

## Biosorption of cadmium(II) from aqueous solution onto *Hydrilla verticillata*

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**Abstract** Biosorption is an effective method to remove heavy metals from wastewater. In this work, the biosorption of Cd(II) onto *Hydrilla verticillata* was examined in aqueous solution with parameters of initial pH, adsorbent dosage, contact time, initial Cd(II) concentration, temperature, and co-existing ion. Linear Langmuir and Freundlich models were applied to describe the equilibrium isotherms, and both of the two models were fitted well. The monolayer adsorption capacity of Cd(II) was found to be 50 mg/g at pH 6 and 20°C. Dubinin–Radushkevich isotherm model was also applied to the equilibrium data. The mean free energy of adsorption (11.18 kJ/mol) indicated that the adsorption of Cd(II) onto *H. verticillata* might be carried out via chemical ion-exchange mechanism. Thermodynamic parameters, including free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ), and entropy ( $\Delta S^0$ ) of adsorption, were also calculated. These results showed that the biosorption of Cd(II) onto *H. verticillata* was a feasible, spontaneous, and exothermic process in

nature. Desorption experiments indicated that 0.01 mol/L EDTA and HNO<sub>3</sub> were efficient desorbents for the recovery of Cd(II) from biomass. IR spectrum analysis suggested that amido, hydroxyl, C=O and C–O could combine strongly with Cd(II). EDX spectrum analysis suggested that an ion exchange mechanism might be involved.

**Keywords** Cd(II) · *Hydrilla verticillata* · Adsorption isotherm · Thermodynamics · EDX

### Introduction

Pollution by toxic heavy metals is a global environmental problem. Heavy metals are nonbiodegradable and can be accumulated in living organisms (Liu and Xu 2007). Cadmium is a dangerous pollutant originating from metal plating, metallurgical alloying, mining, ceramics, and other industrial operations (Ramiro et al. 2004). Cadmium is a nonessential element for organisms and its high toxicity for humans has been recognized (Strobel et al. 2001), for example, it can provoke high blood pressure, kidney damage, and probable cancer (Namasivayam and Ranganathan 1995).

The removal and recovery of heavy metals from wastewater is more important to protect public health and environment (Chen et al. 2008; César and Marco 2004; Francesca et al. 2003; Guangyu and Thiruvenkatachari 2003). Conventional methods of heavy metals to removal at high concentrations from aqueous solutions include ion-exchange (Korchagin and Poluektov 2006), solvent extraction, chemical precipitation, phytoextraction, electrodialysis (Terashima et al. 1986), reverse osmosis and ultrafiltration (Antonina et al. 2004; Blöcher et al. 2003). However, these methods have been found to be inefficient or expensive when heavy metals are presented in low

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concentrations (Deng et al. 2007a). Therefore, it is necessary to develop new technologies or materials for removing heavy metal ions from wastewater.

Biosorption process offers advantages of low operating costs, minimization of the volume of chemical and/or biological sludge to dispose and high efficiency in detoxifying very dilute effluents (Marques et al. 2000). It is an economical and effective method to remove heavy metals from wastewater (Choong and Kwang 2005; Núria et al. 2003; Saadet et al. 2005; Yekta et al. 2005). Marine algae with large available quantities in many regions are a kind of promising biological resources (Deng et al. 2007b). Many studies have shown that algae possess high metal binding capacities, due to the presence of polysaccharides, proteins or lipid on the cell wall surface containing functional groups such as amino, hydroxyl, carboxyl, and sulphate, which could act as binding sites for metals (Deng et al. 2007a; Olga et al. 2008; Patricia et al. 2006; Sheng et al. 2004; Vítor et al. 2007).

*Hydrilla verticillata* is a perennial submerged macrophyte, growing in rivers, lakes, pools, and drain, which also can be easily adapted and comparatively quickly bred. *H. verticillata* grows extensively in shallow lakes in China. Therefore, utilizing these affluent resources to treat wastewater is of much interest and absolutely doable.

## Materials and methods

### Materials

The content of crude cellulose in dry matter is one of the main factors of affecting the biosorption capacity of a submerged aquatic plant, and –OH and –CONH<sub>2</sub> groups of polysaccharides on cell wall are maybe the active center of biosorption. The content of crude cellulose of *H. verticillata* in dry matter almost 30 percent (Table 1), therefore, *H. verticillata* should have greater adsorption capacity.

*H. verticillata* was collected from the pool, not far from the Hunan University in Changsha, Hunan. *H. verticillata* was washed with distilled water to separate the remains of sediment and particulate matters, dried at 70°C for 24 h, then pulverized in a mini-size plant pulverizer and ground to pass through a 0.5 mm sieve.

