
Biosorption of Cu(II) and Zn(II) by intact and pre-treated biomass of *Oscillatoria planctonica*

Hui Peng

College of Resources and Environment,
Hunan Agricultural University, Changsha, China
Fax: +86 731 4617803
E-mail: penny_330@yahoo.com.cn

Yunguo Liu*, Guangming Zeng, Xin Li
and Wei Zhang

College of Environmental Science and Engineering,
Hunan University, Changsha, China
Fax: +86 731 8822829
E-mail: liuyunguo2005@yahoo.com.cn
E-mail: zgming@hnu.cn
E-mail: hgxlixin@hnu.cn
E-mail: zhangweix@hnu.cn
*Corresponding author

Abstract: The biosorption of copper(II) and zinc(II) from aqueous solution by intact and pre-treated biomass of *Oscillatoria planctonica* was studied. The biosorption was pH dependent and the adsorption capacity decreased with the biosorbent to solution ratio increasing. The maximum removal ratios were 84.84% and 68.22% respectively in pre-treated biomass. The biosorption followed both the Langmuir and Freundlich isotherm model and the adsorption equilibrium was reached in about 1 h. The adsorbed Cu(II) and Zn(II) could be desorbed effectively by 0.1 M nitric acid. The experimental results indicated that *Oscillatoria planctonica* was effective in removing Cu(II) and Zn(II) from wastewater.

Keywords: biosorption; *Oscillatoria planctonica*; copper; zinc; pre-treatment; desorption.

Reference to this paper should be made as follows: Peng, H., Liu, Y., Zeng, G.M., Li, X. and Zhang, W. (2009) 'Biosorption of Cu(II) and Zn(II) by intact and pre-treated biomass of *Oscillatoria planctonica*', *Int. J. Environment and Pollution*, Vol. 38, Nos. 1/2, pp.1–14.

Biographical notes: Hui Peng is presently a Lecturer at Hunan Agricultural University. She received her BS Degree and MSc from Hunan University. Her research interests include handling heavy metal contaminated soils and waters. She has published several papers in journals and conference proceedings.

Yunguo Liu received his BS, MSc from Central South University of Forestry and Technology in 1982 and 1987. In 1998, he obtained his PhD Degree from the Institute of Plant Physiology and Ecology Shanghai Institutes for

Biological Sciences, Chinese Academy of Sciences. He is currently Professor at the College of Environmental science and Engineering, Hunan University. His research interests include remediation technologies of contaminated liquids and soils and Environmental ecology. He has published many papers in journals and conference proceedings.

Guangming Zeng received his BS in Hydromechanics and Water Channels Engineering, MSc and PhD in Water Resources and Water Environment from Wuhan University in 1978–1988. He is presently the Head of College of Environmental science and Engineering. His research interests are in the areas of environmental pollution from waters and gases and environmental simulation. He has published lots of papers in journals and conference proceedings.

Xin Li is presently a Senior Lecturer at Hunan University. He received his BS from the University of Northeast, China in 1996. He received his MSc from Hunan University. He has published several papers in journals and conference proceedings.

Wei Zhang is presently a Senior Lecturer at Hunan University. She received her BS Degree in Environmental Engineering from the Hunan University.

1 Introduction

Heavy metals like cadmium, nickel, copper, lead, zinc and chromium have formed a serious threat to human health and the global ecosystem due to their persistence and non-biodegradability. The increase in small-scale industrial activities especially metal finishing, alloy making, electroplating, mining and battery manufacturing has led to many-fold increase in the release of heavy metals because of the low returns from investing in the area of effluent treatment. Copper and zinc are the most important metals often found in effluents discharged from these industries. Though Cu(II) and Zn(II) are necessary as micronutrients for normal development of biological cycles and are potentially less toxic, special attention needs to be taken at their toxicant at high concentrations as a result of their solubility, mobility and accumulation throughout the food chain. A number of methods have been developed for removing heavy metals from waste water include: evaporation, chemical precipitation, electroplating, adsorption, ion-exchange and membrane separation process. However, certain drawbacks of the conventional methods have been noticed such as high cost, generation of toxic wastes and other difficulties (Kapoor and Viraraghavan, 1995; Harry, 1999) which has urged for an alternative process.

