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Biosorption of copper (II) and lead (II) from aqueous solutions by nonliving green algae *Cladophora fascicularis*: Equilibrium, kinetics and environmental effects

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Abstract Biosorption of Cu^{2+} and Pb^{2+} by *Cladophora fascicularis* was investigated as a function of initial pH, initial heavy metal concentrations, temperature and other co-existing ions. Adsorption equilibriums were well described by Langmuir and Freundlich isotherm models. The maximum adsorption capacities were 1.61 mmol/g for Cu^{2+} and 0.96 mmol/g for Pb^{2+} at 298 K and pH 5.0. The adsorption processes were endothermic and biosorption heats calculated by the Langmuir constant b were 39.0 and 29.6 kJ/mol for Cu^{2+} and Pb^{2+}, respectively. The biosorption kinetics followed the pseudo-second order model. No significant effect on the uptake of Cu^{2+} and Pb^{2+} by co-existing cations and anions was observed, except EDTA. Desorption experiments indicated that Na_2EDTA was an efficient desorbent for the recovery of Cu^{2+} and Pb^{2+} from biomass. The results showed that *Cladophora fascicularis* was an effective and economical biosorbent material for the removal and recovery of heavy metal ions from wastewater.

Keywords Biosorption · Heavy metal · Marine algae · Biosorption heat · Wastewater · Desorption · Desorbent

1 Introduction

Heavy metal pollution in wastewater has always been a serious environmental problem because heavy metals are not biodegradable and can be accumulated in living tissues. Copper and lead are widely used in various important industrial applications. Copper at excessive concentration is toxic to living organism of humans and other creatures, especially fish (Terry and Stone, 2002). Lead, one of the three most toxic heavy metals, has long-term potential negative impacts on anemia, encephalopathy, hepatitis and nephritic syndrome (Lo et al., 1999).

The removal and recovery of heavy metals from wastewater is important for the environmental protection and human health. Conventional methods applied to remove excessive heavy metals from aqueous solutions include precipitation, ion exchange, evaporation, electroplating and membrane processes. However, these methods are either inefficient or expensive when heavy metals exist in low concentrations. Additionally, these methods may also risk the generation of secondary wastes, which are difficult to treat (Kuyucak and Volesky, 1998; Alimohamadi et al., 2005). Consequently, it is urgent to find new technologies or materials for removing heavy metal ions from wastewater.

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Biosorption utilizes the ability of certain materials to accumulate heavy metals from aqueous solutions by either metabolically mediated or physico-chemical pathways of uptake (Fourest and Roux, 1992). The most prominent features of biosorption are the use of low cost and highly efficient biomass materials to adsorb heavy metals even present at very low concentrations (Yu et al., 2001). Various types of biomass, including bacteria (Scott and Palmer, 1990; Chang et al., 1997; Selatnia et al., 2004; Iyer et al., 2005), yeast (Huang et al., 1990; Volesky et al., 1993; Seki et al., 2005; Göksungur et al., 2005), fungi (Lewis and Kriff, 1988; Fourest et al., 1994; Dursun et al., 2003; Pal et al., 2006; Tunali et al., 2006), and algae (Xue et al., 1988; Yu et al., 1999; Lodeiro et al., 2005; Hansen et al., 2006; Vijayaraghavan et al., 2005, 2006), have been investigated with the aim of finding more efficient and cost-effective metal-removal biosorbent. Among them, marine algae with large available quantities in many regions are a kind of promising biological resources. Many studies reported biosorption by brown seaweeds such as *Sargassum* sp. (Kratochvil et al., 1997, 1998; Sheng et al., 2004; Diniz and Volesky, 2005; Vijayaraghavan et al., 2006), *Laminaria* sp. (Lodeiro et al., 2005; Figueira et al., 2000; Luo et al., 2006), and *Fucus* sp.(Herrero et al., 2006). Some kinds of green seaweed such as *Ulva* (Sheng et al., 2004; Suzuki et al., 2005), *Cladophora* sp. (Özer et al., 1994, 2004), *Sphaeroplea* (Rao et al., 2005) were also reported to present high adsorption capacities. Algae possess high metal binding capacities, because polysaccharides, proteins or lipid on the surface of their cell walls contain some functional groups such as amino, hydroxyl, carboxyl and sulphate, which can act as binding sites for metals (Holan and Volesky, 1994; Yu et al., 1999).