All chemicals used in this research were of analytical reagent grade. Deionised water was used for all dilutions.

**Table 1** Comparison of chemical components of *Hydrilla verticillata*

Moisture	Dry matter	The content in dry matter						Reference
		Crude protein	Crude fat	Ash content	Crude cellulose	Nitrogen free extract		
91.49	8.51	23.97	2.00	18.45	29.26	26.32		Wei et al. 1996

### Equipments

A E-201-C pH meter (Shanghai China) was used for measuring pH values in the aqueous solution. A Perkin-Elmer Analyst 6800 flame atomic absorption spectrometer with deuterium background corrector was used. All measurements were carried out in air/acetylene flame. A 10 cm long slot burner head, a lamp, and an air/acetylene flame were used. All the measurements were made under optimized parameters given as follows: lamp current 2 mA; wavelength 228.8 nm, bandwidth 0.5 nm, range 0.01–0.4 mg/L.

FT-IR spectroscopy was used to detect vibration frequency change in the *H. verticillata*. The spectra were collected by Avatar-360 spectrometer within the range 400–4,000 per centimeter using a KBr window. The background obtained from the scan of pure KBr was automatically subtracted from the sample spectra. All spectra were plotted using the same scale on the transmittance axis.

The scanning electron microscope (SEM) (JSM-5610LV) was used to take microscopic pictures of the biomass. The SEM is equipped with a spectrometer capable of detecting X-rays emitted by the specimen during electron-beam excitation. These X-rays carry the characteristics of energy and wavelength, which can reveal the elemental composition of the specimen.

### Batch adsorption procedure

To optimize pH, contact time and adsorbent dosage and initial concentration, batch sorption experiments were performed at 20°C. Adsorption experiments for Cd(II) were conducted in the pH range from 1.5 to 7, adsorbent dosage from 0.02 to 0.3 g, initial concentration from 10 to 100 mg/L, and contact time ranging from 10 min to 4 h. The pH value of the solution was adjusted by using 0.1 N NaOH or 0.1 N HNO<sub>3</sub>. The effects of competitive ions were also studied after adding lead, copper and nickel, respectively, and in the combinations of lead + copper, lead + nickel, copper + nickel, and lead + copper + nickel at concentration 50 mg/L, respectively.

To study the thermodynamics of adsorption, a series of experiments were conducted at 20–50°C. Adsorption experiments were carried out at the desired pH value (pH 6), contact time (120 min) and adsorbent dosage (0.1 g)

and different initial concentrations from 10 to 100 mg/L. The samples in PVC bottle were shaken in a thermostatic reciprocating shaker at 200 rpm. The bottle samples were filtered through filter paper, and the filtrate was analyzed for metal concentration by using flame AAS. All the experiments were done in triplicate, and the mean of all the three results were reported.

The percent adsorption of metal ion was calculated as follows:

$$\text{Adsorption (\%)} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

where  $C_0$  and  $C_e$  are the initial and final metal concentrations (mg/L), respectively.

#### Adsorption isotherm models

Three important isotherm models were selected in this study, namely Langmuir, Freundlich, and Dubinin–Radushkevich (D–R) isotherm models.

The mathematical expression of the Langmuir isotherm is:

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

where  $C_e$  is equilibrium concentration of metal (mg/L) and  $q_e$  is the amount of the metal adsorbed (mg) by per unit of the adsorbent (g).  $q_m$  and  $K_L$  are Langmuir constants evaluated from slope and intercept of the linear plots of  $C_e/q_e$  versus  $C_e$ , respectively.

Based on the further analysis of Langmuir equation, the dimensionless parameter of the equilibrium or adsorption intensity ( $R_L$ ) can be expressed by

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

where  $C_0$  (mg/L) is the initial amount of adsorbate. The  $R_L$  parameter is considered as one more reliable indicator in the adsorption. There are four probabilities for the  $R_L$  value: (1) for favorable adsorption,  $0 < R_L < 1$ , (2) for unfavorable adsorption,  $R_L > 1$ , (3) for linear adsorption,  $R_L = 1$ , and (4) for irreversible adsorption,  $R_L = 0$  (Angove et al. 1997; Ho et al. 2002).

The logarithmic form of the Freundlich model is given by the equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where  $K_F$  and  $n$  are Freundlich constants incorporating all factors affecting the adsorption process, such as adsorption capacity and intensity of adsorption. These constants were determined from the intercept and slope of linear plot of  $\log q_e$  versus  $\log C_e$ , respectively.

