Biodegradation (2007) 18:393–402
DOI 10.1007/s10532-006-9074-6

ORIGINAL PAPER

Biosorption of copper(II) from aqueous solutions by green alga *Cladophora fascicularis*

**Liping Deng · Xiaobin Zhu · Xintang Wang ·
Yingying Su · Hua Su**

Received: 15 October 2005 / Accepted: 1 August 2006 / Published online: 8 November 2006

Abstract Biosorption is an effective means of removal of heavy metals from wastewater. In this work the biosorption behavior of *Cladophora fascicularis* was investigated as a function of pH, amount of biosorbent, initial Cu^{2+} concentration, temperature, and co-existing ions. Adsorption equilibria were well described by Langmuir isotherm models. The enthalpy change for the biosorption process was found to be 6.86 kJ mol^{-1} by use of the Langmuir constant *b*. The biosorption process was found to be rapid in the first 30 min. The presence of co-existing cations such as Na^+, K^+, Mg^{2+}, and Ca^{2+} and anions such as chloride, nitrate, sulfate, and acetate did not significantly affect uptake of Cu^{2+} whereas EDTA substantially affected adsorption of the metal. When experiments were performed with different desorbents the results indicated that EDTA was an efficient desorbent for the recovery of Cu^{2+} from biomass. IR spectral analysis suggested amido or hydroxy, C=O, and C–O could combine strongly with Cu^{2+}.

L. Deng · X. Zhu (✉) · X. Wang · Y. Su · H. Su
Institute of Oceanology, Chinese Academy
of Sciences, Qingdao 266071, Peoples Republic
of China
e-mail: xbzhu@ms.qdio.ac.cn

L. Deng · Y. Su · H. Su
Graduate School, Chinese Academy of Sciences,
Beijing 100049, Peoples Republic of China

Keywords Biosorption · Enthalpy of biosorption · Copper(II) · Marine algae · Wastewater

Introduction

The presence of heavy metals in aqueous effluents is a major environmental problem owing to their toxicity to humans and to other life forms. Because copper is widely used in industry, there are many sources of copper pollution. Copper at high concentrations is toxic to living organisms from humans to bacteria, and is especially toxic to fish (Terry and Stone 2002).

The removal and recovery of heavy metals from wastewater is important for environmental protection and human health. Several methods have been used to remove heavy metals in high concentrations from aqueous solutions, including precipitation, ion exchange, evaporation, electroplating, and membrane processes. These methods are, however, either inefficient or expensive when heavy metals are present at low concentrations (Kuyucak and Volesky 1998). It is, therefore, necessary to find new technologies or materials for removing heavy metal ions from wastewater.

Biosorption utilizes the ability of some materials to accumulate heavy metals from aqueous solutions by either metabolically mediated or physicochemical uptake pathways (Fourest and

Roux 1992). The most prominent features of biosorption are the use of low-cost and high-efficiency biomass materials to adsorb heavy metals present at very low concentrations (Yu et al. 2001). Different types of biomass, including bacteria (Mamaril et al. 1997; Selatnia et al. 2004; Iyer et al. 2005), yeast (Huang et al. 1990; Göksungur et al. 2005), fungi (Gharieb 2002; Dursun et al. 2003; Tunali et al. 2006), and algae (Yu et al. 1999; Vijayaraghavan et al. 2005, 2006; Hansen et al. 2006), have been evaluated for use as efficient metal-removing biosorbents. Marine algae are a biological resource which is available in large quantities in many parts of the world. Many studies have shown that algae have high metal-binding capacity (Ramelow et al. 1992; Holan and Volesky 1994), because of the presence, in the cell walls of the algae, of polysaccharide groups that can act as binding sites for metals. The cell wall matrix of green algae contains complex heteropolysaccharides with amino, carboxyl, and sulfate groups (Andradeet al. 2005).

Coastal areas can become eutrophicated because of loading with nutrients from human activity. As a result, large amounts of green seaweeds flourish along the coasts of the world. *Cladophora fascicularis*, a green filamentous macro-alga, is widely distributed in eutrophic wastewater, lagoons, and intertidal zones in many parts of the world. Approximately 40,000 tons of *C. fascicularis* are dumped every year in the brine pans of Jiangsu Province in China. Utilization of these affluent resources to treat wastewater is therefore of much interest. Many studies have reported biosorption by brown seaweed biomass, for example *Sargassum* sp. (Sheng et al. 2004; Diniz and Volesky 2005; Vijayaraghavan et al. 2006), *Laminaria* sp. (Figueira et al. 2000; Lodeiro et al. 2005), and *Fucus* sp. (Herrero et al. 2006). Some kinds of green seaweed, for example *Ulva* (Sheng et al. 2004; Suzuki et al. 2005) and *Cladophora* sp. (Özer et al. 1994; 2004), have been reported to have high adsorption capacity. There has been no study of the utilization of green seaweed *C. fascicularis* for metal removal. In the work discussed in this paper the adsorption behavior of *C. fascicularis* as a function of pH, biosorbent dosage, temperature, initial Cu^{2+} concentration, and co-existing ions were investigated. Equilibrium and kinetic data were obtained from batch experiments. The efficiency of removal of adsorbed Cu^{2+} from the biomass by different desorbents (H_2O, HNO_3, $Ca(NO_3)_2$, Na_2EDTA) was also evaluated. The IR spectrum of biosorbent loaded with Cu^{2+} was also analyzed.