Due to eutrophication, green seaweeds flourish in many coastal areas. *Cladophora fascicularis*, a kind of green filamentous macro-alga, is widely distributed in eutrophic wastewater, lagoon and intertidal zones. In shrimp breeding ponds, *C. fascicularis* may flourish wildly to form "green blankets" which soon make the pond anoxic. About 40 thousand tons of *C. fascicularis* have to be dumped by manpower every year in brine pans of Jiangsu Province in China. Therefore the idea of utilization of *C. fascicularis* as an efficient and cost-effective biosorbent is of much interest and promise. Özer et al. (1994, 2004) studied the adsorption isotherms of copper (II), lead (II) and chromium (VI) on *Cladophora crispate*. Aksu and Kutsal (1998) determined adsorption kinetic parameters of copper (II) on *Cladophora sp.* in a packed bed column reactor. To our best knowledge, there is no report on utilization of green seaweed *C. fascicularis* for heavy metal removal. In this work, adsorption features of *C. fascicularis* were investigated as a function of initial pH, initial heavy metal concentrations, temperature and other co-existing ions. The equilibrium and kinetics were obtained from batch experiments. At last, the efficiencies of different desorbents (H_2O, HNO_3, $Ca(NO_3)_2$, and Na_2EDTA) to remove adsorbed Cu^{2+} and Pb^{2+} from the biomass were also evaluated.

2 Materials and methods

2.1 Preparation of biomass

C. fascicularis was sampled from a shrimp breeding pond, at Qingdao Yihai Well-bred Fish Breeding Center. Before use, the samples were washed several times with distilled water and dried in an oven at 60°C for 24 h. Then they were cut into segments of 4–5 mm.

2.2 Stock solutions

Heavy metal stock solutions (100 mmol/L) were separately prepared by dissolving analytical grade $CuSO_4{\cdot}5H_2O$ and $Pb(NO_3)_2$ in deionized distilled water. Solutions of different concentrations were obtained by diluting the stock solutions. Standard solutions of Cu^{2+} and Pb^{2+} (1000 mg/L) for flame atomic adsorption spectrometry (AAS) were obtained from Beijing NCS Analytical Instruments Co. Ltd.

2.3 General uptake procedure

Experiments were conducted in 250 ml flasks containing 50 ml of heavy metal solutions and 0.1 g of biomass. The pH value was adjusted to the required value with 0.1 mol/L HNO_3 or 0.1 mol/L NaOH hourly throughout the experiment. The mixtures were shaken on a rotary shaker (agitation rate, 200 rpm) for 6 h, and then set still 12 h to reach equilibrium. Then the biosorbent was filtered through an acid-cleaned 0.45 μm Millipore filter and the concentrations of heavy metal ions in the filtrates were analyzed by flame atomic absorption spectrometry (Model AA6800, Shimadzu® Japan). Each experiment was repeated for three times.

All chemicals used in this study were at least analytical reagent.

2.4 Effect of pH on heavy metal uptake

A series of experiments, with Cu^{2+} and Pb^{2+} set to 1 mmol/L respectively, were conducted under different pH to investigate the effect of pH on the adsorption. The pH was first adjusted to a specific value, from 2.0 to 6.0. Then it was measured hourly and maintained steady throughout the experiment.

2.5 Adsorption equilibrium

For equilibrium studies, the concentrations of Cu^{2+} and Pb^{2+} varied from 0.2 to 4.0 mmol/L, while the pH was restricted to 5.0. The mixtures were agitated at constant temperature (298 K, 308 K and 318 K respectively). The amount of heavy metal ions 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 (mmol/g); C_0 is the initial concentration of heavy metal (mmol/L); C_e is the concentration remaining in solution at equilibrium (mmol/L); W is biosorbent dosage (g/L).

2.6 Effect of light metal ions and anionic ligands

By setting biosorbent to 2 g/L and heavy metals to 1 mmol/L, other ions were added to check their effects on the adsorption. They included cations (namely Na^+, K^+, Mg^{2+} and Ca^{2+}) and anions (namely NO_3^-, Cl^-, SO_4^{2-}, $C_2O_4^{2-}$ and EDTA). Blank samples without light metals and anionic ligands were used as controls. The pH of this group was all set to 5.0.

