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ORIGINAL PAPER

Adsorption of lead(II) from aqueous solution onto *Hydrilla verticillata*

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Abstract The adsorption of Pb(II) onto *Hydrilla verticillata* was examined in aqueous solution with parameters of pH, adsorbent dosage, contact time and temperature. The linear Langmuir and Freundlich models were applied to describe equilibrium isotherms, and both models fitted well. The monolayer adsorption capacity of Pb(II) was found as 104.2 mg/g at pH 4 and 25°C. Dubinin–Radushkevich (D–R) isotherm model was also applied to the equilibrium data. The mean free energy of adsorption (15.81 kJ/mol) indicated that the adsorption of Pb(II) onto *H. verticillata* may be carried out via chemical ion-exchange mechanism. Thermodynamic parameters, free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) of adsorption were also calculated. These parameters showed that the adsorption of Pb(II) onto *H. verticillata* was a feasible, spontaneous and exothermic process in nature. The influence of Cd^{2+}, Cu^{2+} and Ni^{2+} on adsorption of Pb^{2+} onto *H. verticillata* was studied, too. In the investigated range of operating conditions, it was found that the existence of Cd $^{2+}$, Cu $^{2+}$ and Ni $^{2+}$ had no impact on the adsorption of Pb^{2+}.

Keywords Pb(II) · *Hydrilla verticillata* · Adsorption isotherm · Thermodynamics

Introduction

Heavy metals are non-degradable in the environment and can be harmful to a variety of living species. Therefore, the removal of these metals from water and wastewater is important in terms of protecting public health and environment (Yan and Thiruvenkatachari 2003; Teixeira and Zezzi Arruda 2004; Pagnanelli et al. 2003). A wide range of industrial applications, including microelectronics, electroplating, battery manufacture, dyestuffs, pharmaceutical and metallurgical chemistry and so on, cause heavy metal pollution in the environment. Therefore, the heavy metal levels in water should be reduced below the maximum permissible concentration. The common methods used for removal of heavy metal ions from aqueous solutions include ion-exchange, solvent extraction, chemical precipitation, ultrafiltration, reverse osmosis, electrodialysis and adsorption (Blöcher et al. 2003; Kryvoruchko et al. 2004; Terashima et al. 1986), among which adsorption is one of the important methods for the removal of heavy metals from the environment (Jeon and Park

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2005; Lâzaro et al. 2003; Saygideger et al. 2005; Liu and Hui 2007).

Lead (Pb) is one of the major environmental pollutants. It enters the water and environment through effluents from lead smelters, battery manufacturers, paper and pulp industries and ammunition industries. The adsorption of Pb(II) from aqueous solution have been investigated by using various adsorbents (Matheickal and Yu 1996; Cabuk et al. 2007; Muraleeddharan et al. 1995; Chang et al. 1997; Martínez et al. 2006; Han et al. 2005; Pavasant et al. 2006; Liu et al. 2006). However, the application of *Hydrilla verticillata* as a cheap and facile adsorbent for the adsorption of metal ion from aqueous solution has not been reported.

Hydrilla verticillata is a perennial submerged plant, growing in rivers, lakes, pools, and drains. It can be adapted easily and bred fairly quickly. *H. verticillata* grows extensively in shallow lakes of our country.

The objective of the present work is to study the adsorption characteristics of the Pb(II) ion from aqueous solution using *H. verticillata*. Well-known isotherm models were applied to analyze the equilibrium data. Thermodynamic parameters were also calculated to describe the adsorption mechanism.

Materials and methods

Materials

Hydrilla 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 60°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. De-ionized water was used for all dilutions.

Equipments

A E-201-C pH meter (Shanghai China) was used for measuring pH values in the aqueous solution.

A PerkinElmer Analyst 700 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 10 mA, wavelength 283.3 nm, bandwidth 0.7 nm; range 0.05–10.0 mg/l.

Batch adsorption procedure

To optimize pH, contact time and *H. verticillata* dosage and initial concentration, batch sorption experiments were performed at 25°C. Sorption experiments for Pb were conducted in the pH range of 1–6, *H. verticillata* dosage of 0.01–0.3 g, initial concentration of 20–500 mg/l and contact time from 10 min to 3 h. pH of the solution was adjusted by using 0.1N NaOH/0.1N HNO_3. The effect of competitive ions was also studied after adding cadmium, copper and nickel, respectively and in the combinations of cadmium + copper, cadmium + nickel, copper + nickel and cadmium + copper + nickel at concentration 100 mg/l, respectively.