Materials and methods

Preparation of biomass

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

Effect of solution pH on heavy metal adsorption

The effect of pH on adsorption of Cu^{2+} was investigated using 2 g L^{-1} biosorbent and a series of 1 mmol L^{-1} solutions of Cu^{2+}. The pH of the solutions was adjusted from 2.0 to 6.0 with 0.1 mol L^{-1} HNO_3 or 0.1 mol L^{-1} NaOH and maintained during the experiment. Blank samples without biomass were used as controls. The mixtures were shaken on a rotary shaker for 6 h at room temperature (25 ± 1°C) and then left stationary for 12 h to reach equilibrium. The biosorbent was removed by filtration through an acid-cleaned 0.45 μm Millipore filter and the filtrates were then analyzed by flame atomic-absorption spectrometry (Shimadzu, Japan, Model AA6800).

Adsorption equilibrium

For equilibrium studies the concentrations of heavy metal solutions varied from 0.2 to 4.0 mmol L^{-1} and the amount of biosorbent used was 2 g L^{-1}. During the reaction process the pH was maintained constant at 5.0 by hourly addition of 0.1 mol L^{-1} HNO_3 or 0.1 mol L^{-1} NaOH. The mixtures were agitated for 6 h at constant temperature (15, 25, 35, or 45°C), and then left stationary for 12 h. The amount of Cu^{2+} uptake by *C. fascicularis* in each flask was determined by use of the mass equation:

$$q = \frac{(C_0 - C_e)}{W} \quad (1)$$

Where q is the amount adsorbed at equilibrium (mmol g^{-1}); C_0 is the initial concentration of heavy metal (mmol L^{-1}); C_e is the concentration in solution at equilibrium (mmol L^{-1}); and W is the amount of biosorbent (g L^{-1}).

Effect of light metal ions and anionic ligands

The effect of light metal ions and anionic ligands was studied by using 2 g L^{-1} biosorbent and 1 mmol L^{-1} Cu^{2+} solution containing the respective light ions and anionic ligands. Blank samples without light metals and anionic ligands were used as controls.

Kinetic experiments

Kinetic experiments were performed in continuously stirred beakers containing 500 mL 1 mmol L^{-1} Cu^{2+} solution (pH 5.0) and 0.5 g biosorbent. Samples of solution (3 mL) were withdrawn at scheduled time intervals and analyzed for residual Cu^{2+} concentration.

Desorption experiments

Desorption studies were conducted with *C. fascicularis* previously loaded with Cu^{2+}. The biomass was filtered, washed three times with distilled water to remove residual heavy metal ions on the surface, and maintained in contact with 50 mL desorbent solution: H_2O, HNO_3, $Ca(NO_3)_2$, or EDTA. The mixtures were shaken on a rotary shaker for 18 h. The filtrates were analyzed to determine the concentrations of Cu^{2+} after desorption. Desorption ratio was calculated from the amount of metal ions adsorbed on the biomass and the final metal ion concentration in the desorption medium, by use of the equation:

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

Infrared spectra of *C. fascicularis*

The IR spectra of native biosorbent and of biosorbent loaded with Cu^{2+} were acquired with a Fourier transform infrared spectrometer (Bio-Rad FTS-40). The alga (5 mg) was mixed with 4.0 mg KBr and compacted into pellet form.

Results and discussion

Effect of solution pH on heavy metal adsorption

Many studies have shown that pH is an important factor affecting biosorption of heavy metals (Huang et al. 1990; Matheickal and Yu 1999; Sanchez et al. 1999). Copper removal by *C. fascicularis* as a function of pH was studied; the results are shown in Fig. 1. At pH 2, the percentage adsorption was 23% and copper removal efficiency was 14% without biosorbent, most of which was removed by the flask wall and on the mesh during filtration. At low pH there was clear competition between Cu^{2+} and protons for biomass adsorption sites. As pH was increased the percentage removal increased; it stabilized between pH 4 and 5. Above pH 6, Cu^{2+} may hydrolyze, resulting in copper deposition, and at pH 6 50% of Cu^{2+} was removed by deposition. Subsequent experiments were therefore conducted at pH 5.0.