2.7 Kinetic experiments

Kinetic experiments were conducted in continuously stirred beakers containing different concentrations of 500 ml heavy metal solutions (1, 2 and 4 mmol/L) and 0.5 g of biosorbent (pH = 5.0). At scheduled time intervals, 3 ml solution samples were drawn out and the concentrations of the residual heavy metals were analyzed.

2.8 Desorption experiments

For the desorption study, 0.1 g of biomass was first contacted with 50 ml heavy metal solutions (3 mmol/L). After adsorption experiment, the biomass was collected by filtration and washed with distilled water for three times, to remove surface-residual heavy metal ions. Then it was transferred into 50 ml desorbent solutions: distilled water, HNO_3 solutions (0.1 and 0.01 mmol/L), $Ca(NO_3)_2$ solutions (0.1 and 0.01 mmol/L) and Na_2EDTA solutions (0.1 and 0.01 mmol/L). The mixtures were shaken for 18 h, and the filtrates were analyzed to determine the concentrations of metal ions after desorption. The 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:

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

3 Results and discussion

3.1 Effect of pH on heavy metal uptake

Many studies showed that pH is an important factor affecting biosorption of heavy metals (Huang et al., 1990; Matheickal et al., 1999; Sanchez et al., 1999). It is well known that pH could affect the protonation of the functional groups on the biomass as well as the metal chemistry. The effect of pH on adsorption was studied and the results were shown in Fig. 1. At pH 2, the removal percentage of Cu^{2+} and Pb^{2+} was small. The removal percentage increased rapidly with increasing pH, and reached a plateau around 90% at pH 5.0. Experiments were not conducted beyond pH 6.0 to avoid precipitation of heavy metal ions. The results showed strong pH dependence of biosorption.

The cell wall matrix of green algae contains complex heteropolysaccharides that can provide amino, carboxyl and sulphate groups (Andrade and Rollemberg, 2005). At low pH, cell wall ligands are protonated and restrict the approach of metal cations as a result of the repulsive force. As pH increases, more ligands such as amino, phosphate and carboxyl

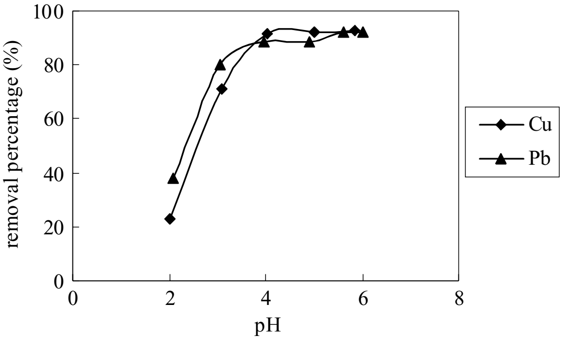

Fig. 1 Removal efficiencies of Cu^{2+} and Pb^{2+} by *C. fascicularis* at different pH

groups would be exposed and carry negative charges with subsequent attraction of metal ions (Dönmez et al., 1999; Aksu, 2001). The effect of pH may be further explained in relation to the competition effect between H_3O^+ and heavy metal ions. At low pH, H_3O^+ occupies the binding sites on the cell walls. As pH increases, the competing effect of H_3O^+ decreases and positively charged metal ions take up the free binding sites. The metal uptake capacity is hence increased (Matheickal et al., 1999).

3.2 Adsorption equilibrium

The capacity of an adsorbent can be described by its 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 isotherm is represented as:

$$q = \frac{q_m b C_e}{1 + b C_e} \tag{3}$$

where q_m is the maximum adsorption capacity (mmol/g) and b is an affinity constant related to the energy of adsorption (L/mmol). The value of b indicates the strength or affinity of the sorbate for the solute (Holan et al., 1993).

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

$$q = K_F C_e^{1/n} \tag{4}$$

where K_F and n are the Freundlich constants related to the adsorption capacity and adsorption intensity of the adsorbent, respectively. The Freundlich model is also widely used but provides no information on the monolayer adsorption capacity, in contrast to the Langmuir model.

