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Biosorption of Cd(II) and Cr(III) from aqueous solution by moss (*Hylocomium splendens*) biomass: Equilibrium, kinetic and thermodynamic studies

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Abstract

The biosorption characteristics of Cd(II) and Cr(III) ions from aqueous solution using the moss (*Hylocomium splendens*) biomass were investigated in terms of equilibrium, kinetics and thermodynamics. Optimum biosorption conditions were determined 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 isotherm of the metal ions by *H. splendens* biomass. Langmuir model fitted the equilibrium data better than the Freundlich isotherm. The maximum biosorption capacity (q_m) of *H. splendens* biomass was found to be 32.5 mg/g for Cd(II) ion and 42.1 mg/g for Cr(III) ion. The mean free energy values evaluated from the D–R model indicated that the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass was taken place by chemical ion-exchange. The calculated thermodynamic parameters, ΔG°, ΔH° and ΔS° showed that the biosorption of Cd(II) and Cr(III) ions onto *H. splendens* biomass was feasible, spontaneous and exothermic under examined conditions. Experimental data were also tested in terms of biosorption kinetics using pseudo-first-order and pseudo-second-order kinetic models. The results showed that the biosorption processes of both metal ions followed well pseudo-second-order kinetics.

Keywords: Biosorption; Cd(II); Cr(III); *Hylocomium splendens*; Kinetics; Thermodynamics

1. Introduction

Industrial heavy metal pollution is a serious environmental problem all over the world in recent years. Besides the toxic and harmful effects to organisms living in water, heavy metals also accumulate throughout the food chain and may affect human beings [1]. Heavy metals such as cadmium (Cd) and chromium (Cr) often present in industrial wastewaters, are hazardous to the aquatic ecosystem and pose possible human health risk. Cadmium is also a dangerous pollutant originating from metal plating, metallurgical alloying, mining, ceramics and other industrial operations [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]. Chromium compounds, mostly in chromium(III), produced by the chemical industry are used for chrome plating, the manufacture of dyes and pigments, leather tanning, and wood preserving [4,5]. Cr(III) is also thought to be an essential nutrient required for sugar and fat metabolism in organisms [6]. However, long time contact causes skin allergic and cancer [7]. Cr(III) can be also oxidized to the more carcinogenic and mutagenic Cr(VI) by MnO_2 in the environment or by some bacteria in soil under proper conditions [8]. Cr(III) is toxic to fish when its concentration in water exceeds 5.0 mg L^{-1} [9].

The most widely used methods for removing heavy metals from wastewaters include ion exchange, chemical precipitation, reverse osmosis, evaporation, membrane filtration, adsorption biological treatment [10]. Most of these methods suffer from some drawbacks, such as high capital and operational cost or the disposal of the residual metal sludge, and are not suitable for small-scale industries [11]. Biosorption plays an important role in the elimination of metal ions from aqueous solutions water pollution control [12,13]. The main advantages of this technique are the reusability of biomaterial, low operating cost, improved

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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 [14]. Various biomasses have been used for removal of Cd(II) and Cr(III) ions from aqueous solution [15–18].

Mosses have been used for more than 20 years as biomonitors for the determination of atmospheric heavy metal deposition because of their high cation exchange capacity [19–21]. Studies on uptake and release of heavy metals by the various species of mosses have also been accomplished [22–25]. As far as the authors are aware, there is no investigation reported in the literature on the biosorption of Cd(II) and Cr(III) by *H. splendens*. In addition, this new material was chosen as biosorbent in this study due to its being of natural, abundantly available and thus low-cost.

The objective of the present work is to investigate the biosorption potential of *H. splendens* biomass in the removal of Cd(II) and Cr(III) ions 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 mechanisms of Cd(II) and Cr(III) ions onto *H. splendens* biomass were also evaluated in terms of thermodynamics and kinetics.

2. Experimental procedures

2.1. Biomass preparation

The moss (*H. splendens*) biomass samples were collected from the East Black Sea region of Turkey. Samples were washed with deionized water and dried in an oven at 70 °C for 48 h. The dried moss biomass was ground and sieved through different sizes and 150–300 μm fraction was used in all experiments.