To study the thermodynamics of adsorption, a series of experiments were conducted at 25–40°C. Adsorption experiments were carried out at desired pH value (pH 4), contact time (30 min) and adsorbent dosage (0.1 g) and different initial concentrations from 20–500 mg/l. The samples in PVC (polyvinyl chloride) bottle were shaken in a thermostatic reciprocating shaker at 200 rpm. The samples of the bottle were filtered through filter paper and the filtrate was analyzed for metal concentration by using flame AAS (atomic absorption spectrometry). All the experiments were done in triplicate and means of all the three results are reported.

The percent adsorption of metal ion was calculated as follows:

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

The amount of metal ion adsorbed by the biomass was calculated using the following equation:

$$q = (C_i - C_f)\frac{V}{m} \tag{2}$$

where C_i and C_f are the initial and final metal concentrations (mg/l), respectively; q is the amount of metal adsorbed by biomass (mg/g), m is the mass of the biomass in the adsorption medium (g), V is the initial volume of the adsorption medium (L).

Adsorption isotherm models

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

Langmuir and Freundlich isotherm models were applied to establish the relationship between the amount of Pb(II) adsorbed onto *H. verticillata* and its equilibrium concentration in aqueous solution. Langmuir adsorption isotherm is applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented in linear form

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \tag{3}$$

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 vs. 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

$$R_L = \frac{1}{1 + K_L C_0} \tag{4}$$

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 adsorption data obtained were then fitted to the Freundlich adsorption isotherm, which is the earliest known relationship describing the adsorption equilibrium and is expressed in linear form by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

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 vs. log C_e, respectively.

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

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \tag{6}$$

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); β, the activity coefficient related to mean sorption energy (mol^2/J^2) and ε 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)

$$E = \frac{1}{\sqrt{2\beta}}. \tag{7}$$

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 (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) associated to the adsorption process were calculated by using following equation (Liu and Hui 2007; El-Shahawi and Nassif 2003).

$$\Delta G^0 = -RT \ln K \tag{8}$$

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

$$\ln K = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}. \tag{9}$$

According to Eq. 9, ΔH^0 and ΔS^0 parameters can be calculated from the slope and intercept of the plot of ln K vs. $1/T$ yields, respectively.

Desorption experiments

For desorption studies, 0.1 g of *H. verticillata* was loaded with Pb^{2+} using 50 ml of 100 mg/l Pb^{2+} solution at pH 4 and contact time 30 min was given at room temperature (25°C). Pb^{2+}-loaded *H. verticillata* was collected, gently washed with distilled water to remove any unadsorbed Pb^{2+}. Subsequently, *H. verticillata* was contacted with 50 ml of various desorbents including ethylendiamine tetraacetic acid (EDTA), HCl and HNO_3. The final concentration of Pb^{2+} ions in the aqueous phase was determined by means of AAS. The desorption ratio of Pb^{2+} ions from *H. verticillata* was calculated from the amount of Pb^{2+} ions adsorbed on the *H. verticillata* and the final concentration of Pb^{2+} ions in the desorption medium.

Results and discussion

Effect of adsorbent dosage

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate at the operating conditions. The influence of adsorbent dosage on the adsorption of Pb(II) is shown in Fig. 1. The adsorption of the metals increased with the increasing dosage of the *H. verticillata*, and the adsorption was almost constant at dosages higher than 0.1 g. With the increasing adsorbent dosage, more surface area was available for adsorption due to increase in active sites on the adsorbent and thus making easier penetration of metal ions to the sorption sites.