Adsorption equilibriums of Cu^{2+} and Pb^{2+} by *C. fascicularis* at different temperatures were well described by Langmuir and Freundlich isotherm models, as Fig. 2 showed. The adsorption data were analyzed by Excel and SigmaPlot. The equilibrium constants, correlation coefficients (R^2) and standard error (SE) of estimate were presented in Table 1. The values of K_F and n (Freundlich constants) showed high adsorption capacity and easy uptake. Since the values of n were higher than 1.0, the strength of metal adsorption by the biosorbent was quite intense (Özer et al., 1994). The maximum adsorption capacities obtained from the Langmuir isotherms increased with the increasing temperature, and the values of q_m were 1.61 mmol/g for Cu^{2+} and 0.96 mmol/g for Pb^{2+} at 298 K and pH 5.0. The adsorption capacities of *C. fascicularis* are fairly high compared with other adsorbents (Table 2).

3.3 The biosorption heats of Cu^{2+} and Pb^{2+} onto *C. fascicularis*

The biosorption heat can be calculated using various methods (Singh and Tiwari, 1997; Sağ and Kutsal, 2000; Özer et al., 2003). Singh and Tiwari calculated the heat of adsorption of Cr (VI) ions on a carbon slurry by using energy change ($\Delta G^0 = \Delta H^0 - T\Delta S^0$) and the equilibrium constant, K_c, obtained at different temperatures. The enthalpy change was also calculated using the Langmuir constant b. They found that values of ΔH obtained 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 the fraction of surface covered by the adsorbed solute.

$$b = b_0 \exp\left(-\frac{\Delta H}{RT}\right) \tag{5}$$

where b_0 is a constant containing the entropy term, ΔH is the heat of the adsorption (kJ/mol), R is universal

Table 1 The Langmuir and Freundlich sorption constants of Cu^{2+} and Pb^{2+} by *C. fascicularis* at different temperatures

		Langmuir constants				Freundlich constants			
Metal	T (K)	q_m (mmol/g)	b (L/mmol)	R^2	SE	K_F	n	R^2	SE
Cu^{2+}	298	1.614	4.141	0.997	0.0688	1.328	2.449	0.998	0.0465
	308	1.681	7.886	0.998	0.0597	1.620	2.853	0.995	0.0926
	318	1.778	11.12	1.000	0.0318	1.889	2.899	0.993	0.1207
Pb^{2+}	298	0.958	8.292	0.998	0.0427	0.789	3.621	0.997	0.0489
	308	1.042	9.017	0.999	0.0306	0.890	3.885	0.995	0.0698
	318	1.099	15.87	0.998	0.0432	1.006	4.175	0.993	0.0867

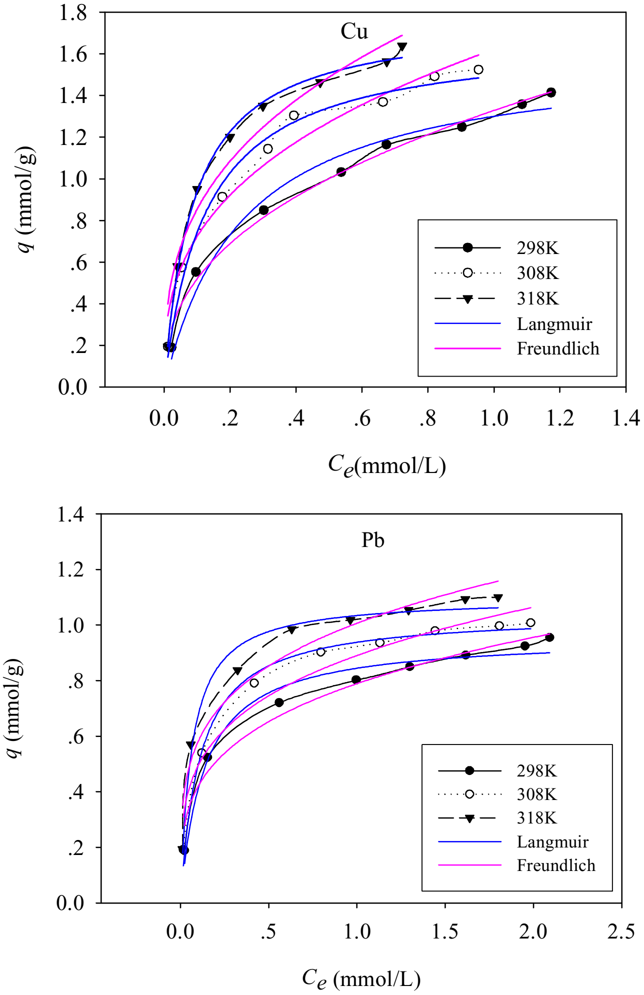

Fig. 2 Adsorption isotherms of Cu^{2+} and Pb^{2+} by *C. fascicularis* at different temperatures

gas constant (J/mol/K) and T is the absolute temperature (K).