2.2. Reagents and equipments

All chemicals used in this work, were of analytical reagent grade and were used without further purification. Double deionised water (Milli-Q Millipore 18.2 MΩ cm^{-1} conductivity) was used for all dilutions. A pH meter, Sartorius pp-15 Model glass-electrode was employed for measuring pH values in the aqueous phase. A PerkinElmer AAnalyst 700 flame atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in an air/acetylene flame. A 10 cm long slot-burner head, a lamp and an air–acetylene flame were used. The operating parameters for working elements were set as recommended by the manufacturer. Fourier transform infrared (FT-IR) spectra of dried unloaded biomass and Cd(II)-loaded biomass and Cr(III)-loaded biomass prepared as KBr discs were recorded at 400–4000 cm^{-1} wavenumber range using a JASCO-430 model FT-IR spectrometer.

2.3. Batch biosorption procedure

Biosorption experiments were optimized out 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. Initial solutions with different concentration of Cd(II) and Cr(III) were prepared by proper dilution from stock 1000 mg/L Cd(II) and Cr(III) 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 110 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 analyzed for metal concentration by using flame AAS. The percent biosorption of metal ion was calculated as follows:

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

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) and 10 mg/L of Cr(III) concentration with a biomass dosage of 4 g/L. Throughout the study, the contact time was varied from 5 to 90 min, the pH from 2 to 8, the initial metal concentration from 10 to 400 mg/L, and the biosorbent dosage from 0.1 to 20 g/L.

3. Results and discussion

3.1. FT-IR analysis

The FT-IR spectroscopy method was used to obtain information on the nature of possible interactions between the functional groups of *H. splendens* biomass and the metal ions. The FT-IR spectra of dried unloaded biomass, Cd(II)-loaded biomass and Cr(III)-loaded biomass are shown in Fig. 1. The broad and strong bands at 3295–3338 cm^{-1} were due to bounded hydroxyl (–CHOH) or amine (–NH$_2$) groups. The peaks at 1623–1638 cm^{-1} were attributed to stretching vibration of carboxyl group (–C=O). The bands observed at 1027–1039 cm^{-1} were assigned to C–O stretching of alcohols and carboxylic acids. The peaks observed at 2898 cm^{-1} can be assigned to the –CH group.

The stretching vibration at 3305 cm^{-1} was shifted to 3295 and 3338 cm^{-1} in case of Cd(II) and Cr(III) biosorption, respectively. The carboxyl peak was shifted from 1631 to 1623 cm^{-1} for Cd(II)-loaded biomass and to 1638 cm^{-1} for Cr(III)-loaded biomass samples, respectively. The peak of C–O group was shifted from 1033 to

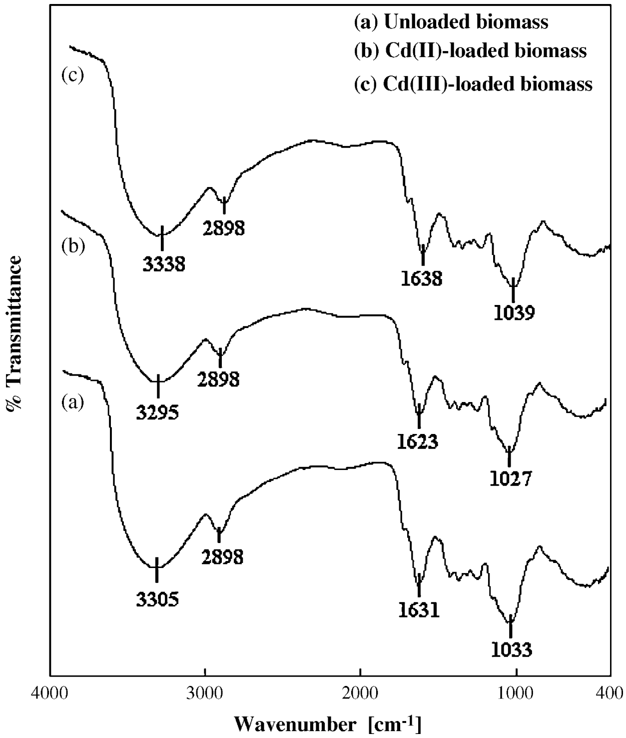

Fig. 1. FT-IR spectrum of dried unloaded biomass, Cd(II)-loaded biomass and Cr(III)-loaded biomass.