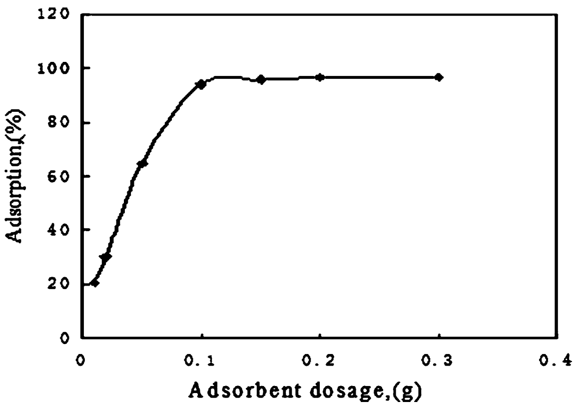


Fig. 1 Effect of adsorbent dosage on the adsorption of Pb(II) onto *Hydrilla verticillata* (Metal concentration: 100 mg/l; pH 4; temperature: 25°C)

Effect of pH

The pH of solution has been identified as the most important variable affecting metal adsorption onto adsorbent (Ho 2005). The removal of Pb(II) as a function of hydrogen ion concentration was examined at pH 1–6. The effect of pH on adsorption efficiency is shown in Fig. 2. The high adsorption was obtained at pH 2.5–6. At pH values higher than 6, the lead hydroxide precipitation was observed. The fact can be explained by competition between protons and lead ions for surface adsorption sites. In addition, as pH is increased there is a decrease of the positive surface charge, which results in a lower coulombic repulsion of lead ions (Martins et al. 2004). The maximum Pb(II) uptake capacity was 48.0 mg/g at pH 4 and this pH value was selected as the optimum pH for further studies.

Effects of contact time and temperature

The effect of contact time on the adsorption of Pb(II) ion onto *H. verticillata* at the temperature range of 25–40°C is shown in Fig. 3. It can be seen that the adsorbed amount of Pb(II) increased with contact time up to 30 min, and after that a maximum removal is attained. Therefore, 30 min was selected as the optimum contact time for all further experiments. Figure 3 also shows the effect of the temperature on

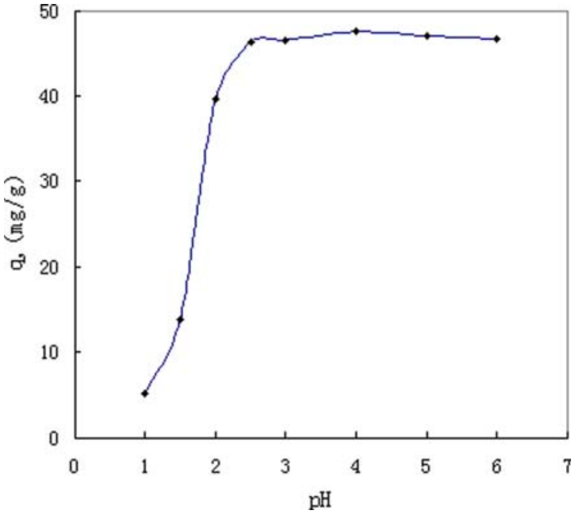


Fig. 2 Effect of pH on the adsorption of Pb(II) onto *H. verticillata* (Metal concentration: 100 mg/l; adsorbent dosage: 0.1 g; temperature: 25°C)

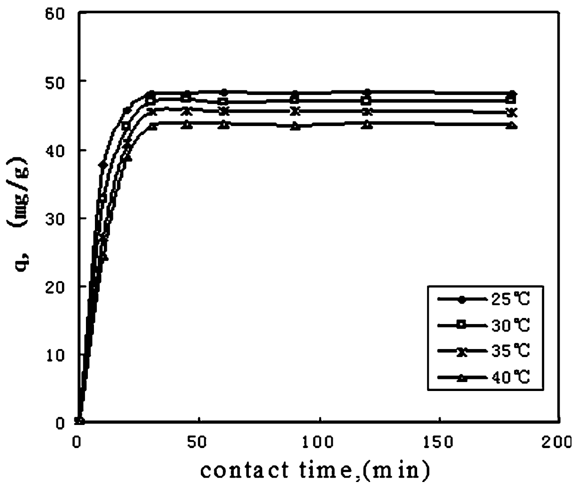


Fig. 3 Effect of contact time and temperature on the adsorption of Pb(II) onto *H. verticillata* (Metal concentration: 100 mg/L; adsorbent dosage: 0.1 g; pH 4)

the adsorption of Pb(II) onto *H. verticillata*. The maximum Pb(II) uptake capacity were found as 48.0, 47.0, 45.5 and 43.5 mg/g at 25, 30, 35 and 40°C, respectively. A decrease in the adsorption of Pb(II) with the rise in temperature was due to the increasing tendency to desorb from the interface to the solution. This result also indicated that the adsorption process of Pb(II) onto *H. verticillata* was exothermic in nature. The optimum temperature for further experiments was selected as 25°C.

