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Sorption and desorption of lead (II) from wastewater by green algae *Cladophora fascicularis*

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Abstract

Biosorption is an effective method to remove heavy metals from wastewater. In this work, adsorption features of *Cladophora fascicularis* were investigated as a function of time, initial pH, initial Pb(II) concentrations, temperature and co-existing ions. Kinetics and equilibria were obtained from batch experiments. The biosorption kinetics followed the pseudo-second order model. Adsorption equilibria were well described by the Langmuir and Freundlich isotherm models. The maximum adsorption capacity was 198.5 mg/g at 298 K and pH 5.0. The adsorption processes were endothermic and the biosorption heat was 29.6 kJ/mol. Desorption experiments indicated that 0.01 mol/L Na$_2$EDTA was an efficient desorbent for the recovery of Pb(II) from biomass. IR spectrum analysis suggested amido or hydroxy, C=O and C–O could combine intensively with Pb(II).
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1. Introduction

Heavy metals are major pollutants in the environment due to their toxicity and threat to creatures and human being at high concentrations. Lead is widely used in many important industrial applications, such as storage battery, manufacturing, printing pigments, fuels, photographic materials, and explosive manufacturing. Lead, one of the three most toxic heavy metals [1], may cause a range of health effects, from behavioral problems and learning disabilities to seizures and death.

The removal and recovery of heavy metals from wastewater is important for the environmental protection and human health. Conventional methods applied to remove heavy metals in high concentration from aqueous solutions, include precipitation, ion exchange, evaporation, electroplating and membrane processes. However, these methods have been found to be inefficient or expensive when heavy metals are present in low concentrations, and they may also generate secondary wastes which are difficult to treat [2,3]. Therefore, it is necessary to find new technologies or materials for removing heavy metal ions from wastewater.

Biosorption utilizes the ability of certain materials to accumulate heavy metal ions from aqueous solutions by either metabolically mediated or physico-chemical pathways of uptake [4]. It is an economical and effective method to remove heavy metals from wastewater. Marine algae with large available quantities in many regions are a kind of promising biological resources. Many studies have showed that algae possess high metal binding capacities [5,6], 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 can act as binding sites for metals. The cell wall matrix of green algae contains complex heteropolysaccharides that can provide amino, carboxyl and sulphate groups [7]. Protein can constitute 10–70% of the green algal cell wall [8,9].

Cladophora fascicularis, a kind of green filamentous macro-alga, is widely distributed in eutrophic wastewater, lagoon and intertidal zones in many parts of the world. Therefore, utilization of these affluent resources to treat wastewater is of much interest. In this work, the influence of several parameters, such as time, initial pH, initial Pb(II) concentrations, temperature and co-existing ions were investigated. The kinetics and adsorption equilibria were obtained from batch experiments. The efficiencies of different desorbents (H$_2$O, HNO$_3$, Ca(NO$_3$)$_2$, Na$_2$EDTA) to remove the adsorbed Pb(II)

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from the biomass were also evaluated. The IR spectrum of the biosorbent with that loaded with Pb(II) was analyzed.

2. Materials and methods

2.1. Preparation of biomass

The biosorbent *C. fascicularis* used in this work was sampled along the seashore of Qingdao, China. Before use, they were washed several times with distilled water to remove dirt and dried in an oven at 60 °C for 24 h. Then they were cut into segments of 4–5 mm.

2.2. Chemicals

All chemicals used in this study were of analytical grade and solutions were prepared using deionized and distilled water. Stock solution of Pb(II) (100 mmol/L) was prepared by dissolving $Pb(NO_3)_2$ in water. Pb(II) solutions of different concentrations were obtained by diluting the stock solution. Standard solution of Pb(II) (1000 mg/L) for flame atomic adsorption spectrometry was obtained from Beijing NCS Analytical Instruments Co. Ltd. To adjust the pH, 0.1 mol/L HNO_3 and NaOH solutions were used. The solutions of 0.1 mol/L $NaNO_3$, KNO_3, $Mg(NO_3)_2$, $Ca(NO_3)_2$, $NaNO_3$, NaCl, $Na_2C_2O_4$ and Na_2EDTA were prepared for the effect of light metal ions and anionic ligands.