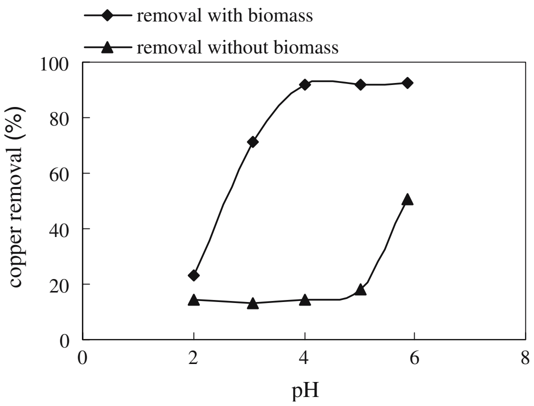

Fig. 1 Efficiency of removal of copper by *C. fascicularis* at different pH

Adsorption equilibrium

The Langmuir model 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:

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

where q_m is the maximum adsorption capacity (mmol g^{-1}) and b is an affinity constant related to the energy of adsorption (L $mmol^{-1}$). The value of b indicates the affinity of the sorbate for the solute (Holan et al. 1993).

To determine equilibrium data, Eq. 3 can be transformed to a linear form as follows:

$$\frac{1}{q} = \frac{1}{q_m bc} + \frac{1}{q_m} \tag{4}$$

Uptake of Cu^{2+} by *C. fascicularis* correlates well with the Langmuir isotherm model, as shown in Fig. 2. Values of q_m and b were obtained from Eq. 4. The value of q_m varied as the amount of biosorbent was changed. There is no criterion for the amount of biosorbent but most studies choose 2 g L^{-1} to determine q_m. For the same concentration of Cu^{2+}, as more biosorbent was added less Cu^{2+} was adsorbed per gram biomass, so the value of q_m only reflects the adsorption capacity of biomass. The maximum adsorption capacity obtained from the Langmuir isotherms was 1.48 mmol g^{-1} (for 1 g L^{-1} biosorbent) and 1.11 mmol g^{-1} (for 2 g L^{-1} biosorbent). The adsorption capacity of *C. fascicularis* is fairly high in comparison with other biosorbents (Table 1).

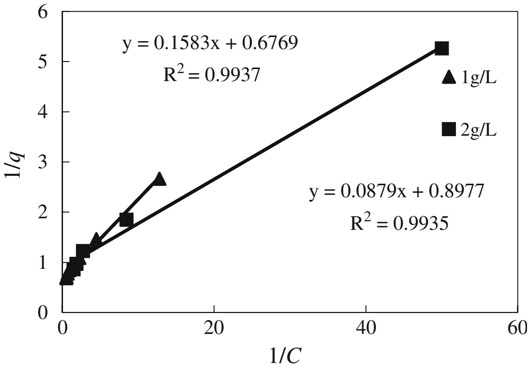

Fig. 2 Langmuir adsorption isotherms for different amounts of biosorbent

The enthalpy of biosorption of Cu^{2+} on to *C. fascicularis*

The enthalpy of biosorption can be calculated by many methods (Singh and Tiwari 1997; Sağ and Kutsal 2000; Özer and Özer 2003). Singh and Tiwari calculated the heat of adsorption of Cr(VI) ions on carbon slurry by using the energy change ($\Delta G° = \Delta H - T\Delta S$) and the equilibrium constant K_c, obtained at different temperatures. The enthalpy change was also calculated using the Langmuir constant b. The values of ΔH obtained using free energy changes, equilibrium constants, and Langmuir constants were almost equal.

The Langmuir model is based on a postulated chemical or physical interaction between the solute and vacant sites on the adsorbent surface, and the enthalpy (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 enthalpy of adsorption (kJ mol^{-1}), R is universal gas constant, and T is the absolute temperature (K).

Eq. 5 can be transformed to:

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

The adsorption isotherms for Cu^{2+} at different temperatures are shown in Fig. 3. The enthalpy of biosorption of Cu^{2+} on to *C. fascicularis* was obtained by calculating the slope of the plot of ln$b$ against $1/T$ (Fig. 4). The negative slope or positive value of enthalpy change indicated biosorption of Cu^{2+} on to *C. fascicularis* was endothermic. This was also supported by the increase of uptake capacity with increasing temperature (Table 2). The enthalpy of biosorption