The adsorption data were also modeled by D–R isotherm to determine the adsorption type (physical or chemical). The linear form of this model is expressed by

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (5)$$

where  $q_e$  is the amount of the metal adsorbed onto per unit dosage of the adsorbent (mol/L);  $q_m$ , the monolayer adsorption capacity (mol/g);  $\beta$ , the activity coefficient related to mean sorption energy (mol<sup>2</sup>/J<sup>2</sup>); and  $\varepsilon$  is the Polanyi potential ( $\varepsilon = RT \ln(1 + 1/C_e)$ ). The mean sorption energy  $E$  (kJ/mol) can be calculated using the following equation (Benhammou et al. 2005; El-Shahawi and Nassif 2003)

$$E = \frac{1}{\sqrt{2\beta}} \quad (6)$$

#### Thermodynamics of adsorption

Thermodynamic parameters can be determined using the equilibrium constant,  $K$  ( $q_e/C_e$ ), which depends on temperature. The change in free energy ( $\Delta G^0$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ ) associated to the adsorption process were calculated by using following equation (El-Shahawi and Nassif 2003; Liu and Xu 2007).

$$\Delta G^0 = -RT \ln K \quad (7)$$

where  $R$  is the universal gas constant (8.314 J/mol K) and  $T$  is temperature (K).

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

According to Eq. 8,  $\Delta H^0$  and  $\Delta S^0$  parameters can be calculated from the slope and intercept of the plot of  $\ln K$  versus  $1/T$  yields, respectively.

#### Effect of competitive ions on adsorption

The effect of competitive ions were studied by using 0.1 g *H. verticillata* and 50 mg/L Cd<sup>2+</sup> solution containing lead, copper and nickel separately and in the combinations of lead + copper, lead + nickel, copper + nickel, and lead + copper + nickel at concentration 50 mg/L, respectively.

#### Desorption experiments

For desorption studies, 0.1 g of *H. verticillata* was loaded with Cd<sup>2+</sup> using 50 mL of 50 mg/L Cd<sup>2+</sup> solution at pH 6 at room temperature (25°C) for 120 min of contact time. Cd<sup>2+</sup>-loaded *H. verticillata* was collected, gently washed with distilled water. Then, the *H. verticillata* was contacted with 50 mL of various desorbents including ethylenediamine tetraacetic acid (EDTA), HCl, and HNO<sub>3</sub> (Deng et al. 2007a).

The final concentration of  $\text{Cd}^{2+}$  in the aqueous phase was determined by Atomic Absorption Spectrometry (AAS). The desorption ratio of  $\text{Cd}^{2+}$  from *H. verticillata* was calculated from the amount of  $\text{Cd}^{2+}$  adsorbed on the *H. verticillata* and the final concentration of  $\text{Cd}^{2+}$  in the desorption medium.