$1027\,cm^{-1}$ and $1039\,cm^{-1}$ for Cd(II)-loaded and Cr(III)-loaded biomasses, respectively. The results indicated that the chemical interactions as ion-exchange between the hydrogen atoms of carboxyl (–COOH), hydroxyl (–CHOH), and amine ($-NH_2$) groups of the biomass and the metal ions were mainly involved in the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass. In addition, no frequency change was observed in the of –CH group of the biomass after biosorption of metal ions. This suggested that this group did not participate in the biosorption process.

3.2. *Effect of pH*

One of the more important factors affecting biosorption of metal ions is acidity of solution. This parameter directly related with competition ability of hydrogen ions with metal ions to active sites on the biosorbent surface [26]. Generally, metal biosorption involves complex mechanisms of ion exchange, chelation, adsorption by physical forces, and ion entrapment in interand intrafibrillar capillaries and spaces of the cell structural network of a biosorbent [27–29]. 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 [30]. The effect of pH can be explained by ion-exchange mechanism of sorption in which the important role is played by the functional groups of the biomass that have cation-exchange properties [20,21,31].

The effect of pH on the biosorption of Cd(II) and Cr(III) ions onto *H. splendens* biomass was studied at pH 2–8 and the results were presented in Fig. 2. The biosorption efficiency was increased from 25 to 83% for Cd(II) biosorption and from 50 to 92% for Cr(III) ion, respectively as pH was increased from 2 to 4. The maximum biosorption was found to be 98% for Cd(II) and 99% for Cr(III) ions at pH 5. Therefore, all the biosorption experiments were carried out at pH 5. At high pH values ($pH > 5$), the biosorption yields for Cd(II) and Cr(III) ions were dramatically decreased. The pH dependency of biosorption efficiency could be explained by the functional groups involved in metal uptake and the metal chemistry [32]. At low pH values ($pH < 2.0$), the poor biosorption of Cd(II) could be due to competition with the H^+ ions for metal binding sites on the cell of the biomass. When the pH values increased (pH 2–5), biosorbent surface were more negatively charged and the functional groups of the biomass were more deprotonated and thus available for metal ions. Especially, carboxyl groups have the highest affinity for metal ions, since they are deprotonated in a wide range of pH [30]. 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 [30,33].

3.3. *Effect of biomass dosage*

The biomass dosage is an important parameter because this determines the capacity of a biosorbent for a given initial concentration. The biosorption efficiency for Cd(II) and Cr(III) ions as a function of biomass dosage was investigated (Fig. 3). The percentage of the metal biosorption steeply increases with the biomass loading up to 4 g/L. The maximum biosorption, 97% for Cd(II) and 99% for Cr(III), of the metal ions was attained at biomass dosage, 4 g/L and the increase was insignificant at higher dosages, 10 and 20 g/L. Therefore, the amount of biomass was selected as 4 g/L for further experiments.

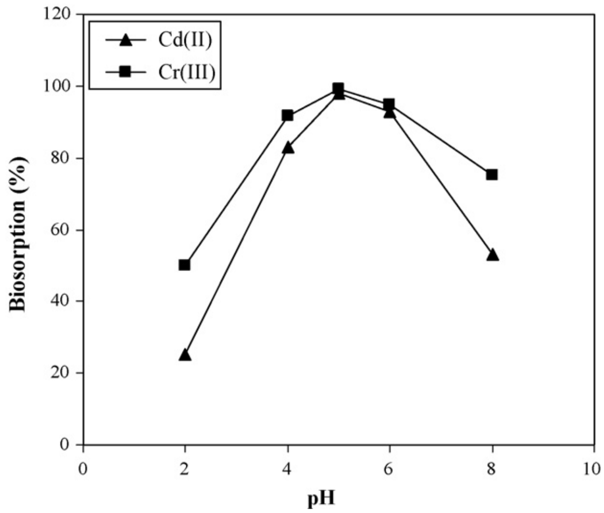

Fig. 2. Effect of pH on the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass (metal concentration:10 mg/L; temperature: 20 °C).