Equation (5) can be altered as:

$$\ln b = \ln b_0 - \frac{\Delta H}{RT} \tag{6}$$

The biosorption heats of Cu^{2+} and Pb^{2+} onto *C. fascicularis* were obtained by calculating the slope of ln$b$ versus $1/T$, as shown in Fig. 3. The biosorption heats were 39.0 kJ/mol and 29.6 kJ/mol for Cu^{2+} and Pb^{2+}, respectively. The positive values of ΔH indicated

Table 2 Uptake capacities for Cu^{2+} and Pb^{2+} of various adsorbents

	q_m (mmol/g)			
Adsorbent	Cu^{2+}	Pb^{2+}	pH	Literature
Powder activated carbon	–	0.10	–	Matheickal and Yu, 1996
Granulated activated carbon, F-400	0.03	0.15	–	Muraleedharan et al.,1995
Pseudomonas aeruginosa	0.29	0.33	5.5	Chang et al.,1997
grape stalks	0.16	0.24	5.5	Villaescusa et al., 2004; Martínez et al., 2006
chaff	–	0.06	5.5	Han et al., 2005
Cephalosporium aphidicola	–	0.18	5.0	Tunali et al., 2006
Padina sp.	0.80	–	5.0	Kaewsarn, 2002
Rhizopus arrhizus	0.76	0.27	5.0	Alimohamadi et al., 2005
Durvillaea potatorum	1.30	1.55	5.0	Matheickal et al., 1999
Ecklonia radiata	1.11	1.26	5.0	Matheickal et al., 1999
Sargassum sp.	0.99	1.16	5.0	Sheng et al., 2004
Ulva sp.	0.75	1.46	5.0	Sheng et al., 2004
Ulva (Alkila pretreated)	0.90	–	7.8	Suzuki et al., 2005
Sphaeroplea	2.21	–	4.0	Rao et al., 2005
Sphaeroplea (Acid pretreated)	3.41	–	4.0	Rao et al., 2005
Cladophora crispate	1.03	1.21	4.5	Özer et al., 1994, 2004
C. fascicularis	1.61	0.96	5.0	This study

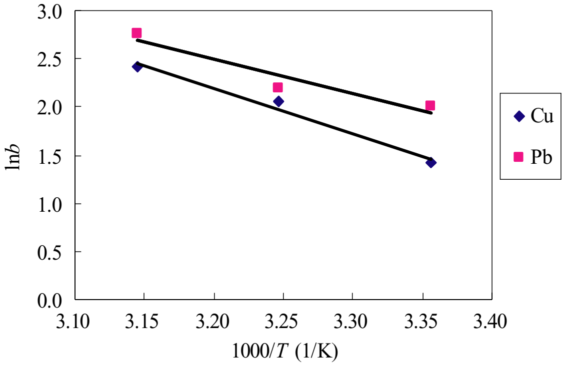

Fig. 3 Determination of biosorption heats of Cu^{2+} and Pb^{2+}

that biosorption of Cu^{2+} and Pb^{2+} onto *C. fascicularis* was endothermic. This was also supported by the increase of uptake capacity with the increasing temperature. The magnitude of the ΔH value gives an indication on the type of adsorption, which can be either physical or chemical. Although there are no certain criteria related to the ΔH value that defines the adsorption type, 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 to 100 kcal/mol (20.9–418.4 kJ/mol) (Treybal, 1980; Smith, 1981). Physical adsorption phenomenon is associated with the presence of weak van der Waal's forces. Equilibrium between the cell surface and the metal ions is usually rapidly attained and easily reversible, because the energy requirement is small. Chemisorption involves essentially the formation of a chemical bond between the sorbate and the surface of the adsorbent. The biosorption heats of Cu^{2+} and Pb^{2+} onto *C. fascicularis* were of the same magnitude as the heat of chemisorption. The values of ΔH obtained showed that chemisorption also took part in the adsorption process with chelating effect of the functional groups available on the surface of biosorbent.

