be noteworthy that the *D. dichotoma* alga has important potential for the removal of Cd(II) ions from aqueous solution.

4. Conclusion

In this study, the biosorption characteristics of cadmium(II) from aqueous solution using brown alga (*D. dichotoma*) were investigated in terms of equilibrium, thermodynamics and kinetics. The experimental parameters, pH of solution, biomass concentration, contact time and temperature, were effective on the biosorption of Cd(II) using *D. dichotoma* biomass. The maximum biosorption capacity of *D. dichotoma* was found to be 75 mg/g at pH 5, contact time of 30 min, biomass concentration of 4 g/L and temperature of 20°C. The calculated mean free energy (9.17 kJ/mol) from the D–R model indicated that the biosorption of Cd(II) using *D. dichotoma* took place by chemisorption. The calculated thermodynamic parameters showed that the biosorption of Cd(II) onto *D. dichotoma* was feasible, spontaneous and exothermic under studied experimental conditions.

The kinetic results revealed that the pseudo-second-order model was the best kinetic model for the description of the biosorption mechanism. XPS and FT-IR analysis showed similar chelating characteristics of metal coordination to the functional groups in the cell wall of the brown algae. The functional groups involved in Cd(II) biosorption included carboxyl, ether, alcoholic and amino groups. The findings of this study revealed that the brown alga *D. dichotoma* is a promising biosorbent for the removal of cadmium from aqueous solutions.

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