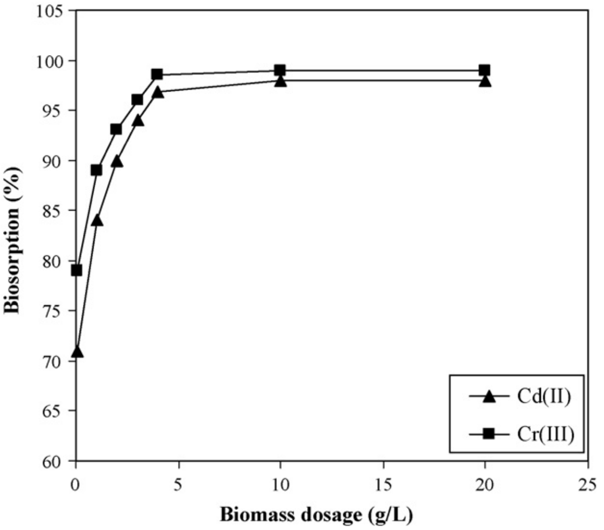

Fig. 3. Effect of biomass dosage on the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass (metal concentration:10 mg/L; pH: 5; temperature: 20 °C).

3.4. Effects of contact time and temperature

Contact time is one of the important parameters for successful use of the biosorbents for practical application and rapid sorption is among desirable parameters [34]. Fig. 4 shows the effect of contact time on the biosorption of Cd(II) and Cr(III) ions onto *H. splendens*. The biosorption yield of Cd(II) and Cr(III) increased considerably with increasing contact time up to 60 min and after then, it was nearly constant. For instance, during 60 min (at 20 °C), when the biosorption efficiency was 97% and 98% for Cd(II) and Cr(III), respectively, it was 98 and 99%, respectively during 90 min (at 20 °C). Therefore, the optimum contact time was selected as 60 min for further experiments.

Temperature of the medium affects on the removal efficiency of the pollutant from aqueous solution. Fig. 4 also shows the biosorption of Cd(II) and Cr(III) ions as a function of the temperature. The biosorption percentage decreased from 97 to 82% for Cd(II) and from 99 to 86% for Cr(III) as temperature was increased from 20 to 50 °C for the equilibrium time, 60 min. These results indicated the exothermic nature of Cd(II) and Cr(III) biosorption onto *H. splendens* biomass. A decrease in the biosorption of Cd(II) and Cr(III) ions with the rise in temperature may be due to either the damage of active binding sites in the biomass [35] or increasing tendency to desorb metal ions from the interface to the solution [36]. Optimum temperature was selected as 20 °C for further biosorption experiments.

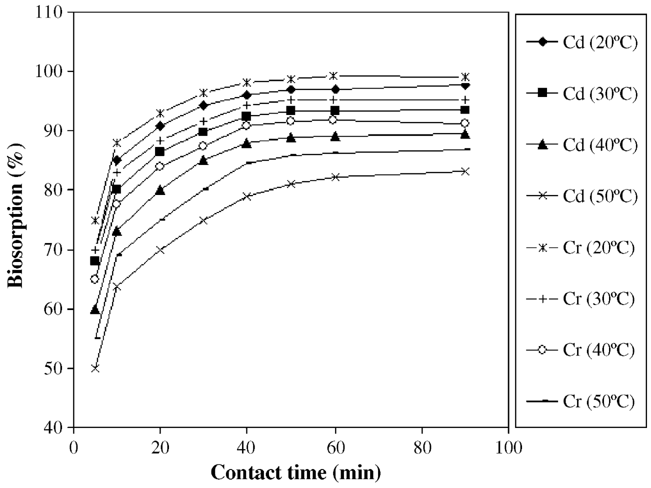

Fig. 4. Effect of contact time and temperature on the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass (metal concentration:10 mg/L; biomass dosage: 4 g/L; pH: 5).

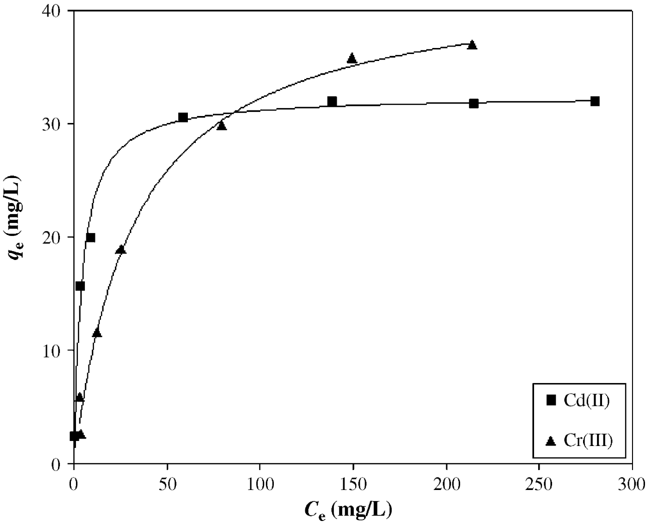

Fig. 5. Langmuir isotherm plots for the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass (biomass dosage: 4 g/L; contact time: 60 min; pH: 5; temperature: 20 °C).