Table 1 Uptake capacities of different biosorbents for Cu^{2+}

Biosorbent	q_m (mmol g^{-1})	pH	Literature
Ecklonia radiata ($CaCl_2$-pretreated)[a]	1.11	5.0	Matheickal and Yu (1999)
Durvillaea potatorum ($CaCl_2$-pretreated)[a]	1.30	5.0	Matheickal and Yu (1999)
Sargassum vulgare[a]	0.93	4.5	Davis et al. (2000)
Laminaria japonica[a]	1.59	4.5	Fourest and Volesky (1997)
Fucus vesiculosus[a]	1.18	4.5	Fourest and Volesky (1997)
Padina sp.[a]	0.80	5.0	Kaewsarn (2002)
Ulva onoi (Alkali-pretreated,1 g L^{-1})	0.90	7.8	Suzuki et al. (2005)
Cladophora crispate (1 g L^{-1})	1.03	4.5	Özer et al. (2004)
Cladophora fascicularis (1 g L^{-1})	1.48	5.0	This study
Cladophora fascicularis (2 g L^{-1})	1.11	5.0	This study

[a] The amount of biosorbent was 2 g L^{-1}

of Cu^{2+} was determined to be 6.86 kJ mol^{-1}. The enthalpy of physical adsorption is typically of the order of 10 kJ mol^{-1} (Smith 1981; Satterfield 1980). The enthalpy of biosorption of Cu^{2+} on to *C. fascicularis* was of the same magnitude as the enthalpy of physical adsorption.

Effect of light metal ions and anionic ligands on biosorption

Industrial wastewater often contains other ions, for example Na^+, K^+, Mg^{2+}, and Ca^{2+} which may interfere with uptake of heavy metal ions by biomass. The effect of these metal ions on Cu^{2+} adsorption capacity was studied; the results are shown in Fig. 5. It was evident that the effect of Na^+ and K^+ on the uptake of Cu^{2+} was very small, even at initial concentrations of 10 mmol L^{-1}. In contrast, the amount of Cu^{2+} removed dropped with increasing concentration of Mg^{2+} and Ca^{2+}. The presence of 10 mmol L^{-1} Mg^{2+} and Ca^{2+} caused the percentage removal to drop by 8% and 10%, respectively. The effect of light metal ions on uptake was because of competition with heavy metal ions for the binding sites. With decreasing hydrated ionic radius and increasing ionic charge the amount of ionic polarization increases, so the affinity of Ca^{2+} for the biosorbent was stronger than for the other ions.

The effect of five anions, chloride, nitrate, sulfate, acetate, and EDTA, as the sodium salts, was also investigated (the above experiment had shown the effect of sodium on adsorption of Cu^{2+} was negligible). Fig. 6 shows that the presence of chloride, nitrate, sulfate, and acetate did not substantially affect copper removal. Acetate at 10 mmol L^{-1} caused the removal efficiency to drop by 9%. It was obvious that EDTA substantially affected adsorption. The presence of 1 mmol L^{-1} EDTA caused the efficiency of copper removal to drop by 78%. When the concentration of EDTA was increased to 10 mmol L^{-1}

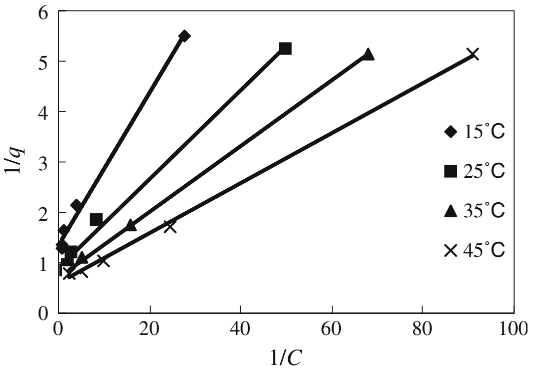

Fig. 3 Langmuir adsorption isotherms at different temperatures

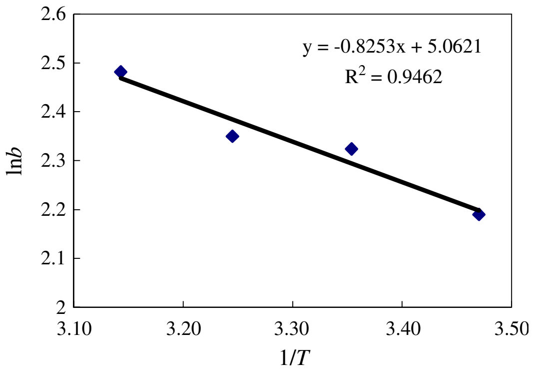

Fig. 4 Determination of the enthalpy of biosorption for Cu^{2+}

Table 2 Langmuir constants for adsorption of Cu^{2+} by *C. fascicularis* at different temperatures

T (°C)	*b* (L mmol^{-1})	q_m (mmol g^{-1})
15	8.93	0.74
25	10.21	1.11
35	10.48	1.46
45	11.96	1.74

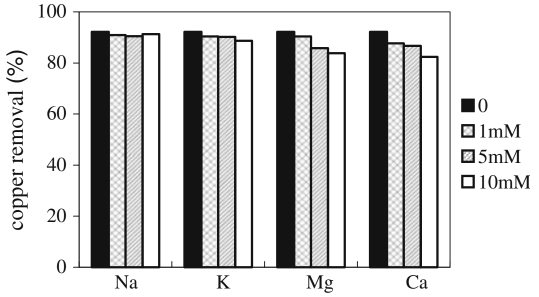

Fig. 5 Efficiency of removal of copper by *C. fascicularis* in the presence of light metal ions

the efficiency of removal was reduced to less than 10%. This was because Cu^{2+} could combine strongly with EDTA rather than with the biomass. EDTA can therefore be used as an effective agent for recovering Cu^{2+} from loaded biosorbent.