3.4 Effect of light metal ions and anionic ligands

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 these light metal ions on adsorption was studied and the results were shown in Fig. 4. It was evident that the removal percentage dropped with increasing concentrations of light metal ions. The effect of Na^+, K^+ and Mg^{2+} on uptake of Cu^{2+} and Pb^{2+} was very small. The presence of 10 mmol/L Mg^{2+} caused the removal percentage to drop by 8.3% for Cu^{2+} and 7.4% for Pb^{2+},

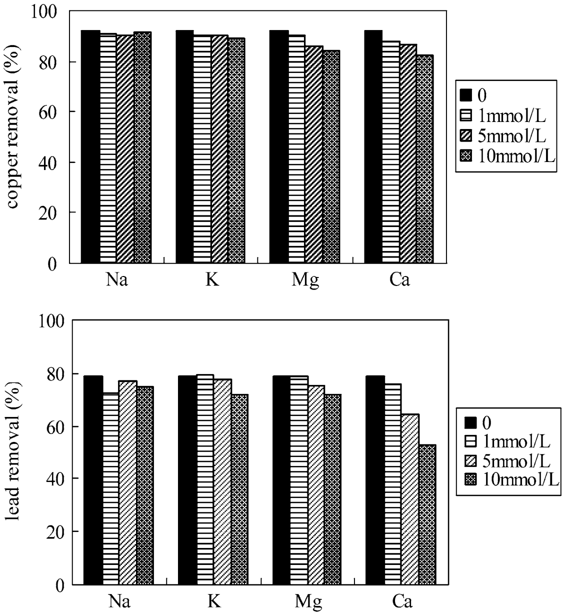

Fig. 4 Removal efficiencies of Cu^{2+} and Pb^{2+} by *C.fascicularis* in the presence of light metal ions

while 10 mmol/L Ca^{2+}caused the removal percentage to drop by 9.7% for Cu^{2+} and 26.0% for Pb^{2+}. The effect of light metal ions on adsorption was due to the competition with heavy metal ions for the binding sites. With the decrease of hydrated ionic radius and the increase of ionic charges, the degree of ionic polarization increases. So appetence of Ca^{2+} with the biosorbent is stronger than other light metal ions.

The influence of anions was investigated as well, including sodium salts of chloride, nitrate, sulphate, acetate and EDTA. The influence of Na^+ on the adsorption of Cu^{2+} and Pb^{2+} could be negligible as shown in above experiments. Figure 5 showed that the presence of chloride, nitrate, sulphate and acetate did not greatly affect adsorption. Acetate, at 10 mmol/L, caused the removal efficiencies to drop by 8.7% for Cu^{2+} and 8.5% for Pb^{2+}. It was obvious that EDTA affected the adsorption remarkably. At the presence of 1 mmol/L EDTA, copper removal efficiency dropped by 77.9% and lead dropped by 76.8%. As EDTA increased to 10 mmol/L, the removal efficiencies for both Cu^{2+} and Pb^{2+} reduced to less than 10%. This was because Cu^{2+} and Pb^{2+} could combine with EDTA strongly rather than the biomass. Therefore, EDTA could be used as an effective agent for heavy metal recovery from loaded biosorbent.

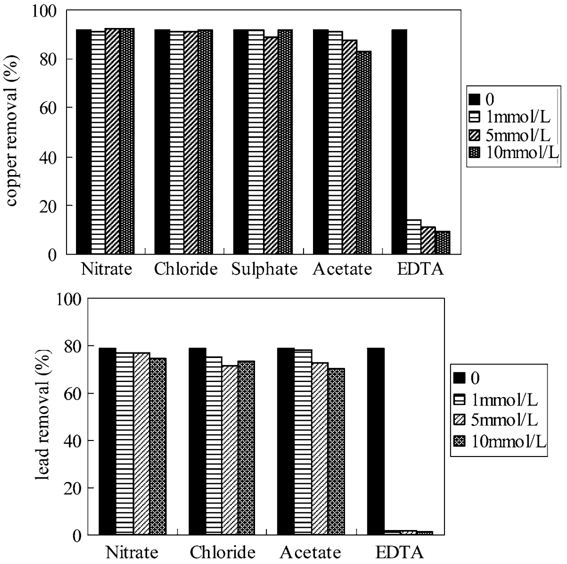

Fig. 5 Removal efficiencies of Cu^{2+} and Pb^{2+} by *C.fascicularis* in the presence of anionic ligands

3.5 Kinetics of biosorption

A number of models have been developed to describe the kinetics of heavy metal biosorption (Yang and Volesky, 1999; Hashim and Chu, 2004; Gupta et al., 2001, 2006). The pseudo-second order kinetic model based on the sorption capacity of solid phase can be used in this case assuming that measured concentrations are equal to cell surface concentrations. The linearized form of the pseudo-second order model was proposed by Ho and McKay (1998, 1999, 2000) and has been widely applied to the sorption of metal ions, dyes, herbicides, oil, pesticides, and organic substances from aqueous solutions (Ho, 2005).