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. The biosorption isotherms were investigated using three equilibrium models, which are namely the Langmuir, Freundlich and Dubinin–Radushkevich (D–R) isotherm models were analyzed.

The Langmuir sorption isotherm has been successfully applied to many pollutant biosorption processes and has been the most widely used isotherm for the biosorption of a solute from a liquid solution. A basic assumption of the Langmuir theory is that sorption takes place at specific homogeneous sites within the sorbent. This model can be written in non-linear form [37].

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_e is the equilibrium metal ion concentration on the adsorbent (mg/g), C_e 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) related with the free energy of biosorption.

Fig. 5 indicates the linear relationship between the amount (mg) of Cd(II) and Cr(III) ions sorbed per unit mass (g) of

Table 1
Comparison of biosorption capacity of *H. splendens* biomass for Cd(II) and Cr(III) with that of different biosorbents

Biosorbent	Biosorption capacity (mg/g)		Reference
	Cd(II)	Cr(III)	
Activated carbon prepared by apricot stone	–	29.3	[11]
Chlorella miniata	–	41.18 (pH 4.5)	[38]
Carrot residues	–	45.1 (pH 4)	[39]
Eggshells	–	160.0	[30]
Modified peanut sawdust	–	7.7 (pH 4)	[40]
Dunaliella sp.	–	58.3	[41]
Rhizopus oligosporus	–	126.0	[42]
Yellow passion-fruit shell	–	85.1	[43]
Animal bones	–	60.9	[44]
Spirulina sp.	159.0 (pH 7)	185.0 (pH 7)	[28]
Sargassum sp.	120.0	–	[45]
Fucus vesiculosus	73.0	–	[46]
Aquatic plant (*Najas graminea*)	28.0	–	[47]
Bifurcaria bifurcata	61.0	–	[48]
Gracillaria sp.	33.7	–	[49]
Aquatic moss (*Rhytidiadelphus sq.*)	16.7	–	[50]
Chlorella minutissima	11.1	–	[51]
Rhizopus arrhizus	27.0	–	[52]
Aquatic moss (*Fontinalis antipyretica*)	28.0	–	[1]
H. splendens	32.5	42.1	Present study

H. splendens biomass against the concentration of Cd(II) and Cr(III) ions remaining in solution (mg/L). The coefficients of determination (R^2) were found to be 0.991 and 0.993 for Cd(II) and Cr(III) biosorption, respectively. These results indicate that the biosorption of the metal ions onto *H. splendens* biomass fitted well the Langmuir model. In other words, the sorption of Cd(II) and Cr(III) ions onto *H. splendens* was taken 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 *H. splendens* biomass was found to be 32.5 mg/g for Cd(II) ion and 42.1 mg/g for Cr(III) ion. Moreover, the K_L value was found as 0.2 L/mg for Cd(II) ion and 0.03 L/mg for Cr(III) ion.

On the other hand, Table 1 presents the comparison of biosorption capacity (q_m; mg/g) of *H. splendens* biomass for Cd(II) and Cr(III) ions with that of various biomasses reported in literature [1,11,28,30,38–52]. The biosorption capacity of *H. splendens* biomass for Cd(II) and Cr(III) is higher than that of the majority of other biomasses mentioned. Therefore, it can be noteworthy that the *H. splendens* biomass has important potential for the removal of Cd(II) and Cr(III) ions from aqueous solution.

The Freundlich model assumes a heterogeneous adsorption surface and active sites with different energy. The Freundlich model [53] is

$$q_e = K_f C_e^{1/n} \tag{3}$$

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 non-linear Freundlich isotherms which were obtained by plotting q_e versus C_e values. From these plots the values of K_f and $1/n$ were found to be 1.2 and 0.2 for Cd(II) biosorption and 4.3 and 0.4 for Cr(III) biosorption. The $1/n$ values were between 0 and 1 indicating that the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass was favourable at studied conditions. However, the R^2 values were found to be 0.898 for Cd(II) biosorption and 0.957 for Cr(III) biosorption. These results indicate that the Freundlich model was not able to adequately to describe the relationship between the amounts of sorbed metal ions and their equilibrium concentration in the solution. Therefore, it can be concluded that the Langmuir isotherm model best fitted the equilibrium data since it presents higher R^2 values.