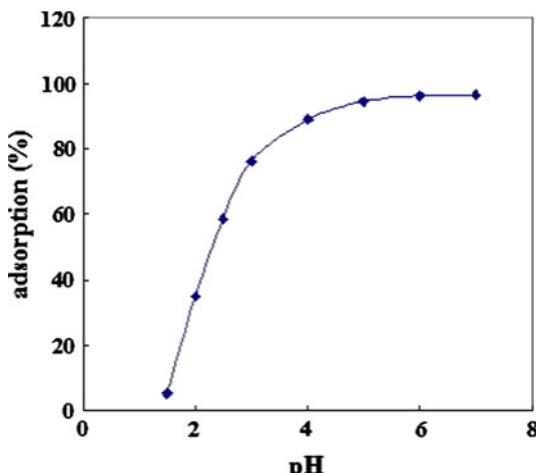
## Results and discussion

### Effect of pH

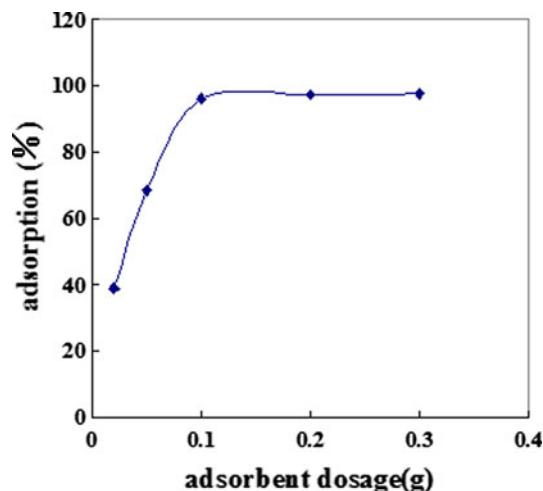
The pH of solution has been identified as the most important variable affecting metal adsorption onto adsorbent (Ho 2005). This is partly because hydrogen ions themselves are strongly competing with adsorbate. The removal of  $\text{Cd}^{2+}$  as a function of hydrogen ion was examined at pH 1.5–7. The removal efficiency was found to be highly dependent on hydrogen ion concentration of solution. The effect of pH on adsorption efficiency was shown in Fig. 1. At low pH, there was clear competition between  $\text{Cd}^{2+}$  and protons for biomass adsorption sites. As pH was increased, the adsorption efficiency increased, and the high adsorption efficiency was obtained at pH 5–7. At pH values higher than 7, the cadmium hydroxide precipitation was observed. The adsorption efficiency was 96% at pH 6, and this pH value was selected as the optimum pH for further studies.

### Effect of adsorbent dosage

The influence of adsorbent dosage on the adsorption of  $\text{Cd}^{2+}$  is shown in Fig. 2. The adsorption of the metals increased with the increasing dosage of the *H. verticillata*, and the adsorption was almost constant at dosages higher



**Fig. 1** Effect of pH on the adsorption of Cd(II) onto *Hydrilla verticillata*



**Fig. 2** Effect of adsorbent dosage on the adsorption of Cd(II) onto *Hydrilla verticillata*

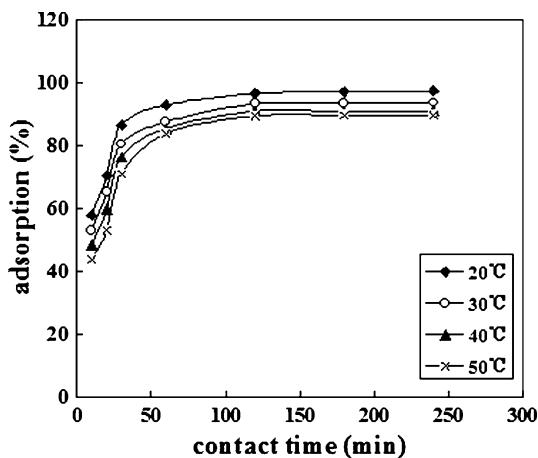
than 0.1 g. With the adsorbent dosage increases, more surface area was available for adsorption due to the increase in active sites on the adsorbent, which resulted in easier penetration of metal ions to the sorption sites (Ahmed et al. 2007).

### Effects of contact time and temperature

The effect of contact time on the adsorption of  $\text{Cd}^{2+}$  onto *H. verticillata* at the temperature range from 20 to 50°C was shown in Table 2 and Fig. 3. It can be seen that the adsorbed amount of  $\text{Cd}^{2+}$  increased with contact time up to 120 min, and on this point, it attained the maximum removal. Therefore, 120 min was selected as the optimum contact time for all further experiment. Figure 3 also showed the effect of the temperature on the adsorption of Cd(II) onto *H. verticillata*. The maximum adsorption ratios were found to be 96, 93, 91, and 89% at 20, 30, 40, and 50°C, respectively. A slow decrease in the adsorption of Cd(II) with the rise in temperature was due to the

**Table 2** Effect of contact time and temperature on the adsorption of Cd(II) onto *Hydrilla verticillata* (metal concentration 50 mg/L, adsorbent dosage 0.1 g, pH 6)

Contact time (min)	$C_e$ (mg/L)				Adsorption (%)			
	20°C	30°C	40°C	50°C	20°C	30°C	40°C	50°C
10	21.15	23.6	25.95	28.2	57.7	52.8	48.1	43.6
20	14.85	17.4	20.25	23.55	70.3	65.2	59.5	52.9
30	6.8	9.85	11.9	14.6	86.4	80.3	76.2	70.8
60	3.6	6.25	7.2	8.2	92.8	87.5	85.2	83.6
120	1.75	3.4	4.6	5.4	96.5	93.2	90.8	89.2
180	1.55	3.35	4.6	5.3	96.9	93.3	90.8	89.4
240	1.4	3.25	4.5	5.25	97.2	93.5	91.0	89.5



**Fig. 3** Effect of contact time and temperature on the adsorption of Cd(II) onto *Hydrilla verticillata*

increasing tendency to desorb from the interface to the solution. This result also indicated that the adsorption process of Cd(II) onto *H. verticillata* was exothermic.