Table 2 Uptake capacities for Pb(II) of various adsorbents (at room temperature)

Adsorbent	q_m (mg/g)	pH	Literature
Powder activated carbon	20.7		11
Granulated activated carbon, F-400	31.1		13
Pseudomonas aeruginosa	68.4	5.5	14
Grape stalks	49.7	5.5	15
Chaff	12.4	5.5	16
Caulerpa lentillifera	28.7	5.0	17
Pang Da Hai	27.1	6.5	18
H. verticillata	104.2	4.0	This study

Adsorption isotherms

The isotherm has been of importance in the wastewater treatment by adsorption technique, as it provides estimation of sorption capacity of the adsorbent. The adsorption data obtained for lead using *H. verticillata* as adsorbent were analyzed using Langmuir, Freundlich and D–R equations. The linear plot of C_e/q_e vs. C_e was examined to determine q_m and K_L values. The values are given in Table 1. The Langmuir adsorption maxima q_m was 104.2 mg/g. The adsorption capacity of *H. verticillata* is fairly high in comparison with other adsorbents at room temperature, as shown in Table 2. The high coefficient of determination ($R^2 = 0.9937$) of the plot shows that the linear Langmuir equation gives a good fit to the adsorption isotherm for the adsorption of Pb(II) onto *H. verticillata* at 25°C.

From Eq. 4 the variation of the adsorption intensity (R_L) with the initial concentration of the solution (C_0; mg/l) were calculated. The R_L value ranges from 0.018 to 0.32 between 20 and 500 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 Pb(II) from aqueous solution.

The equilibrium data were also fitted to linear Freundlich equation (Eq. 5) for the adsorption of Pb(II) onto *H. verticillata*. A fairly satisfactory empirical isotherm can be used for non-ideal adsorption because the coefficient of determination (R^2) was 0.9614 (Table 1). From the linear plot of Freundlich isotherm, K_F and $1/n$ were found as 20.7 and 0.2896, respectively. The Freundlich constant $1/n$ smaller than

Table 1 Adsorption isotherm constants for the adsorption of Pb(II) onto *Hydrilla verticillata*

Langmuir	Freundlich	D–R
$q_{max} = 104.2$ mg/g $= 5.03 \times 10^{-4}$ mol/g	$1/n = 0.307$	$q_m = 9.96 \times 10^{-4}$ mol/g
$K_L = 0.108$ l/g	$K_F = 20.7$ l/g^{-}	$\beta = 2 \times 10^{-3}$ mol^2/kJ^2
$r^2 = 0.9937$	$r^2 = 0.9614$	$r^2 = 0.9813$
		$E = 15.81$ kJ/mol

one indicates that the adsorption of Pb(II) onto *H. verticillata* was favorable under studied conditions.

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. 6) for the adsorption of Pb(II) onto *H. verticillata*. The β constant and monolayer sorption capacity (q_m) were calculated from the slopes and intercept of the plot. The β constant and the q_m value were found to be 2×10^{-3} mol^2/kJ^2 and 9.96×10^{-4} mol/g, respectively (Table 1).

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. 7 the numerical value of E was calculated as 15.81 kJ/mol, indicating the adsorption process may be carried out via chemical ion-exchange mechanism.

Thermodynamic parameters of adsorption

From Eq. 8, Gibbs free energy change of adsorption (ΔG^0) was calculated using ln K values for different temperatures. It was found as −3.88, −3.73, −3.52 and −3.38 kJ/mol for the adsorption of Pb(II) onto *H. verticillata* at 298, 303, 308 and 313 K, respectively. The negative ΔG^0 values indicated that the adsorption of Pb(II) onto *H. verticillata* was feasible and spontaneously thermodynamical. In addition, the decrease in ΔG^0 values with increase in temperature showed that the adsorption was not favorable at higher temperatures. The enthalpy change (ΔH^0) and entropy change (ΔS^0) for the adsorption process were obtained from the ln K vs. 1/T plot (Fig. 4). The ΔH^0 parameter had a value of −13.97 kJ/mol. The negative ΔH^0 value indicated exothermic nature of the adsorption. The ΔS^0 parameter was found to be −33.85 J/mol K, implying that the Pb(II) in bulk phase (aqueous solution) was in a much more chaotic distribution compared to the relatively ordered state of solid phase (surface of adsorbent).