The pseudo-second order kinetic rate equation is expressed as:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{7}$$

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:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where k_2 is the second order biosorption rate constant (g/mmol/min); q_e and q_t are the amounts of adsorbed

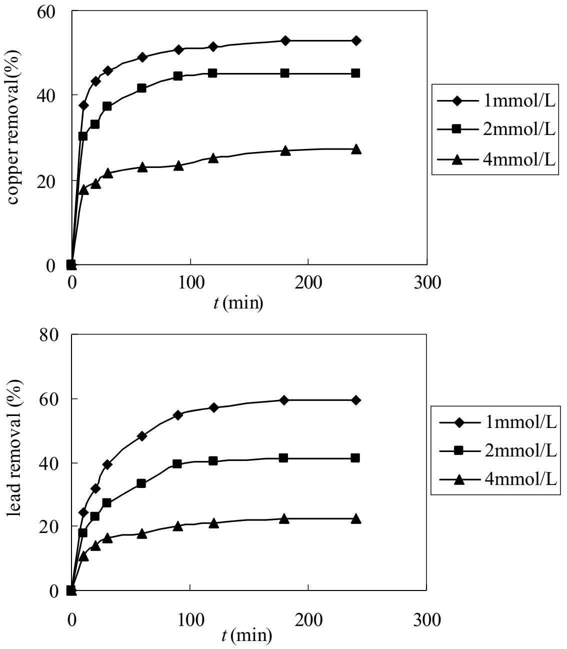

Fig. 6 Adsorption kinetics at different initial concentrations

metal ions on the biosorbent at the equilibrium and at any time *t*, respectively.

The removal rate of Cu^{2+} and Pb^{2+} by *C. fascicularis* was rapid in the first 30 min, and leveled off after 1 to 2 h (Fig. 6). The adsorption capacity increased with increasing initial concentrations of Cu^{2+} and Pb^{2+}, apparently because of the much higher probability of collision between heavy metal ions and biosorbent particles. The kinetic data were analyzed in term of the pseudo-second order. Figure 7 showed the plots of t/q vs. t at various initial concentrations. The values of k_2 and q_e were presented in Table 3. The adsorption of Cu^{2+} and Pb^{2+} onto *C. fascicularis* followed the second order model very well ($R^2 > 0.998$), 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. This was also supported by biosorption heat.

3.6 Desorption and reuse

Table 3 The pseudo-second order adsorption constants

Metal	C_0 (mmol/L)	q_e (mmol/g)	k_2 (g/mmol/min)	R^2
Cu^{2+}	1	0.56	0.34	0.999
	2	1.06	0.14	0.999
	4	1.14	0.08	0.998
Pb^{2+}	1	0.70	0.078	0.999
	2	0.92	0.064	0.999
	4	0.98	0.058	0.998

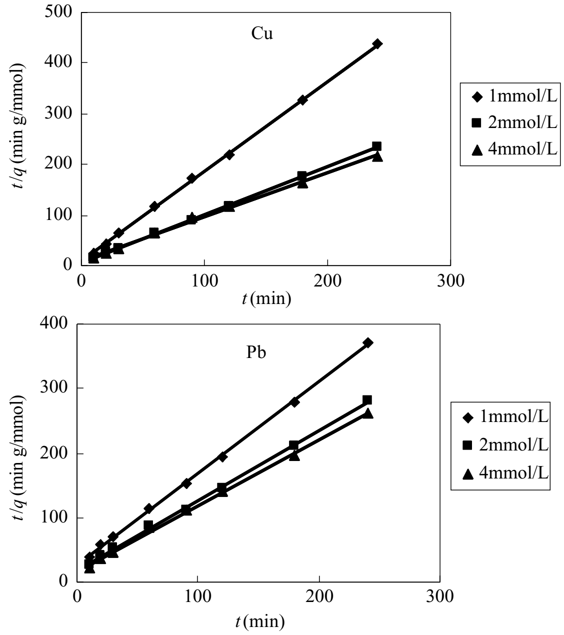

Fig. 7 Linearized pseudo-second order kinetics at different initial concentrations