2.3. Kinetic experiments

Kinetic experiments were performed in continuously stirred beakers containing 500 ml Pb(II) solutions at different concentrations (225.4, 426.0 and 838.3 mg/L) and 0.5 g of biosorbent. Samples of 3 ml solution were withdrawn at scheduled time intervals and analyzed for residual Pb(II) concentration by flame atomic absorption spectrometry at 283.3 nm (Model AA6800, Shimadzu Japan).

2.4. Effect of pH on Pb(II) adsorption

A series of experiments, with 225.4 mg/L Pb(II) solutions, were conducted under different pH to investigate the effect of pH on the adsorption. The pH was first adjusted to a designed value, from 2.0 to 6.0 with HNO_3 or NaOH. Then it was measured hourly and maintained steady throughout the experiment.

2.5. Adsorption equilibrium

For equilibrium studies, the concentrations of Pb(II) solutions varied from 45.0 to 901.6 mg/L and biosorbent dosage was 2 g/L. The pH was adjusted to 5.0 using HNO_3 or NaOH hourly throughout the experiment. The mixtures were agitated on a rotary shaker (agitation rate, 200 rpm) for 6 h at constant temperature (298, 308 and 318 K, respectively), and then set still 12 h. Then the biosorbent was filtered through an acid-cleaned 0.45 μm Millipore filter. The amount of Pb(II) uptake by *C. fascicularis* in each flask was determined using the mass balance

equation:

$$q = \frac{C_0 - C_e}{W} \tag{1}$$

where q is the adsorption amount at equilibrium (mg/g), C_0 the initial concentration of heavy metal (mg/L), C_e the concentration remaining in solution at equilibrium (mg/L) and W is the biosorbent dosage (g/L).

2.6. Effect of cations and anions on biosorption

The effect of light metal ions and anionic ligands were studied by using 2 g/L biosorbent and 225.4 mg/L Pb(II) solution containing respective cations (Na^+, K^+, Mg^{2+} and Ca^{2+}) and anions (NO_3^-, Cl^-, $C_2O_4^{2-}$ and EDTA). Blank samples without light metals and anionic ligands were used as controls.

2.7. Desorption experiments

For the desorption study, 0.10 g biomass was contacted with 50 ml Pb(II) solution (676.2 mg/L). After adsorption experiment, the biomass was collected by filtration and washed with distilled water for three times, to remove residual Pb(II) on the surface. Then it was transferred to 50 ml desorbent solutions: HNO_3, $Ca(NO_3)_2$, EDTA (0.10 and 0.01 M, respectively) and H_2O. The mixtures were shaken for 18 h, then the filtrates were analyzed to determine the concentration of Pb(II) after desorption. Desorption ratio was calculated from the amount of metal ions adsorbed on the biomass and the final metal ion concentration in desorption medium, as the following equation:

$$\text{Desorption ratio} = \frac{\text{Amount of metal ions desorbed}}{\text{Amount of metal ions adsorbed}} \times 100 \tag{2}$$

2.8. IR spectrum of C. fascicularis

The IR spectrum of the biosorbent with that loaded with Pb(II) was analyzed using a Fourier transform infrared spectrometer (BIO-RAD FTS-40). Amount of 5 mg algae was mixed with 4.0 mg of KBr and compacted in pellet form.

3. Results and discussion

3.1. Kinetics of biosorption

Fig. 1 depicted Pb(II) removal percentage versus t profiles by *C. fascicularis* at different initial Pb(II) concentrations. The removal rate was rather fast in the first 30 min, but then the rate significantly decreased and eventually reached a plateau after 90 min. This was the same for all the initial Pb(II) concentrations. The uptake capacities increased with increasing initial Pb(II) concentrations, because of much bigger probability of collision between Pb(II) and biosorbent particles.

A number of models have been developed to describe the kinetics of heavy metal biosorption [10–13]. The pseudo-second order kinetic model based on the sorption capacity of solid phase can be used in this case assuming that measured concentrations
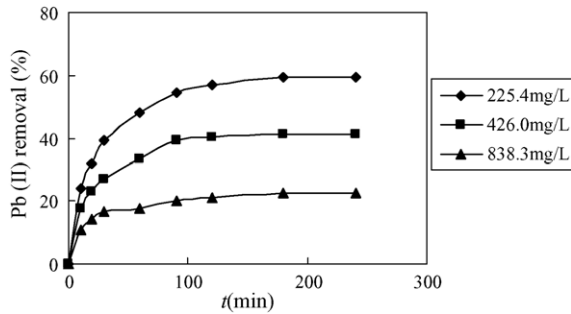
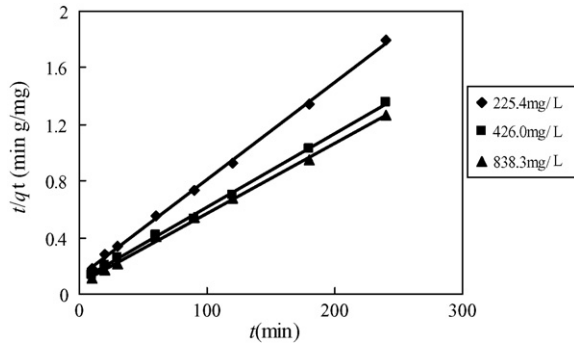Fig. 1. Adsorption rate at different initial Pb(II) concentrations.