The equilibrium data were also subjected to the D–R isotherm model to determine the nature of biosorption processes as phys-

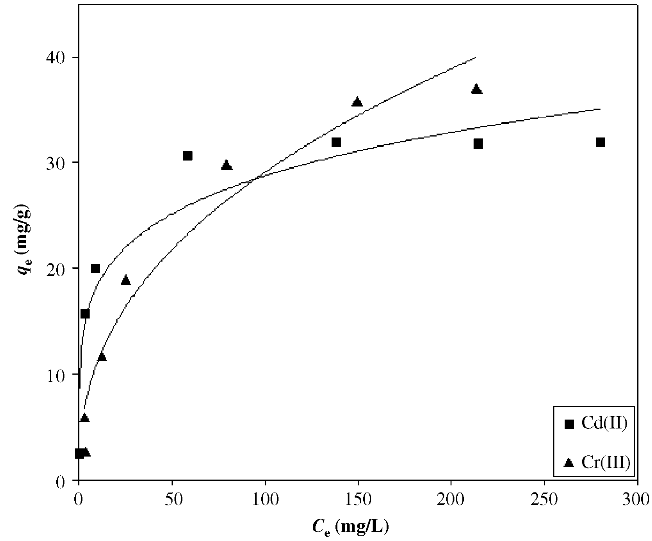

Fig. 6. Freundlich isotherm plots for the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass (biomass dosage: 4 g/L; contact time: 60 min; pH: 5; temperature: 20 °C).

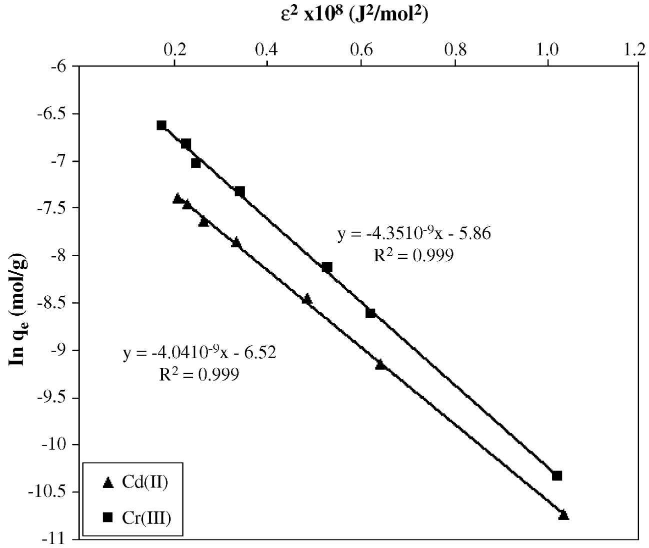

Fig. 7. D–R isotherm plots for the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass (pH: 5; adsorbent dosage: 4 g/L; contact time: 60 min; temperature: 20 °C).

ical 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 [54]. The linear presentation of the D–R isotherm equation [55] is expressed by

$$\ln q_{\mathrm{e}} = \ln q_{\mathrm{m}} - \beta\varepsilon^2 \qquad (4)$$

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

The D–R isotherm model well fitted the equilibrium data since the R^2 value was found to be 0.999 for biosorption of both metal ions (Fig. 7). The q_{m} value was found using the intercept of the plots to be 1.5×10^{-3} mol/g for Cd(II) biosorption and 2.9×10^{-3} mol/g for Cr(III) biosorption. The biosorption mean free energy (E; kJ/mol) is as follows

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

The biosorption mean free energy gives information about biosorption mechanism. If E value is between 8 and 16 kJ/mol, the biosorption process follows by chemical ion-exchange and if $E < 8$ kJ/mol, the biosorption process is of a physical nature [18,56,57]. The mean biosorption energy was calculated as 11.2 and 10.7 kJ/mol for the biosorption of Cd(II) and Cr(III) ions, respectively. These results suggest that the biosorption processes of both metal ions onto *H. splendens* biomass could be taken place by chemical ion-exchange mechanism because the sorption energies lie within 8–16 kJ/mol.

3.6. Biosorption kinetics

The prediction of biosorption rate gives important information for designing batch biosorption systems. Information on the kinetics of pollutant uptake is required for selecting optimum operating conditions for full-scale batch process. In order to clarify the biosorption kinetics of Cd(II) and Cr(III) ions onto *H. splendens* biomass two kinetic models, which are Lagergren's pseudo-first-order and pseudo-second-order model were applied to the experimental data.