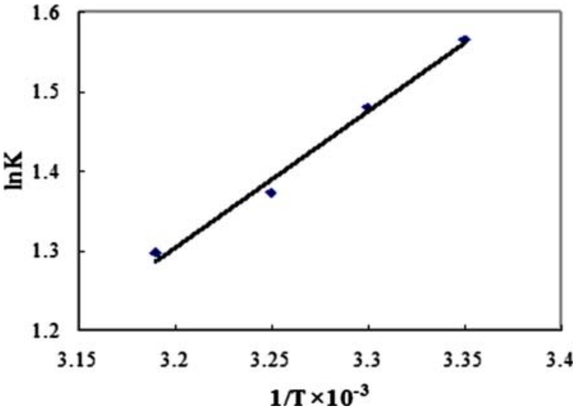


Fig. 4 Plot of ln K vs. 1/T for estimation of thermodynamic parameters for the adsorption of Pb(II) onto *H. verticillata*

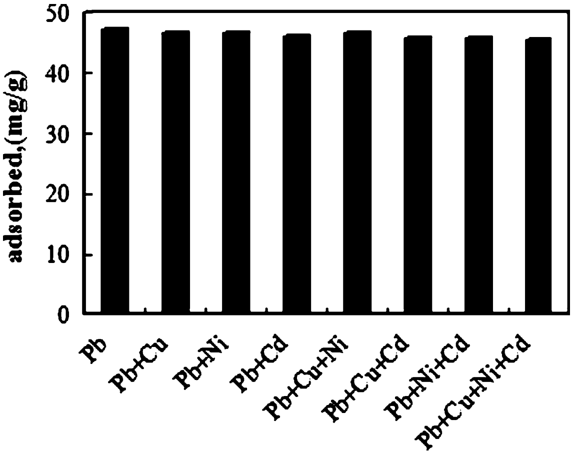


Fig. 5 Effect of competitive ions on the adsorption of Pb(II) onto *H. verticillata* (Metal concentration: 100 mg/l; adsorbent dosage: 0.1 g; temperature: 25°C; pH: 4; contact time: 30 min)

Effect of competitive ions

Effect of competitive ions was studied after addition of cadmium, copper and nickel separately and in the combinations of cadmium + copper, cadmium + nickel, copper + nickel and cadmium + copper + nickel at concentration 100 mg/l, respectively. The influence of competitive ions on adsorption of Pb^{2+} onto *H. verticillata* is shown in Fig. 5. It was found that the existence of Cd^{2+}, Cu^{2+} and Ni^{2+} had no influence on the adsorption of Pb^{2+}.

FT-IR spectrum of *Hydrilla verticillata*

The absorbance spectrum of *H. verticillata* with that loaded with Pb(II) was shown in Fig. 6. Some intense characteristic bands were obtained from the functional groups presented in proteins and polysaccharides. The

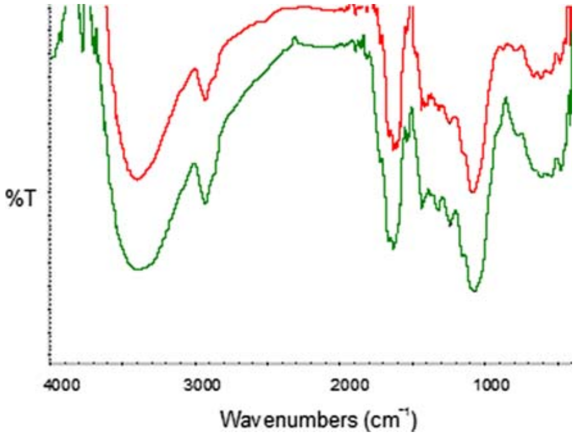


Fig. 6 FT-IR spectrum of the *H. verticillata*

broad bands observed at 3,400 cm^{-1} was due to O–H and N–H stretching vibration. The spectra bands at 1,634, 1,542 and 1,438 cm^{-1} reflected acylamide I (–C=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 cm^{-1} represented C–OH stretching vibration. Some bands in the fingerprint region could be attributed to phosphate groups. After adsorbing Pb(II),the peaks at 3,400, 1,634, and 1,088 cm^{-1} were shifted to 3,385, 1,618, and 1,067 cm^{-1}, respectively, which suggested that amido, hydroxyl, C=O and C–O could combine strongly with Pb(II).