Biosorption, the process of passive binding by non-living biomass, represent a potentially cost effective and efficient way of removing heavy metals from an aqueous solution (Thomas et al., 2003). It is a rapid, economical and reversible technology in contrast to conventional methods and could be employed most effectively in a concentration range below 100 mg/L, where other techniques are ineffective or costly (Schiewer and Volesky, 1995; Palmieri et al., 2002; Nuhoglu, 2002). Furthermore, it appears to present specific advantages in comparison to bioaccumulation, another dissolved metal removal bioprocess which requires the metabolic activity of a living organism. For instance, non-living biomass eliminates the problem of heavy metal

toxicity and the need of nutrient requirement for metabolism. Wide variety of biomass for removal of heavy metals such as fungi, algae, bacteria and yeast have been studied for the last two decades with very encouraging results (Veglio and Beolchini, 1997; Bakkaloglu et al., 1998; Thomas et al., 2003; Neetu et al., 2005; Márcia et al., 2005). These microbes are known to remove metal ions by interaction between metal cations and the cell surface which contain polysaccharides as basic building blocks. The polysaccharides are also recommended as surface-active agents for heavy metal removal which provide amino, hydroxyl, carboxylate, sulphate and phosphate (Özer et al., 1994; Ariff et al., 1999).

The present study was focused on copper and zinc biosorption by a fresh water cyanobacterium *Oscillatoria planctonica*, which is one of the most common algae considered as bioindicators of eutrophication. The biomass was pre-treated by CaCl₂ solution to improve the stability and the metal removal capacity (Pairat, 2002). The objective of this investigation was to study the equilibrium, kinetics and mechanism of Cu(II) and Zn(II) biosorption by both intact and pre-treated biomass and the desorption, assay the effect of pre-treatment and some physical or chemical parameters on the biosorption.

2 Materials and methods

2.1 Biomass and culture medium

Oscillatoria planctonica was obtained from the Freshwater Algae Culture Collection of the Institute of Hydrobiology, the Chinese Academy of Sciences (FACHB-Collection). It was cultured in the HGZ medium adjusted to pH 8–8.5, maintained at 25 ± 1°C with 12 : 12 h of light/dark cycle using 2000 lx light intensity. After a 14-day cultivation period cells were harvested by centrifugation and were washed three times with deionised water in order to remove remaining culture medium, dried at 80°C for 12 h and then sieved for particle size of 150 µm.

HGZ medium was prepared with analytical grade reagents. The working solution had solution PIV 3 mL/L and the following macronutrient composition in g/L : NaNO₃, 0.496; K₂HPO₄, 0.039; MgSO₄ · 7H₂O, 0.075; CaCl₂ · 2H₂O, 0.036; Na₂SiO₃ · 9H₂O, 0.058. Solution PIV contained in mg/L: Na₂EDTA, 750; FeCl₃ · 6H₂O, 97; MnCl₂ · 4H₂O, 41; ZnCl₂, 5; CoCl₂ · 6H₂O, 2; Na₂MoO₄ · 2H₂O, 4.

2.2 Biomass pre-treatment

Pre-treatment of the biomass was carried out as follow. A sample of 20 g of dry biomass was treated with 0.2 M CaCl₂ solution (400 mL) for 24 h under slow stirring. The solution pH was kept at pH 5.0 by using 0.1 M HNO₃ or NaOH solution. The calcium treated biomass was washed three times with deionised water to remove excess calcium from the biomass. The biomass was then heated in an oven at 60°C for 24 h and made into powder of 150 µm.