The linear form of the pseudo-first-order rate equation by Lagergren [58] is given as

$$\ln(q_{\mathrm{e}} - q_{\mathrm{t}}) = \ln q_{\mathrm{e}} - k_1 t \qquad (6)$$

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 equation (min^{-1}). The biosorption rate constants (k_1) can be determined experimentally by plotting of ln ($q_{\mathrm{e}} - q_{\mathrm{t}}$) versus t.

The plots of ln ($q_{\mathrm{e}} - q_{\mathrm{t}}$) 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. It can be concluded from the R^2 values in Table 2 that the biosorption mechanisms of Cd(II) and Cr(III) ions onto *H. splendens* biomass does not follow the pseudo-first-order kinetic model. Moreover, from Table 2, it can be seen that the experimental values of $q_{\mathrm{e,exp}}$ are not in good agreement with the theoretical values calculated ($q_{\mathrm{e1,cal}}$) from Eq. (6). Therefore, the pseudo-first-order model is not suitable for modeling the biosorption of Cd(II) and Cr(III) onto *H. splendens*.

Table 2
Kinetic parameters obtained from pseudo-first-order and pseudo-second-order for Cd(II) and Cr(III) bisorption onto *H. splendens* biomass at different temperatures

	Temperature (°C)	$q_{\mathrm{e,exp}}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
			k_1 (1/min)	$q_{\mathrm{e1,cal}}$ (mg/g)	R^2	k_2 (g/mg min)	$q_{\mathrm{e2,cal}}$ (mg/g)	R^2
Cd(II)	20	0.87	6.6×10^{-2}	0.34	0.974	0.52	1.03	0.995
	30	0.84	5.3×10^{-2}	0.32	0.962	0.43	0.97	0.998
	40	0.82	4.9×10^{-2}	0.27	0.972	0.35	0.94	0.997
	50	0.68	3.8×10^{-2}	0.21	0.967	0.23	0.93	0.998
Cr(III)	20	0.90	6.4×10^{-2}	0.30	0.972	0.36	1.11	0.999
	30	0.87	5.1×10^{-2}	0.27	0.985	0.35	1.07	0.999
	40	0.82	4.3×10^{-2}	0.22	0.963	0.29	0.99	0.998
	50	0.73	3.2×10^{-2}	0.21	0.955	0.16	0.97	0.999

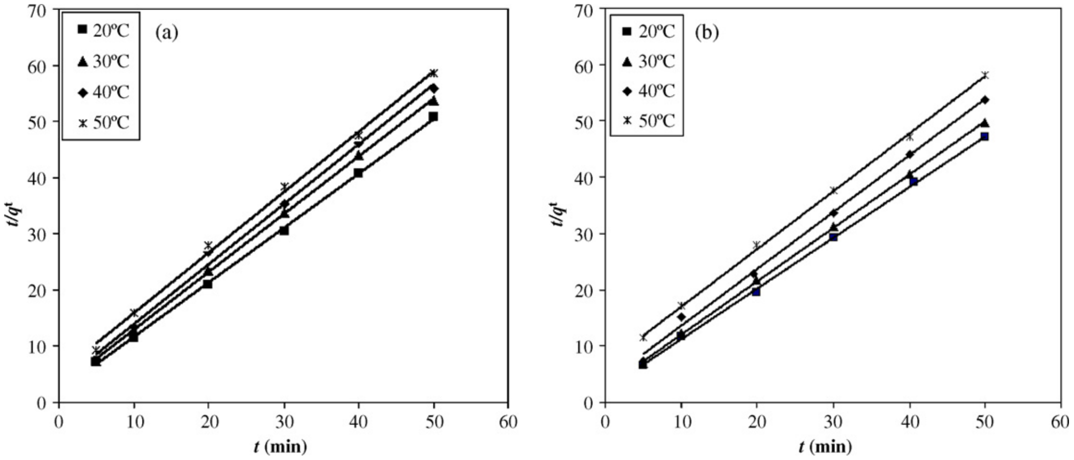

Fig. 8. Pseudo-second-order kinetic plots at different temperatures: (a) for Cd(II) biosorption (b) for Cr(III) biosorption.