Fig. 2. Plots of t/q vs. t obtained at different initial Pb(II) concentrations.

are equal to cell surface concentrations. The pseudo-second order kinetic rate equation is expressed as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{3}$$

Integrating for the boundary condition conditions $q_t = 0$ at $t = 0$ and q_t at time t, the linearized form of pseudo-second order model is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 is the second order biosorption rate constants (g/mg min^{-1}), q_e and q_t are the amounts of sorbed metal ions on the biosorbent at the equilibrium and at any time t, respectively. The kinetic data was analyzed in term of the pseudo-second order. Fig. 2 showed the plots of t/q_t versus t at various initial concentrations. The values of parameters k_2, q_e and correlation coefficients were presented in Table 1. The correlation coefficients obtained were greater than 0.998. It suggested that the sorption of Pb(II) onto *C. fascicularis* followed the second order model very well and based on the assumption that the rate limiting step may be chemisorption involving valence forces through sharing or exchange of electrons between sorbent and sorbate.

Table 1
The pseudo-second order adsorption constants

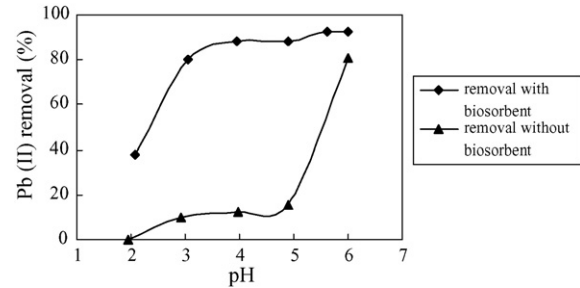| C_0 (mg/L)	q_e (mg/g)	k_2 ($\times 10^3$ g/mg min^{-1})	R^2
225.4	144.9	0.376	0.999
426.0	192.3	0.309	0.999
838.3	204.0	0.280	0.998

Fig. 3. Pb(II) removal efficiencies by *C. fascicularis* at different pH.

3.2. Effect of pH on Pb(II) adsorption

Many studies have shown that pH is an important factor affecting biosorption of heavy metals [14–16]. It is well known that pH affects the protonation of the functional groups on the biomass as well as the metal chemistry. The effect of pH on Pb(II) adsorption was studied and the results were shown in Fig. 3. At pH 2, the percentage of adsorption was 38%, while removal percentage was zero without biosorbent. There was a clear competition for sorption sites between Pb(II) and protons at low pH. As pH increased, the removal percentage with biosorbent increased and stabilized around 90%. Pb(II) may hydrolyze resulting in lead deposition at high pH, and 81% of Pb(II) was removed by depositing at pH 6. Therefore, the whole experiment was conducted at pH 5.0.

3.3. Adsorption isotherms

The capacity of an adsorbent can be described by equilibrium sorption isotherm, which is characterized by certain constants whose values express the surface properties and affinity of the adsorbent.

The Langmuir isotherm is probably the most widely applied adsorption isotherm. A basic assumption of this model is that adsorption takes place at specific homogeneous sites within the adsorbent. The saturated monolayer isotherm is represented as

$$q = \frac{q_m b C_e}{1 + b C_e} \tag{5}$$

where q_m is the maximum adsorption capacity and b is an affinity constant related to the energy of adsorption. The value of b indicates the strength or affinity of the sorbate for the solute [17].

The Freundlich isotherm is an empirical isotherm that can be used for non-ideal adsorption and expressed as follows:

$$q = K_F C_e^{1/n} \tag{6}$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively.