#### Adsorption isotherms

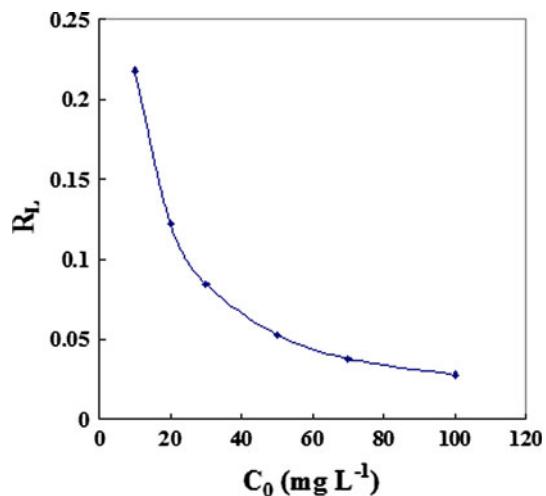
The equilibrium data (Table 3) obtained for the adsorption of Cd(II) onto *H. verticillata* were fitted to linear Langmuir equation (Eq. 2). Linear plot of  $C_e/q_e$  versus  $C_e$  was examined to determine  $q_m$  and  $K_L$  values. The values were given in Table 2. The high coefficient of determination ( $R^2 = 0.9852$ ) and the low standardized residual ( $\sigma_r = 0.0151$ ) of the plot show that the linear Langmuir equation gives a good fit to the adsorption isotherm for the adsorption of Cd(II) onto *H. verticillata* at 20°C.

The variation of the adsorption intensity ( $R_L$ ) with the initial concentration of the solution ( $C_0$ , mg/L) was shown in Fig. 4. The  $R_L$  value ranges from 0.028 to 0.218 between 10 and 100 mg/L and approaches zero with increase in the  $C_0$  value. This parameter ( $0 < R_L < 1$ ) indicates that the *H. verticillata* is a suitable adsorbent for the adsorption of Cd(II) from aqueous solution.

The equilibrium data were also fitted to linear Freundlich equation (Eq. 4) for the adsorption of Cd(II) onto *H. verticillata*. A fairly satisfactory empirical isotherm can

**Table 3** Adsorption isotherms data (adsorbent dosage 0.1 g, pH 6, temperature 20°C)

No	$C_0$ (mg/L)	$C_e$ (mg/L)	$q_e$ (mg/g)	$C_e/q_e$	$\lg C_e$	$\lg q_e$	$R_L$
1	10	0.2	4.9	0.04	-0.7	0.69	0.218
2	20	0.56	9.72	0.06	-0.25	0.99	0.122
3	30	1.26	14.4	0.09	0.1	1.16	0.085
4	50	3.45	23.5	0.13	0.54	1.37	0.053
5	70	6.09	32.0	0.19	0.78	1.51	0.038
6	100	14.6	42.7	0.34	1.16	1.63	0.028



**Fig. 4** Variation of adsorption intensity ( $R_L$ ) with initial metal concentration ( $C_0$ : mg/L)

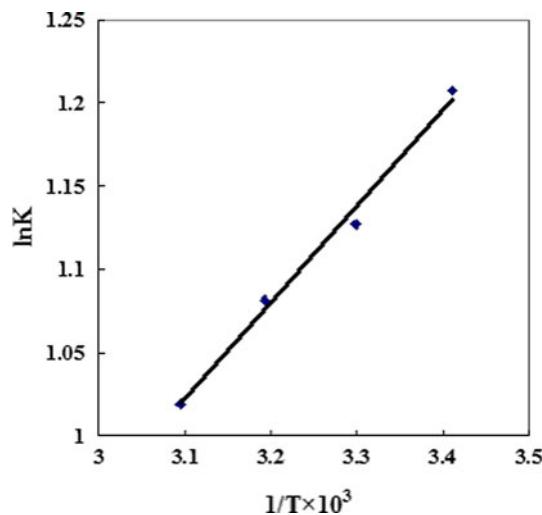
be used for nonideal adsorption because the coefficient of determination ( $R^2$ ) was 0.9901 and the standardized residual ( $\sigma_r$ ) was 0.0388 (Table 2). From the linear plot of Freundlich isotherm,  $K_F$  and  $1/n$  were found to be 12.2 L/g and 0.5061, respectively. The Freundlich constant  $1/n$  smaller than 1 indicates that the adsorption of Cd(II) onto *H. verticillata* was favorable under the studied conditions. However, the Freundlich isotherm model ( $R^2 = 0.9901$ ) fitted the equilibrium data better than the Langmuir isotherm model ( $R^2 = 0.9852$ ) obtained for the biosorption of Cd(II) onto *H. verticillata*. The similar results were reported for Cd(II) biosorption onto biomatrix from rice husk (Krishnani et al. 2008).