The amounts of Cu^{2+} and Pb^{2+} adsorbed by *C. fascicularis* and recovery percentage with different desorbents were shown in Table 4. It was observed that Na$_2$EDTA and 0.1 mol/L HNO$_3$ were more efficient than other desorbents, while desorption using distilled water was almost negligible. The biosorbent was oxidized to be yellow in 0.1 mol/L HNO$_3$ and the biosorption capacity could not be recovered because of strong oxidation by HNO$_3$. 0.01 mol/L Na$_2$EDTA recovered 94.7% of Cu^{2+} and 82.5% of Pb^{2+} bound to the biomass. This can be explained by the high values of the conditional formation constants of the complex Cu-EDTA ($K'_f = 2.24 \times 10^{12}$, pH = 5.0) and Pb (II)-EDTA ($K'_f = 3.55 \times 10^{11}$, pH = 5.0), which favor desorption of heavy metals from the biomass. Copper and lead were recovered in the form of CuS and PbS by adding 0.1 mol/L Na$_2$S to the desorption solutions that contained Cu-EDTA or Pb-EDTA. Then the residual solutions mainly contained Na$_2$EDTA, which can be used as desorbent again. The reuse of the biomass and

Table 4 The amounts of Cu^{2+} and Pb^{2+} adsorbed by *C. fascicularis* and recovery percentage by different desorbents

	Adsorption		Recovery	
Desorbent	Cu^{2+} (mmol/g)	Pb^{2+} (mmol/g)	Cu^{2+} (%)	Pb^{2+} (%)
Distilled H_2O	0.92	0.61	0.27	0.77
0.1 mol/L HNO_3	0.93	0.67	72.1	84.8
0.01 mol/L HNO_3	0.96	0.63	53.0	24.0
0.1 mol/L $Ca(NO_3)_2$	0.94	0.67	11.2	33.6
0.01 mol/L $Ca(NO_3)_2$	0.93	0.65	3.03	11.0
0.1 mol/L Na_2EDTA	1.00	0.68	82.6	79.73
0.01 mol/L Na_2EDTA	0.91	0.63	94.7	82.5

desorbent is an important feature for its possible utilization in continuous systems in industrial processes.

4 Conclusion

The biosorption properties of Cu^{2+} and Pb^{2+} by *C. fascicularis* were studied in this work. The biosorption processes were pH dependent. The equilibrium data fitted well to the Langmuir and Freundlich isotherm models and the maximum adsorption capacities were 1.61 mmol/g for Cu^{2+} and 0.96 mmol/g for Pb^{2+} at 298 K and pH 5.0. The adsorption processes were endothermic and the biosorption heats were 39.0 and 29.6 kJ/mol for Cu^{2+} and Pb^{2+}, respectively. Kinetics followed the pseudo-second order kinetic model. Desorption experiments proved that 0.01 mol/L Na_2EDTA was an efficient desorbent for the recovery of Cu^{2+} and Pb^{2+} from biomass. With high metal ions biosorption and desorption capacities, the biomass of *C. fascicularis* has the potential to be used as an effective and economic biosorbent for the removal and recovery of toxic heavy metals from wastewater.

Nomenclature

q	the adsorption amount at equilibrium (mmol/g)
C_0	the initial concentration of heavy metal (mmol/L)
C_e	the concentration in solution at equilibrium (mmol/L)
W	biosorbent dosage (g/L)
q_m	the maximum adsorption capacity (mmol/g)
b	an affinity constant related to the energy of adsorption (L/mmol)
K_F	Freundlich constant related to the adsorption capacity
n	Freundlich constant related to adsorption intensity of the adsorbent
b_0	a constant containing the entropy term
R^2	correlation coefficient
ΔH	the heat of the adsorption (kJ/mol)
R	universal gas constant (J/mol/K)
T	the absolute temperature (K)
t	the contact time (min)
k_2	the second order biosorption rate constant (g/mmol/min)
q_e	the amount of sorbed metal ions on the biosorbent at the equilibrium (mmol/g)
q_t	the amount of sorbed metal ions on the biosorbent at any time (mmol/g)
K'_f	conditional equilibrium constant

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