2.3 Biosorption studies

The biosorption of Cu(II) and Zn(II) on intact and pre-treated algal biomass was studied by batch technique. Stock solutions (2000 mg/L) of Cu(II) and Zn(II) were prepared by

dissolving $\text{Cu}(\text{NO}_3)_2$ or $\text{Zn}(\text{NO}_3)_2$ (analytical grade) in deionised water. The test solutions of various concentrations ranged from 10 mg/L to 200 mg/L were prepared from the stock solution. The general method used for this study was described as follows: a known weight of biomass was mixed with 50 mL known concentration of metal solution in 100 mL shaking flasks. The solution pH was adjusted using 0.1 M HNO_3 or NaOH at the beginning of the experiment and not controlled afterwards. The flasks were shaken at 200 rpm and $25 \pm 1^\circ\text{C}$ for 12 h in a temperature controlled rotatory shaker.

To determine the effect of dose of adsorbent on adsorption, different amounts of adsorbent were added to vary the solid/liquid ratio in the range of 0.2–3 g/L at pH 4.5 and the metal concentration was 50 mg/L. Effect of pH and temperature on biosorption were investigated at pH values of 2.0–5.5 and four different temperatures (i.e., 15, 25, 35 and 45°C) at 50 mg/L initial metal concentration. To examine the effect of initial concentration of Cu(II) or Zn(II) on the biosorption rate and capacity, the initial concentration was varied between 25–300 mg/L at pH 4.5 and $25 \pm 1^\circ\text{C}$. Kinetic experiments were conducted in batch samples containing 50 mg biomass and 50 mL metal solution (50 mg/L) at pH 4.5 and $25 \pm 1^\circ\text{C}$. The residual metal concentration was measured for 12 h: every 10 min for the first hour and every two hours afterwards.

After agitating the flasks for predetermined time intervals, each reaction mixture was centrifuged at 5000 rpm for 10 min and then the supernatant solution was used to analyse for the heavy metal concentration by Atomic Adsorption Spectrophotometer (PE700). Metal uptake (q_{eq}) was calculated using the following equation (1):

$$q_{eq} = \frac{(C_0 - C_{eq})V}{W} \quad (1)$$

where q_{eq} (mg/g) is the amount of Cu(II) or Zn(II) adsorbed onto the unit amount of the biomass, C_0 (mg/L) is the initial metal concentration, C_{eq} (mg/L) is the equilibrium metal concentration after biosorption, V (L) is the initial volume of metal solution, and W (g) is the adsorbent weight. All experiments were conducted in triplicate and mean values were used in the analysis of data.

2.4 FT-IR spectroscopy

About 0.1 g intact biomass (before and after pre-treatment or biosorption) was mixed with KBr for FT-IR spectra analysis (Nexus 670, Nicolet).

2.5 Desorption

Desorption of Cu(II) and Zn(II) from previously loaded *Oscillatoria planctonica* was performed by 0.1 M HNO_3 and EDTA. The algal biomass loaded with heavy metal ions was placed in desorption medium and stirred at 200 rpm for 90 min at $25 \pm 1^\circ\text{C}$, the supernatant was analysed for the metal concentration. Desorption ratios were calculated from the equation (2):

$$R = \frac{A_{de}}{A_{ad}} \times 100\% \quad (2)$$

where R is the desorption ratio, A_{de} (mg/g) is the amount of metal desorbed, A_{ad} (mg/g) is the amount of metal adsorbed.