On the other hand, the adsorption data were also applied to the D–R isotherm model based on the heterogeneous surface of the adsorbate in order to distinguish between physical and chemical adsorption. The equilibrium data were also fitted to linear D–R equation (Eq. 5) for the adsorption of Cd(II) onto *H. verticillata* at 20°C. The  $\beta$  constant and monolayer sorption capacity ( $q_m$ ) were calculated from the slopes and intercept of the plot. The  $\beta$  constant and the  $q_m$  value were found to be  $4 \times 10^{-3}$  mol<sup>2</sup>/kJ<sup>2</sup> and  $2.47 \times 10^{-3}$  mol/g, respectively (Table 2).

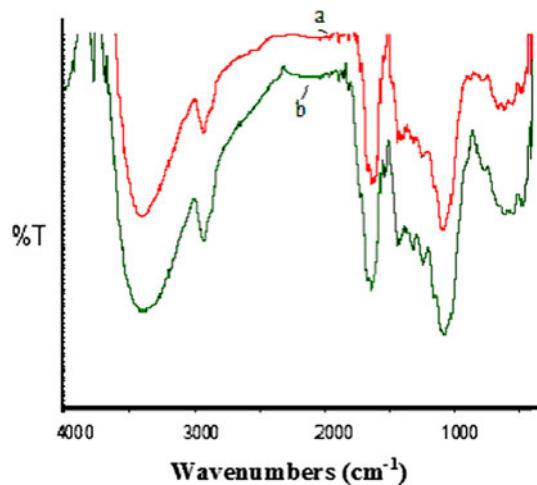
The mean sorption energy  $E$  can judge adsorption mechanism as chemical ion-exchange or physical adsorption. If  $E$  value is between 8 and 16 kJ/mol, the adsorption process follows chemical ion-exchange, and if  $E < 8$  kJ/mol, the adsorption is physical in nature (Ho and McKay 1998). From Eq. 6, the numerical value of  $E$  was calculated as 11.18 kJ/mol, indicating that the adsorption process may be carried out via chemical ion-exchange mechanism.

#### Thermodynamic parameters of adsorption

From Eq. 7, Gibbs free energy change of adsorption ( $\Delta G^0$ ) was calculated using  $\ln K$  values for different temperatures.



**Fig. 5** Plot of  $\ln K$  versus  $1/T$  for estimation of thermodynamic parameters for the adsorption of Cd(II) onto *Hydrilla verticillata*



**Fig. 6** FT-IR spectrum of the *Hydrilla verticillata* (a) and Cd-loaded (b)

It was found to be  $-2.94$ ,  $-2.84$ ,  $-2.82$  and  $-2.72$  kJ/mol for the adsorption of Cd(II) onto *H. verticillata* at  $293$ ,  $303$ ,  $313$ , and  $323$  K, respectively. The negative  $\Delta G^0$  values

indicated that the adsorption of Cd(II) onto *H. verticillata* was feasible and spontaneously thermodynamical. In addition, the increase in  $\Delta G^0$  values with increase in temperature showed that the adsorption was not favorable at higher temperatures. The enthalpy change ( $\Delta H^0$ ) and entropy change ( $\Delta S^0$ ) for the adsorption process were obtained from the  $\ln K$  versus  $1/T$  plot (Fig. 5). The  $\Delta H^0$  parameter had a value of  $-4.99$  kJ/mol. The negative  $\Delta H^0$  value indicated exothermic nature of the adsorption (Ahmel et al. 2007). The  $\Delta S^0$  parameter was found to be  $-7.00$  J/mol/K. The negative value of  $\Delta S^0$  suggested a decrease in the randomness at solid/solution interface during the adsorption of Cd(II) ion onto *H. verticillata* (Ahmel et al. 2007).