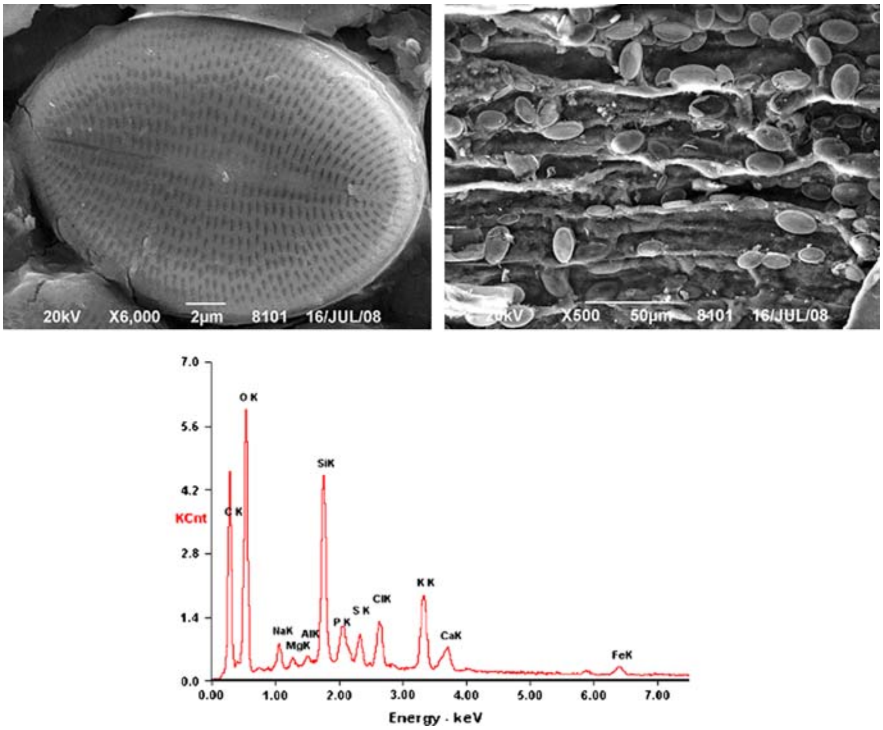
Table 3 Element concentration change of *H. verticillata* (μg/g)

Element	K	Ca	Mg	Na	Pb
Before biosorption	32,500	18,400	2,051	1,100	22
After biosorption	3,354	16,812	1,250	334	37,912

ICP analysis of *Hydrilla verticillata*

In order to investigate the mechanisms of heavy metal biosorption by *H. verticillata*, the amounts of metal ions of biosorbent before and after biosorption were measured by using inductively coupled plasma (ICP) Atomic Emission Spectrometer. Table 3 shows the amounts (μg/g) of biosorbed Pb^{2+} on *H. verticillata* as well as light metal ions (K^{+}, Ca^{2+}, Mg^{2+} and Na^{+}) released into the solution during biosorption experiment. As shown in Table 3, the amount of released K^{+} is far larger than the other three light metal ions (Ca^{2+}, Mg^{2+} and Na^{+}). The simultaneous release of light

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



metals with the uptake of Pb^{2+} by *H. verticillata* may indicate that an ion exchange mechanism would be involved.

EDX spectrum of *Hydrilla verticillata*

Fresh and the Pb^{2+}-loaded *H. verticillata* were analyzed by SEM equipped with EDX (Figs. 7, 8). For the fresh *H. 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 Pb signal was not detected in the EDX spectrum of the fresh *H. verticillata*, i.e., there was no Pb present or the amount of Pb could be negligible in the fresh *H. verticillata*. After Pb^{2+} biosorption, the Pb signal was clearly observed in Fig. 8 for the Pb^{2+}-loaded *H. verticillata*, i.e., a remarkable amount of Pb was adsorbed by *H. verticillata*.

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_3 were used for desorption of lead ions from *H. verticillata*.