3 Result and discussion

3.1 Influence of pH value

Solution pH is an important parameter in biosorption of heavy metals, not only because pH can significantly influence the cell surface metal binding sites but also it can affect the availability of heavy metal ions. The influence of pH on copper and zinc biosorption by *Oscillatoria planctonica* was studied in range of 2–5.5 because pH value higher than 5.5 promoted the heavy metal precipitation (Nuhoglu, 2002). As shown in Figures 1 and 2, at pH less than 2, the amount of biosorption was less for both copper and zinc, especially the adsorption of zinc by intact biomass at pH 2 was almost negligible. Biosorption of both Cu(II) and Zn(II) increased with increasing pH levels. Within the pH range of 2–4, the biosorption capacity of both intact and pre-treated biomass increased rapidly, and in the pH range of 4–5.5, tended to a maximum value. The maximum removal capacity of the pre-treated biomass was 25.14 mg/g for Cu(II) and 21.3 for Zn(II) at pH 5.5. Similar trends have been also reported by other authors for heavy metal biosorption (Pairat and Qiming, 2001; Osman et al., 2005; Renmin et al., 2005). Various reasons might be suggested to explain the metal adsorption behaviour of the biomass relative to solution pH. The biosorption of Cu(II) or Zn(II) on biomass is mainly due to ionic attraction between cations and the active sites on the cell surface. At low pH, the heavy metal ions are in competition with the H⁺, but the binding sites are closely linked to the H⁺ ions for their high concentration. However, with an increase in pH, the competing effect of H⁺ ions decreases and the binding of heavy metal cations is hence increased (Prerna et al., 1999; Pairat and Qiming, 2001). For further biosorption studies pH value 4.5 was selected to prevent H⁺ competition and to fit the pH range from 3.0 to 5.0 of the typical wastes produced by many manufacturers (Flávia et al., 2005). The optimal pH value of 4.5 was also used for biosorption of copper and zinc by various algae (Sánchez, 1999; Nuhoglu, 2002).

Figure 1 Influence of pH on copper biosorption by *O. planctonica* (Cu(II) concentration: 50 mg/L; biosorbent dose: 1 g/L; temperature: 25°C; contact time: 12 h)

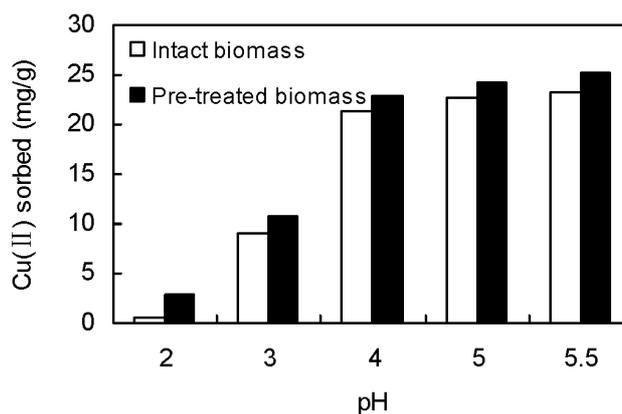
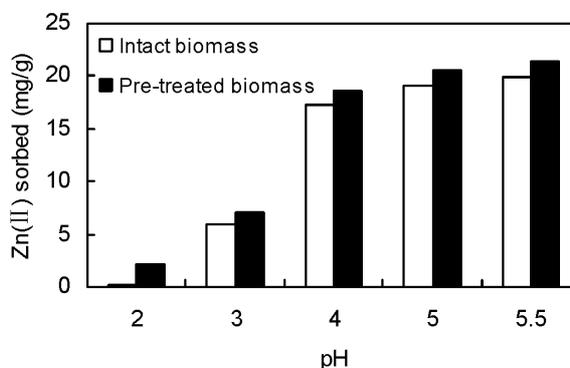


Figure 2 Influence of pH on zinc biosorption by *O. planctonica* (Zn(II) concentration: 50 mg/L; biosorbent dose: 1 g/L; temperature: 25°C; contact time: 12 h)



3.2 Effect of dose of adsorbent and temperature

The effect of biomass concentrations on copper and zinc biosorption by *Oscillatoria planctonica* was shown in Figures 3 and 4, where the amounts of metal adsorbed onto the unit amount of biomass and the percentages of metal adsorbed were plotted against biosorbent/solute ratio. When the biosorbent doses were increased from 0.2 g/L to 3.0 g/L, the percentages of Cu(II) adsorbed increased from 18.74% to 79.62% in intact biomass and from 20.91% to 84.84% in pre-treated biomass, but the amounts of Cu(II) adsorbed reduced from 46.85 mg/g to 13.27 mg/g and 52.27 mg/g to 14.14 mg/g in intact and pre-treated biomass, respectively. Similarly, for zinc, the percentages of adsorption increased from 15.80% to 65.60% and 17.20% to 68.22%, but the amount of Zn(II) adsorbed on unit weight of adsorbent decreased from 39.50 mg/g to 10.93 mg/g and 43.00 mg/g to 11.37 mg/g, respectively for intact and pre-treated biomass. Increased amount of biosorbent resulted in higher removal of heavy metals from the solution as is expected because the total sites of adsorption increased. But the interference and competition between available binding sites at higher biomass densities caused decrease in the specific adsorption capacity of the biosorbent.