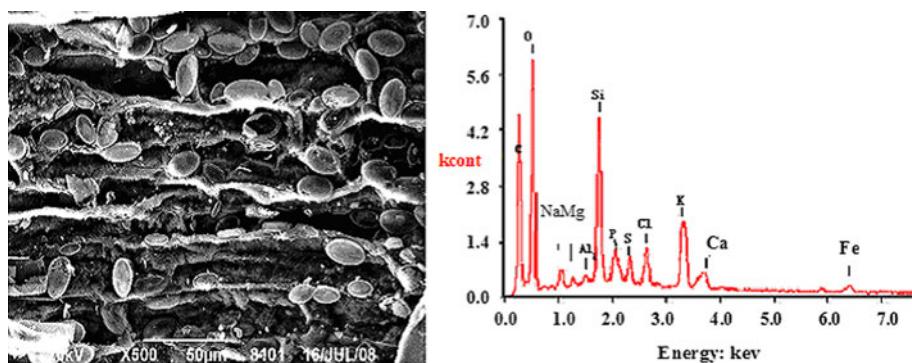
#### FT-IR spectrum of *Hydrilla verticillata*

The absorbance spectrum of *H. verticillata* and that loaded with Cd(II) was shown in Fig. 6. Some intense characteristic bands were obtained from the functional groups presented in proteins and polysaccharides. The broad bands observed at  $3,400$  per centimeter were due to O–H and N–H stretching vibration. The spectra bands at  $1,634$ ,  $1,542$ , and  $1,438$  per centimeter reflected acylamide I ( $-\text{C}=\text{O}$  stretching vibration), acylamide II (N–H bending vibration and C–N stretching vibration) and acylamide III (C–N bending vibration and stretching vibration), respectively. The spectra peak at  $1,088$  per centimeter represented C–OH stretching vibration. Some bands in the fingerprint region could be attributed to phosphate groups (Chen et al. 2000). After adsorbing Cd(II), the peaks at  $3,400$ ,  $1,634$ , and  $1,088$  per centimeter were shifted to  $3,385$ ,  $1,624$ , and  $1,080$  per centimeter, respectively, which suggested that amido, hydroxyl,  $\text{C}=\text{O}$  and  $\text{C}–\text{O}$  could combine strongly with Cd(II).

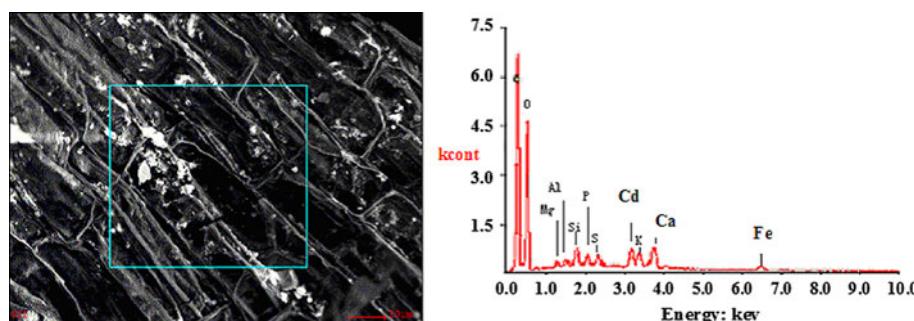
#### EDX spectrum of *Hydrilla verticillata*

Fresh and the  $\text{Cd}^{2+}$ -loaded *H. verticillata* were analyzed by SEM equipped with EDX (Figs. 7, 8). For the fresh *H.*

**Fig. 7** SEM image and EDX spectrum of *Hydrilla verticillata*



**Fig. 8** SEM image and EDX spectrum of Cd<sup>2+</sup>-loaded *Hydrilla verticillata*



*verticillata*, Fig. 7 showed that C, O and Si constituted the three major elements of *H. verticillata*, K, Ca, Na, Mg, and Fe constituted major metal elements of *H. verticillata*, and Cd signal was not detected in the EDX spectrum of the fresh *H. verticillata* (i.e., there was no Cd present or the amount of Cd could be negligible in the fresh *H. verticillata*). After Cd<sup>2+</sup> biosorption, the Cd signal was clearly observed in Fig. 8 for the Cd<sup>2+</sup>-loaded *H. verticillata* (i.e., a remarkable amount of Cd was adsorbed by *H. verticillata*). Simultaneously, Fig. 8 showed that the peaks of K and Na were reduced, which suggested that an ion exchange mechanism might be involved.