Table 4 Desorption ratio of Pb^{2+} ions for various desorbents

Desorbent	Concentration (mol/l)	Desorption ratio (%)
EDTA	0.10	86
	0.05	85
	0.01	82
	0.005	78
HCl	0.10	82
HNO_3	0.10	86

As shown in Table 4, percent desorption ratio of lead ions using EDTA, HCl and HNO_3 were about 86, 86 and 82%, respectively.

Conclusions

In this study, batch adsorption experiments for the removal of Pb(II) from aqueous solution by using *H. verticillata* have been carried out. The obtained results can be summarized as follows:

1. For the maximum adsorption, the optimal operating parameters, pH of solution, adsorbent dosage,

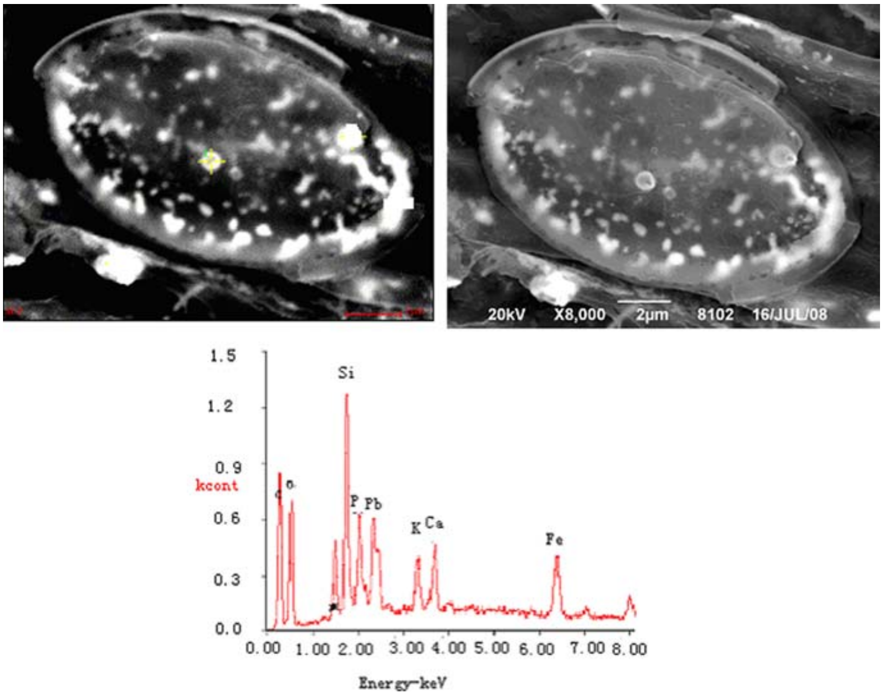


Fig. 8 SEM image and EDX spectrum of Pb^{2+}-loaded *H. verticillata* (Initial Pb^{2+} concentration: 100 mg/l; adsorbent dosage: 0.1 g; pH 4; temperature: 25°C)

contact time and temperature were selected as 4, 0.1 g, 30 min and 25°C, respectively.

2. The linear Langmuir and Freundlich isotherm models were used to represent the experimental data. Both models were fitted well. The monolayer adsorption capacity was obtained as 104.2 mg/g at optimal experimental conditions.
3. The mean free energy of adsorption *E* (15.81 kJ/mol) calculated from examination of D–R isotherm indicated that the adsorption of Pb(II) onto *H. verticillata* may be carried out via chemical ion-exchange mechanism.
4. The negative ΔG^0 values showed that the adsorption of Pb(II) onto *H. verticillata* was feasible and spontaneous. The negative ΔH^0 value depicted exothermic nature of the adsorption. The negative ΔS^0 value revealed that the orderliness of the adsorbed system was higher than that in the solution phase before adsorption.
5. FT-IR spectrum analysis suggested amido, hydroxyl, C=O and C–O could combine strongly with Pb(II).
6. ICP analysis may indicate that an ion exchange mechanism would be involved.
7. EDX spectrum showed that a remarkable amount of Pb was adsorbed by *H. verticillata*.
8. Lead ions adsorbed on *H. verticillata* were desorbed effectively about 86, 86 and 82% by 0.10 mol/l EDTA, HCl and HNO_3, respectively.

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