Figure 3 Effect of biosorbent dose on copper or zinc removal by *O. planctonica* (Cu(II) or Zn(II) concentration: 50 mg/L; pH: 4.5; temperature: 25°C; contact time: 12 h)

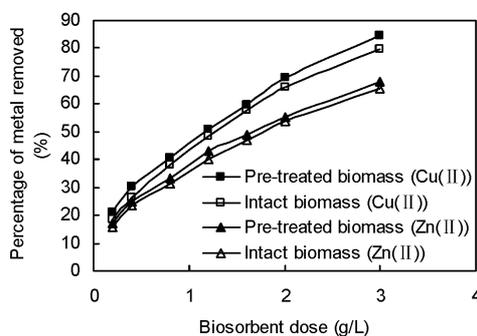
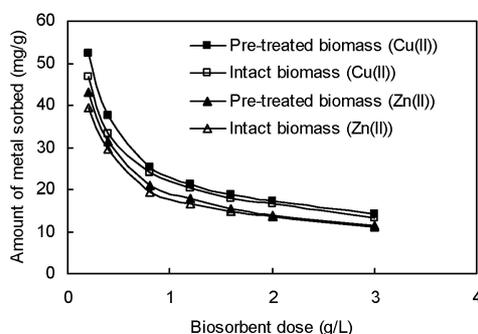
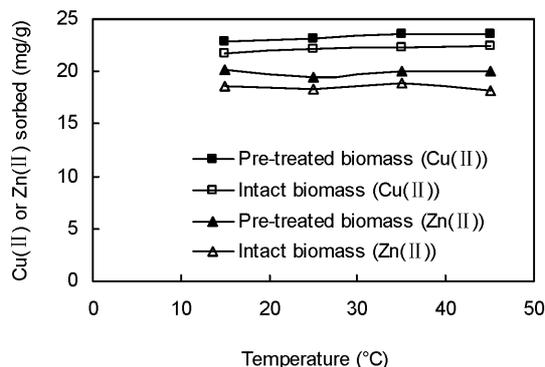


Figure 4 Effect of biosorbent dose on copper or zinc biosorption by *O. planctonica* (Cu(II) or Zn(II) concentration: 50 mg/L; pH: 4.5; temperature: 25°C; contact time: 12 h)



As shown in Figure 5, the temperature has no significant effect on the biosorption of copper and zinc over the tested temperature range of 15–45°C at pH 4.5. The temperature independent biosorption of copper and zinc in this study is in accordance with the studies of Perna et al. (1999), Wallace et al. (2003) and Vitor et al. (2005), indicating biosorption to be a passive energy independent process.

Figure 5 Influence of temperature on copper or zinc biosorption by *Oscillatoria planctonic* (biosorbent dose: 1 g/L; pH: 4.5; metal concentration: 50 mg/L; contact time: 12 h)