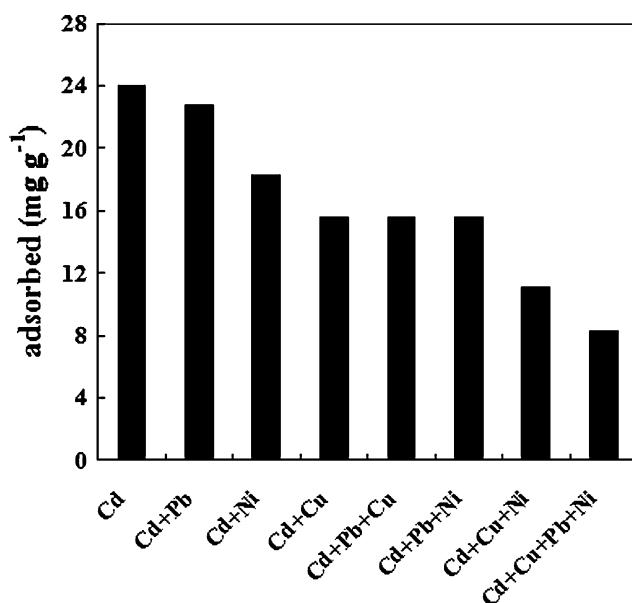
#### Effect of competitive ions

Effect of competitive ions was studied after addition of lead, copper and nickel separately and in the combinations of lead + copper, lead + nickel, copper + nickel, and lead + copper + nickel at concentration 50 mg/L, respectively. The

influence of competitive ions on adsorption of Cd<sup>2+</sup> onto *H. verticillata* was shown in Fig. 9. It was found that the influence increased in the order of Pb(II) < Ni(II) < Cu(II) < Pb(II) + Cu(II) < Pb(II) + Ni(II) < Ni(II) + Cu(II) < Pb(II) + Ni(II) + Cu(II). The observed reduction in the biosorption of Cd(II) in the presence of competitive ions could be attributed to the difference in their class behavior on the basis of their covalent indices. Pb(II) is classified as a class b ions, while Cu(II) and Ni(II) are classified as borderline ions. Based on this argument, it is possible to explain the competition effects observed in the present study.

#### Desorption characteristics

In order to apply biosorbent to real wastewater, desorption process of heavy metal ions is very important. In this study, EDTA, HCl, and HNO<sub>3</sub> were used for desorption of lead ions from *H. verticillata*. As shown in Table 3, desorption ratio of cadmium ions using EDTA, HCl, and HNO<sub>3</sub> reached about 85, 79, and 85%, respectively (Tables 4, 5).



**Fig. 9** Effect of competitive ion on the adsorption of Cd(II) onto *Hydrilla verticillata*

**Table 4** Adsorption isotherm constants for the adsorption of Cd(II) onto *Hydrilla verticillata*

Langmuir	Freundlich	D-R
$q_{\max} = 50.0 \text{ mg/g}$	$1/n = 0.5061$	$q_m = 2.47 \times 10^{-3} \text{ mol/g}$
$K_L = 0.3597 \text{ L/g}$	$K_F = 12.2 \text{ L/g}$	$\beta = 4 \times 10^{-3} \text{ mol}^2/\text{kJ}^2$
$r^2 = 0.9852$	$r^2 = 0.9901$	$r^2 = 0.9982$
$\sigma_r = 0.0151$	$\sigma_r = 0.0388$	$E = 11.18 \text{ kJ/mol}$
		$\sigma_r = 0.0386$

**Table 5** Desorption ratio of Cd(II) ions for various desorbents

Desorbent	Concentration (mol/L)	Desorption ratio (%)
EDTA	0.10	85
HCl	0.10	79
HNO <sub>3</sub>	0.10	85

## Conclusions

- For the maximum adsorption, the optimal operating parameters, pH of solution, adsorbent dosage, contact time, and temperature were optimized as 6, 0.1 g, 120 min and 20°C, respectively.
- Linear Langmuir and Freundlich isotherm models were used to represent the experimental data, and both of the two models were fitted well. The monolayer adsorption capacity was obtained as 50 mg/g at the optimal experimental condition.
- The mean free energy of adsorption  $E$  (11.18 kJ/mol) calculated from examination of D–R isotherm indicated that the adsorption of Cd(II) onto *H. verticillata* might be carried out via chemical ion-exchange mechanism.
- The negative  $\Delta G^0$  values showed that the adsorption of Cd(II) onto *H. verticillata* was feasible and spontaneous. The negative  $\Delta H^0$  value depicted exothermic nature of the adsorption. The negative  $\Delta S^0$  value revealed that the orderliness of the adsorbed system was higher than that in the solution phase before adsorption.
- FT-IR spectrum analysis suggested that amido, hydroxyl, C=O and C–O could combine strongly with Cd(II).
- EDX spectrum analysis suggested that an ion exchange mechanism might be involved.
- Cadmium ions adsorbed on *H. verticillata* were desorbed effectively by about 85, 79, and 85% by 0.10 mol/L EDTA, HCl, and HNO<sub>3</sub>, respectively.

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