Kinetics of biosorption

Several models have been developed to describe the kinetics of heavy metal biosorption in many systems (Yang and Volesky 1999; Hashim and Chu 2004; Gupta et al. 2001). The mathematical model describing the relationship between contact time and percentage removal was used to determine the adsorption kinetics constants for the alga.

$$R_0 = at^b \tag{7}$$

The linearized version of this equation can be expressed as:

$$\lg R_0 = \lg a + b \lg t \tag{8}$$

Where R_0 is the percentage removal, *a* and *b* are the kinetics constants, and *t* is the contact time. The values of constants *a* and *b* were calculated and are listed in Table 3.

Figure 7 shows the profiles of percentage copper removal against time for Cu^{2+} uptake by *C. fascicularis* for different initial metal concentrations. Removal of Cu^{2+} was rather rapid in the first 30 min but then decreased significantly and the plots eventually reach a plateau. Uptake capacities increased with increasing initial concentrations of Cu^{2+}, because of the much greater probability of collision of Cu^{2+} with biosorbent particles.

Desorption and reuse

The amounts of Cu^{2+} recovered by different desorbents arre shown in Fig. 8. It was observed that chelating agent EDTA was more efficient than other desorbents. The biosorbent was oxidized, giving a yellow product, in 0.1 mol L^{-1} HNO_3, and biosorption capacity could not be recovered because of strong oxidation by HNO_3. EDTA at a concentration of 0.01 mol L^{-1} removed 94.7% of the Cu^{2+} bound to the biomass

Fig. 6 Efficiency of removal of copper by *C. fascicularis* in the presence of different anionic ligands

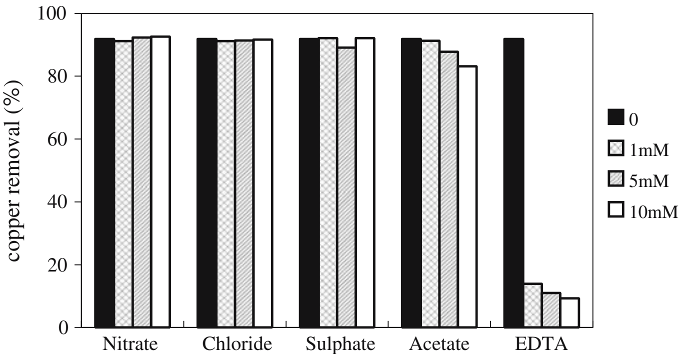

Table 3 Values of the adsorption kinetic constants

Cu^{2+} (mmol L^{-1})	a	B
1	29.44	1.321
2	21.40	1.429
4	5.635	2.004

and did not cause loss of biosorption capacity (i.e. the observed decrease of biosorption capacity did not exceed 10%). This can be explained by the high value of the conditional formation constant of the complex Cu–EDTA ($K_f' = 2.24 \times 10^{12}$, pH 5.0), which favors desorption of heavy metal from the biomass. The high percentage recovery by 0.01 mol L^{-1} EDTA enables reuse of the biomass. This is an important aspect of use of continuous systems in industrial processes.