Adsorption equilibria of Pb(II) by *C. fascicularis* at different temperatures were well described by Langmuir and Freundlich isotherm models, as shown in Fig. 4. The equilibrium constants and correlation coefficients (R^2) were presented in Table 2. The values of K_F and n (Freundlich constants) showed high
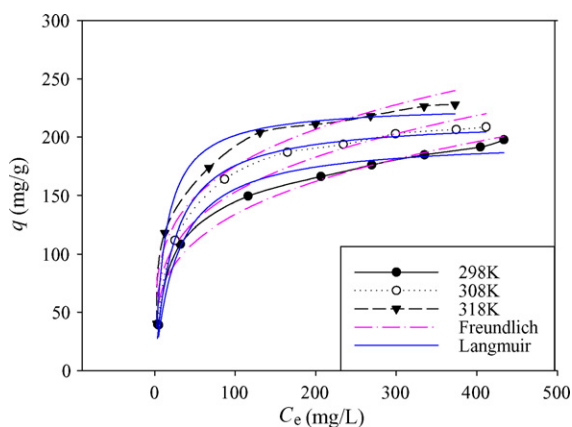
Fig. 4. Adsorption isotherms of Pb(II) by *C. fascicularis* at different temperatures.

adsorption capacity and easy uptake. The maximum adsorption capacity obtained from the Langmuir isotherm increased with increasing temperature, and the value of q_m was 198.5 mg/g at 298 K and pH 5.0. The adsorption capacity of *C. fascicularis* is fairly high in comparison with other adsorbents at room temperature, as shown in Table 3.

3.4. The biosorption heat of Pb(II) onto C. fascicularis

The biosorption heat can be calculated using many methods [24–26], Singh and Tiwari calculated the heat of adsorption of Cr(VI) ions on carbon slurry by using energy change ($\Delta G = \Delta H - T \Delta S$) and equilibrium constant K_c, obtained at different temperatures. The enthalpy change was also calculated using the Langmuir constant b. The values of ΔH obtained by using these two methods were almost equal.

The Langmuir model is based on a postulated chemical or physical interaction between solute and vacant sites on the adsorbent surface, and the heat (ΔH) of adsorption is independent of

Table 2
The Langmuir and Freundlich sorption constants for biosorption of Pb(II) at different temperatures

T (K)	Langmuir constants			Freundlich constants		
	q_m (mg/g)	b (L/mg)	R^2	K_F	n	R^2
298	198.5	0.0359	0.998	37.46	3.621	0.997
308	215.8	0.0435	0.999	46.72	3.885	0.995
318	227.7	0.0766	0.998	58.08	4.175	0.993

Table 3
Uptake capacities for Pb(II) of various adsorbents (at room temperature)

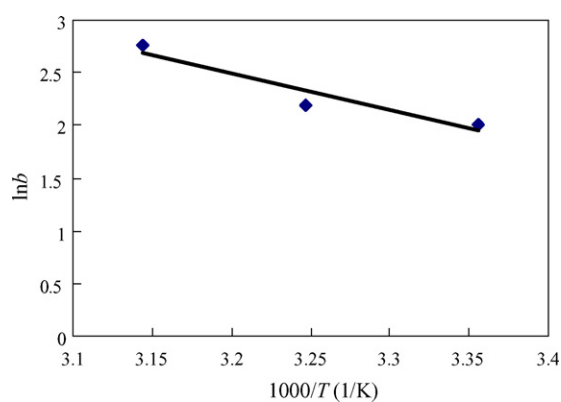| Adsorbent	q_m (mg/g)	pH	Literature
Powder activated carbon	20.7	–	[15]
Granulated activated carbon, F-400	31.1	–	[18]
Pseudomonas aeruginosa	68.4	5.5	[19]
Grape stalks	49.7	5.5	[20]
Chaff	12.4	5.5	[21]
Caulerpa lentillifera	28.7	5.0	[22]
Pang Da Hai	27.1	6.5	[23]
Cladophora fascicularis	198.5	5.0	This study

Fig. 5. Determination of biosorption heat of Pb(II) onto *C. fascicularis*.

the fraction of surface covered by the adsorbed solute.

$$b = b_0 \exp\left(-\frac{\Delta H}{RT}\right) \tag{7}$$

where b_0 is a constant containing the entropy term, ΔH the heat of the adsorption (kJ/mol), R the universal gas constant (J/mol K^{-1}) and T is the absolute temperature (K).