Experimental data were also tested by the pseudo-second-order kinetic model which is given in the following form [59]:

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

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 [60]. The linear plots of t/q_t versus t for the pseudo-second-order model for the biosorption of Cd(II) and Cr(III) ions onto *H. splendens* at 20–50 °C were shown in Fig. 8a and b, respectively. The rate constants (k_2), the R^2 and q_e values are given in Table 2. It is clear from these results that the R^2 values are very high (in range of 0.995–0.998 for the Cd(II) biosorption and 0.998–0.999 for the Cr(III) biosorption). In addition, the theoretical $q_{e2,cal}$ values were closer to the experimental $q_{e,exp}$ values (Table 2). 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 Cd(II) and Cr(III) onto *H. splendens* in contrast to the pseudo-first-order model.

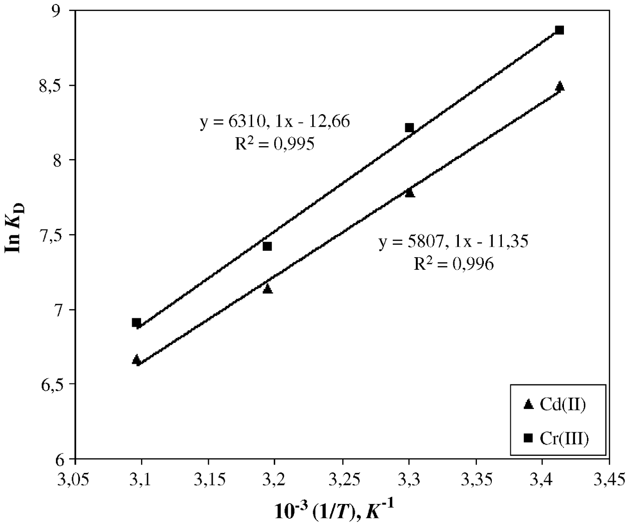

Fig. 9. Plot of ln K_D vs. $1/T$ for the estimation of thermodynamic parameters for biosorption of Cd(II) and Cr(III) onto *H .splendens* biomass.

3.7. Biosorption thermodynamics

In order to describe thermodynamic behaviour of the biosorption of Cd(II) and Cr(III) ions onto *H. splendens* biomass, thermodynamic parameters including the change in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were calculated from following equations

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

where R is the universal gas constant (8.314 J/mol K), T the temperature (K) and K_D (q_e/C_e) is the distribution coefficient [61,62].

The enthalpy (ΔH°) and entropy (ΔS°) parameters were estimated from the following equation

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

According to Eq. (9), the ΔH° and ΔS° parameters can be calculated from the slope and intercept of the plot of ln K_D versus $1/T$ yields, respectively (Fig. 9). Gibbs free energy change (ΔG°) was calculated to be −16.8, −15.0, −13.7, and −12.1 kJ/mol for Cd(II) biosorption and −20.7, −19.6, −18.6, and −17.9 kJ/mol for the biosorption of Cr(III) 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 ΔH° parameter was found to be −48.3 and −52.5 kJ/mol for Cd(II) and Cr(III) biosorption, respectively. The negative ΔH° indicates the exothermic nature of the biosorption processes at 20–50 °C. The ΔS° parameter was found to be −97.8 J/mol K for Cd(II) biosorption and −105.2 J/mol K for Cr(III) 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) and Cr(III) ions onto *H. splendens* biomass from aqueous solution. The operating parameters, pH of solution, biomass dosage, contact time, and temperature, were effective on the biosorption efficiency of Cd(II) and Cr(III). The monolayer biosorption capacity of *H. splendens* biomass was found to be 34.3 and 41.2 mg/g for Cd(II) and Cr(III) ions, respectively. The mean free energy values evaluated from the D–R model indicated that the biosorption of Cd(II) and Cr(III) onto *H. splendens* biomass was taken place by chemical ion-exchange. The kinetic data signified that the biosorption of Cd(II) and Cr(III) ions onto *H. splendens* followed well the pseudo-second-order kinetic model. The thermodynamic calculations showed the feasibility, exothermic and spontaneous nature of the biosorption of Cd(II) and Cr(III) ion onto *H. splendens* biomass at 20–50 °C. It can be also concluded that the *H. splendens* is an effective and alternative biomass for the removal of Cd(II) and Cr(III) ions from aqueous solution because of its reasonable biosorption capacity and its being of natural and abundant available, and thus cost-effective.

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