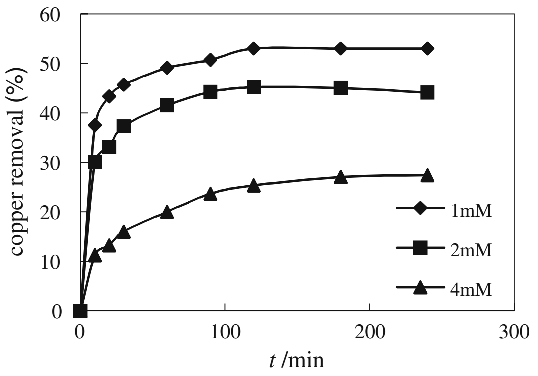

Fig. 7 Kinetics of adsorption for different initial concentrations of Cu^{2+}

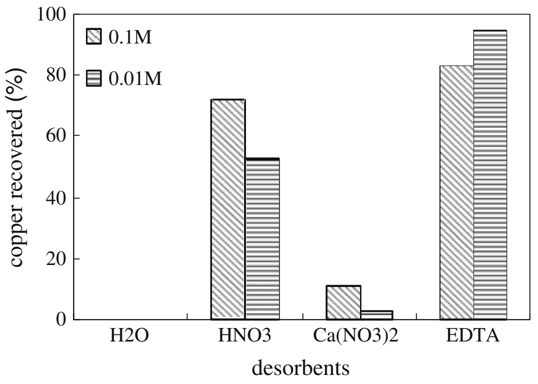

Fig. 8 Amount of Cu^{2+} recovered by use of different desorbents

IR spectrum of *C. fascicularis*

The IR spectrum of *C. fascicularis* is shown in Fig. 9. Intense characteristic bands were obtained from the functional groups present in the proteins and polysaccharides. The intense peak at 3376.39 cm^{-1} was caused by hydroxyl stretching of carboxyl groups and stretching of amido. The strong peaks at 1660.12 and 1246.96 cm^{-1} were assigned to C=O and sulfate, respectively. The peaks at 1116.93 and 1062.26 cm^{-1} were because of the presence of C–O. Some bands in the fingerprint region could be attributed to phosphate groups. The absorbance spectrum of *C. fascicularis* loaded with Cu^{2+} (Fig. 10) was compared with that of native biomass (Table 4). The peaks at 3376.39, 1660.12, and 1062.26 cm^{-1} were shifted to 3351.68, 1649.99, and 1033.47cm^{-1} respectively, which suggested that amido, hydroxy, C=O and C–O combine strongly with Cu^{2+}.

Conclusion

The characteristics of biosorption of Cu^{2+} by *C. fascicularis* were studied as a function of pH, initial Cu^{2+} concentration, temperature, and co-existing ions. The isotherms for adsorption of Cu^{2+} by different amounts of *C. fascicularis* at different temperatures was well described by the Langmuir isotherm model. The adsorption capacity of *C. fascicularis* was fairly high in comparison with some other biosorbents. The biosorption process was endothermic and the heat of biosorption was determined to be 6.86 kJ mol^{-1}. Removal was rapid in the first 30 min. The presence of the common background cations Na^+, K^+, Mg^{2+}, and Ca^{2+} and the anions chloride, nitrate, sulfate, and acetate did not substantially affect uptake of Cu^{2+} by *C. fascicularis*. The efficiency of removal of copper did, however, decrease substantially when EDTA was present. Desorption experiments proved that 0.01 mol L^{-1} EDTA was an efficient desorbent for recovery of Cu^{2+} from biomass. IR spectra of *C. fascicularis* suggested amido, hydroxy, C=O, and C–O could combine strongly with Cu^{2+}. It can be concluded that *C. fascicularis* has the potential to be used as an effective and economic biosorbent material for removal and recovery of Cu^{2+} from wastewater.