Eq. (7) can be altered as

$$\ln b = \ln b_0 - \frac{\Delta H}{RT} \tag{8}$$

The biosorption heat of Pb(II) onto *C. fascicularis* was obtained by calculating the slope of $\ln b$ versus $1/T$, as shown in Fig. 5. The negative slope value indicated biosorption of Pb(II) onto *C. fascicularis* to be endothermic. This was also supported by the increase of uptake capacity with the increasing temperature. The biosorption heat for Pb(II) was determined to be 29.6 kJ/mol. The magnitude of the ΔH value gives an indication on the type of adsorption, which can be either physical or chemical. The heat of adsorption, ranging from 0.5 to 5 kcal/mol (2.1–20.9 kJ/mol), is said to be physical adsorption, and the activation energy for chemical adsorption is of the same magnitude as the heat of chemical reactions, 5–100 kcal/mol (20.9–418.4 kJ/mol) [27,28]. The biosorption heat of Pb(II) onto *C. fascicularis* was of the same magnitude as the heat of chemisorption. The ΔH value obtained showed that chemisorption also took part in the adsorption process with chelating effect of the functional groups available on the surface of biosorbent.

3.5. Effect of cations and anions on biosorption

Industrial wastewater often contains other ions such as Na$^+$, K$^+$, Mg^{2+} and Ca^{2+}, which may interfere with the uptake of heavy metal ions by biomass. The effect of cations on adsorption was studied and the results were shown in Fig. 6. It was evident that the effect of Na$^+$, K$^+$ and Mg^{2+} on adsorption of Pb(II) was very small. In contrast, Pb(II) removal percentage dropped with increasing concentration of Ca^{2+}. The presence of Ca^{2+} at 10 mmol/L caused removal percentage to drop by 26%. The effect of Ca^{2+} on uptake is due to the competition with Pb(II) for the binding sites.

The influence of four types of anions was investigated, including sodium salts of chloride, nitrate, acetate and EDTA. The influence of Na^+ on the adsorption of Pb(II) could be negligent as shown in above experiment. The presence of chloride, nitrate and acetate did not greatly affect the Pb(II) removal (Fig. 7). Acetate, at 10 mmol/L, caused the removal efficiency to drop by 8%. It was obvious that EDTA affected the adsorption remarkably. At the presence of 1 mmol/L EDTA, Pb(II) removal efficiency dropped by 78%. As EDTA increased to 10 mmol/L, the removal efficiency reduced nearly to zero. This is because Pb(II) can combine with EDTA strongly instead of biomass.

3.6. Desorption of lead ions

Fig. 8 showed the percentage of Pb(II) released after treatment with different desorbents. It was observed that EDTA and HNO_3 were more efficient than other desorbents, while desorption using distilled water was almost negligible. The recovery with 0.1 mol/L HNO_3 was 85%, but HNO_3 could nitrify the

Fig. 9. IR spectrum of *C. fascicularis* (top: native algae; bottom: algae loaded with Pb(II)).

Table 4
Removal of heavy metal ions from industry wastewater by *C. fascicularis*

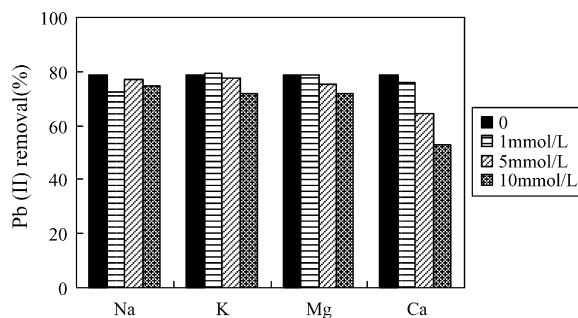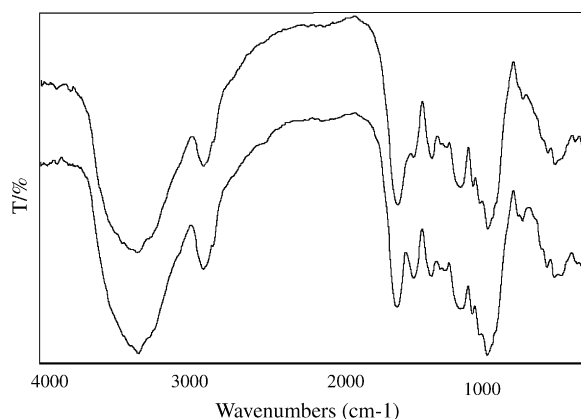| Pollutant	Initial concentration (mg/L)	Final concentration (mg/L)	Wastewater discharge standard in China (mg/L)
Cu	28.03	1.52	2.0
Pb	3.69	0.044	1.0
Cr	5.68	0.015	0.5
Cd	0.88	0.075	0.1