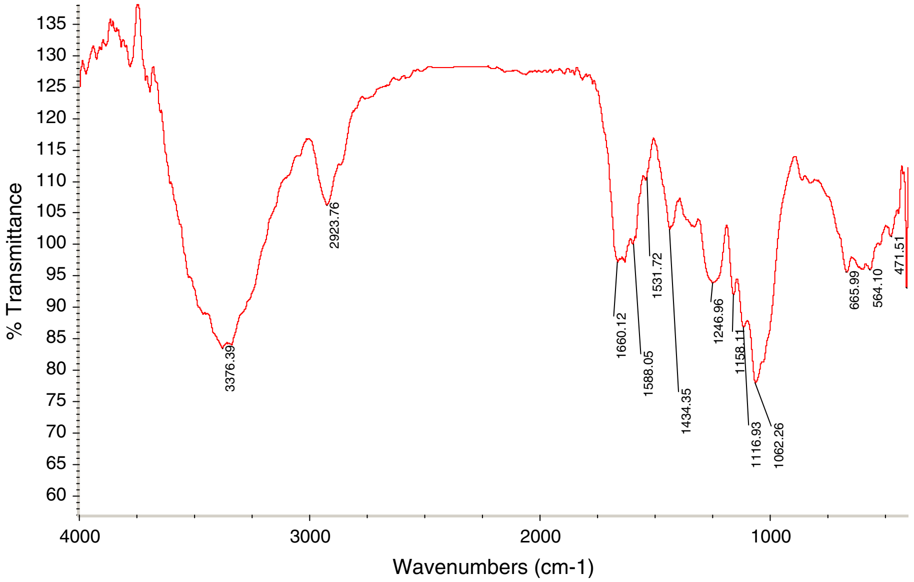

Fig. 9 IR spectrum of native *C. fascicularis*

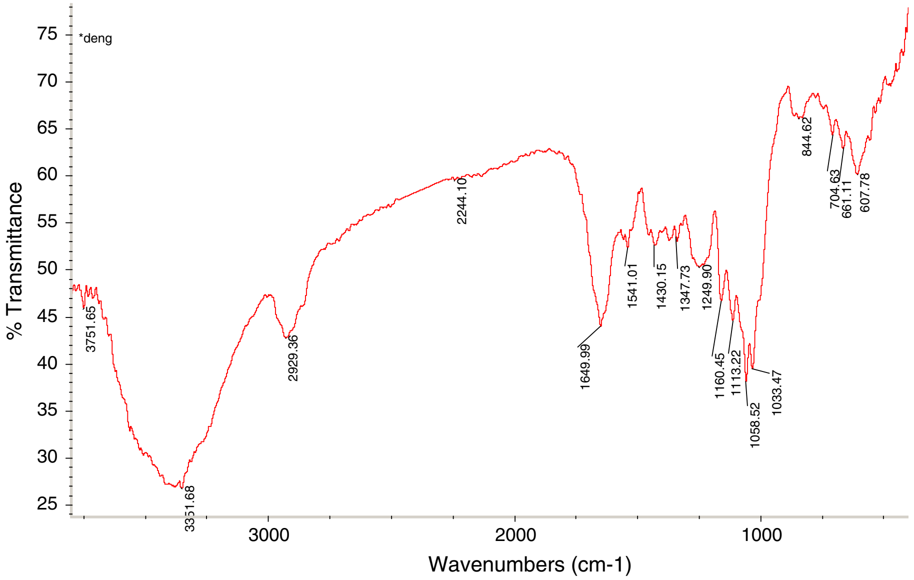

Fig. 10 IR spectrum of *C. fascicularis* loaded with Cu^{2+}

Table 4 Red-shift of the peaks of *C. fascicularis* loaded with Cu^{2+}

Functional groups	*C. fascicularis* (cm^{-1})	*C. fascicularis* loaded with Cu^{2+} (cm^{-1})
-OH, -NH_2	3376.39	3351.68
C = O	1660.12	1649.99
C-O, C-O-C	1062.26	1033.47

Acknowledgments This work was supported by the Major Project Supported by National Science Foundation of China (30530080) and Project 973 of China (No. 20028CB412402).

References

Andrade AD, Rollemberg MCE (2005) Proton and metal binding capacity of the green freshwater alga *Chactophora elegans*. Process Biochem 40(5):1931–1936s

Davis TA, Volesky B, Vieira RHSE (2000) *Sargassum* seaweed as biosorbent for metals. Wat Res 34(17):4720–4728

Diniz V, Volesky B (2005) Biosorption of La, Eu and Yb using *Sargassum* biomass. Wat Res 39(1):239–247

Dursun AY, Uslu G, Cuci Y, Aksu Z (2003) Bioaccumulation of copper(II), lead (II) and chromium (VI) by growing *Aspergillus niger*. Process Biochem 38(12):1647–1651

Figueira MM, Volesky B, Ciminelli VST, Roddick FA (2000) Biosorption of metals in brown seaweed biomass. Wat Res 34(1):196–204

Fourest E, Roux J (1992) Heavy metal biosorption by fungal mycelial by product: mechanism and influence of pH. Appl Microbiol Biotechnol 37:399–403

Fourest E, Volesky B (1997) Alginate properties and heavy metal biosorption by marine algae. Appl Biochem Biotechnol 67(3):215–226

Gharieb MM (2002) Biosorption and solubilization of copper oxychloride fungicide by *Aspergillus niger* and the influence of calcium. Biodegradation 13:191–199

Göksungur Y, Üren S, Güvenç U (2005) Biosorption of cadmium and lead ions by ethanol treated waste baker's yeast biomass. Bioresource Technol 96(1):103–109

Gupta VK, Shrivastara AK, Jain N (2001) Biosorption of chromium (VI) from aqueous solutions by green *Spirogyra* species. Wat Res 35(7):4079–4085

Hashim MA, Chu KH (2004) Biosorption of cadmium by brown, green and red seaweeds. Chem Eng J 97(2–3):249–255

Hansen HK, Ribeiro A, Mateus E (2006) Biosorption of arsenic (V) with *Lessonia nigrescens*. Miner Eng 19(5):486–490

Herrero R, Cordero B, Lodeiro P, Rey-Castro C, Sastre de Vicente ME (2006) Interactions of cadmium (II) and protons with dead biomass of marine algae *Fucus* sp. Mar Chem 99(1–4):106–116

Holan ZR, Volesky B (1994) Biosorption of lead and nickel by biomass of marine algae. Biotechnol Bioeng 43:1001–1009

Holan ZR, Volesky B, Prasetyo I (1993) Biosorption of cadmium by biomass of marine algae. Biotechnol Bioeng 41:819–825