Fig. 6. The effect of cations on Pb(II) adsorption.
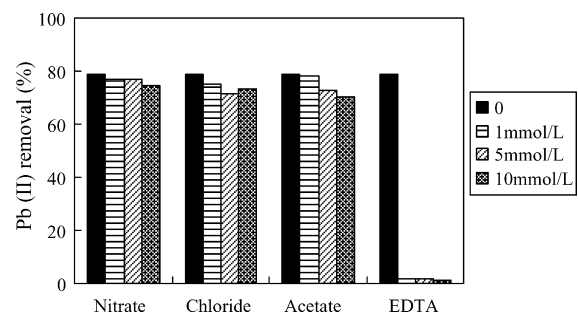
Fig. 7. The effect of anions on Pb(II) adsorption.
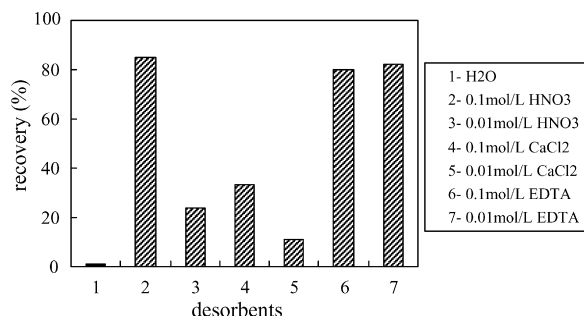
Fig. 8. Pb(II) recovery by different desorbents.

biosorbent. 0.01 mol/L EDTA can recover 82% of Pb(II) bound to the biomass. This fact can be explained by the high value of the conditional formation constant of the complex Pb(II)-EDTA ($K'_F = 3.55 \times 10^{11}$, pH 5.0), which favors the desorption of Pb(II) from the biomass. The high recovery percentage of Pb(II) by EDTA allows the reuse of biomass. It is an important feature to use *C. fascicularis* to remove Pb(II) in continuous systems in industrial processes.

3.7. IR spectrum of C. fascicularis

The absorbance spectrum of *C. fasciculari* with that loaded with Pb(II) was shown in Fig. 9. Some intense characteristic bands were obtained from the functional groups presented in proteins and polysaccharides. The intense peak at 3376.39 cm^{-1} was caused by the hydroxy stretching of carboxylic groups and also stretching of amido. The strong peaks at 1660.12 and 1246.96 cm^{-1} were assigned to C=O and sulphate, respectively. The peaks at 1116.93 and 1062.26 cm^{-1} were due to C–O existence. Some bands in fingerprint region could be attributed to the phosphate groups. After adsorbing Pb(II), the peaks at 3376.39, 1660.12 and 1062.26 cm^{-1} reduced to 3350.29, 1654.22 and 1060.98 cm^{-1}, respectively, which suggested amido, hydroxy, C=O and C–O could combine intensively with Pb(II).

3.8. Industry wastewater sorption experiments

Actual industry wastewater was used to evaluate the practicality of the biomass. The pH of the solution was adjusted to 5.0 and the biomass was 2 g/L. The mixture was shaken for

12 h. The results were shown in Table 4. All the metal ions we detected were under the wastewater discharge standard in China. The biomass was effective for removal of heavy metal ions from industry wastewater.

4. Conclusions

This study indicated that green marine algae *C. fascicularis*, which is widely available at low cost, can be used as an efficient biosorbent material for removal of Pb(II) from wastewater. The removal rate was fast in the first 30 min, and kinetics followed the pseudo-second order kinetic model. The adsorption isotherms at different temperatures could be well described by the Langmuir and Freundlich isotherm models. The maximum adsorption capacity was 198.5 mg/g at 298 K and pH 5.0. The adsorption processes were endothermic and the biosorption heat was of the same magnitude as the heat of chemisorption. No significant effect on the uptake of Pb(II) by co-existing cations and anions was observed, except EDTA. Desorption experiments proved that 0.01 mol/L Na$_2$EDTA was an efficient desorbent for the recovery of Pb(II) from biomass. IR spectrum analysis suggested amido or hydroxy, C=O and C–O could combine intensively with Pb(II).

Acknowledgments

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