Huang JP, Huang CP, Morehart AL (1990) Removal of Cu (II) from dilute adqueous solutions by *Saccharomyces cerevisiae*. Wat Res 24(4):433–499

Iyer A, Mody K, Jha B (2005) Biosorption of heavy metals by a marine bacterium. Mar Pollut Bull 50(3):340–343

Kaewsarn P (2002) Biosorption of copper(II) from aqueous solution by pre-treated biomass of marine algae *Padina* sp. Chemosphere 47(10):1081–1085

Kuyucak N, Volesky B (1998) Biosorbent for recovery of metals from industrial solutions. Biotechnol Lett 10:137–142

Lodeiro P, Cordero B, Barriada JL, Herrero R, Sastre de Vicente ME (2005) Biosorption of cadmium by biomass of brown marine macroalgae. Bioresource Technol 96(16):1796–1803

Mamaril JC, Paner ET, Alpante BM (1997) Biosorption and desorption studies of chromium (III) by free and immobilized *Rhizobium* (BJVr 12) cell biomass. Biodegradation 8:275–285

Matheickal JT, Yu Q (1999) Biosorption of lead (II) and copper(II) from aqueous solutions by pre-treated biomass of Australian marine algae. Bioresource Technol 69:223–229

Özer A, Özer D (2003) Comparative of the biosorption of Pb(II), Ni(II) and Cr(VI) ions onto *S cerevisiae*: determination of biosorption heats. J Hazard Mater 100:219–229

Özer A, Özer D, İbrahim Ekİz H (2004) The equilibrium and kinetic modelling of the biosorption of copper(II) ions on *Cladophora crispate*. Adso 10(4):317–326

Özer D, Asksu Z, Kutsal T, Caglar A (1994) Adsorption isotherms of lead (II) and chromium (VI) on *Cladophora crispat*. Environ Technol 15(5):439–448

Ramelow GJ, Fralick D, Zhao Y (1992) Factors affecting the uptake of aqueous metal ions by dried seaweed biomass of marine algae. Microbios 72:81–93

Sağ Y, Kutsal T (2000) Determination of the biosorption heats of heavy metal ions on *Zooloea ramigera* and *Rhizopus arrhizus*. Biochem Eng J 6:145–151

Sanchez A, Balleste A, Blazquez ML, González F, Muñoz J, Hammaini A (1999) Biosorption of copper and zinc by *Cymodocea nodosa*. FEMS Microbiol Rev 23(5):527–536

Satterfield CN (1980) Heterogeneous Catalysis in Practice. McGraw–Hill, New York, pp 35–41

Selatnia A, Boukazoula A, Kechid N, Bakhti MZ, Chergui A, Kerchich Y (2004) Biosorption of lead (II) from aqueous solution by a bacterial dead *Streptomyces rimosus* biomass. Biochem. Eng. J 19(2):127–135

Sheng PX, Ting YP, Chen JP, Hong L (2004) Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: characterization of biosorptive capacity and investigation of mechanisms. J Colloid Interface Sci 275(1):131–141

Singh VK, Tiwari PN (1997) Removal and recovery of chromium (VI) from industry waster water. J Chem Technol Biotechnol 69:376–382

Smith JM (1981) Chemical Engineering Kinetics, third ed. McGraw–Hill, New York, pp 310–322

Suzuki Y, Kametani T, Maruyama T (2005) Removal of heavy metals from aqueous solution by nonliving *Ulva* seaweed as biosorbent. Wat Res 39(9):1803–1808

Terry PA, Stone W (2002) Biosorption of cadmium and copper contaminated water by *Scenedesmus abundans*. Chemosphere 47(3):249–255

Tunali S, Akar T, Özcan AS, Kiran I, Özcan A (2006) Equilibrium and kinetics of biosorption of lead (II) from aqueous solutions by *Cephalosporium aphidicola*. Sep. Purif Technol 47(3):105–112

Vijayaraghavan K, Jegan J, Palanivelu K, Velan M (2005) Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column. Chemosphere 60(3):419–426

Vijayaraghavan K, Padmesh TVN, Palanivelu K, Velan M (2006) Biosorption of nickel (II) ions onto *Sargassum wightii*: application of two-parameter and three-parameter isotherm models. J Hazard Mater 13(1–3):304–308

Yang J, Volesky B (1999) Biosorption of uranium on *Sargassum* biomass. Wat Res 33(15):3357–3363

Yu Q, Pairat K, Ma W, Jose TM, Yin P (2001) Removal of heavy metal ions from wastewater by using biomass from marine algae—A cost effective new technology. Chinese J of Chem Eng 9(2):133–136

Yu Q, Matheickal JT, Kaewsarn P (1999) Heavy metal uptake capacities of common marine macro algal biomass. Wat Res 33:1534–1537