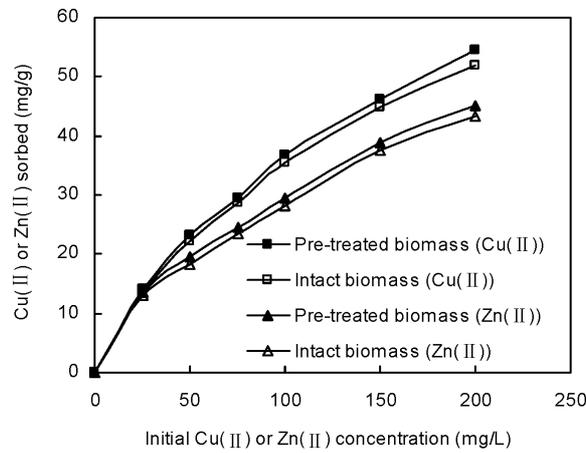


3.3 Effect of initial heavy metal concentration on biosorption and the adsorption isotherms

Biosorption capacities for Cu(II) and Zn(II) of both intact and pre-treated biomass were presented as a function of the initial concentration between 25–200 mg/L as shown in Figure 6. It was noted that, as the initial concentration increased the sorption of Cu(II) or Zn(II) increased as is generally expected due to equilibrium process. For example, when the initial heavy metal concentration increased from 25 mg/L to 200 mg/L, the amount of Zn(II) adsorbed by pre-treated biomass increased from 13.65 mg/g to 45.2 mg/g, and from 14.1 mg/g to 54.4 mg/g for Cu(II) adsorbed. This indicated that initial heavy metal concentration is important for biosorption. Higher initial metal concentration provides higher availability of metal ions in the solution and driving force to overcome all mass transfer resistance of metal ions between the aqueous and solid phases, resulting in higher

probability of collision between metal ions and biosorbents. As seen in Figure 6, pre-treatment by 0.2 M CaCl₂ enhanced both Cu(II) and Zn(II) biosorption compared to the intact form. The pre-treatment was a two-stage process of thermal and chemical modification of the native biomass. It prevented leaching of alginate from the biomass, improved the chemical stability of biosorbents by reducing the amount of total organic carbon content (Pairat and Qiming, 2001). The CaCl₂ pre-treatment may also improved the mechanical stability of biomass by reducing the swelling volumes and the attrition loss, facilitated the separation of the solution and biosorbent. However, the increases in the biosorption capacity of *Oscillatoria planctonica* after CaCl₂ pre-treatment in this study were not so significant as the study of Renmin et al. (2005) due to the different characters of the two algae.

Figure 6 Effect of initial concentration of copper or zinc on its biosorption by *O. planctonica* (biosorbent dose: 1 g/L; pH: 4.5; contact time: 12 h; temperature: 25°C)



The adsorption isotherms generally used for the design of the equilibrium established between adsorbed phase on the biosorbents and that in solution. The Langmuir and Freundlich isotherm equations are the most commonly used for modelling equilibrium. The mathematical description of the Langmuir model is as follows:

$$q_{eq} = \frac{Q_{max} b C_{eq}}{1 + b C_{eq}} \quad (3)$$

where C_{eq} (mg/L) and q_{eq} (mg/g) show the residual metal concentration and the amount of metal adsorbed on the adsorbent at equilibrium, respectively. Q_{max} (mg/g) and b (L/mg) are Langmuir constants denoting maximum adsorption capacity and the affinity of the binding sites, respectively. Langmuir isotherm equation is based on monolayer sorption onto a surface with finite number of identical sites, which are homogeneously distributed over the adsorbent surface, and the energy of adsorption is constant. The Freundlich equation takes the form:

$$q_{eq} = K_f C_{eq}^{1/n} \quad (4)$$

where K_f and n are Freundlich constants related to sorption capacity and sorption intensity, respectively. Freundlich equation is the empirical relationship whereby it is assumed that the adsorption energy of a metal binding to a site on an adsorbent depends on whether or not the adjacent sites are already occupied. To obtain the adsorption isotherm parameters, experimental data were fitted by linear transfer of both equations to:

$$\frac{C_{eq}}{q_{eq}} = \frac{1}{Q_{max}} C_{eq} + \frac{1}{bQ_{max}} \quad (5)$$

$$\ln q_{eq} = \frac{1}{n} \ln C_{eq} + \ln K_f. \quad (6)$$

The Langmuir and Freundlich adsorption constants calculated from the corresponding isotherms with the correlation coefficients are presented in Table 1. The maximum adsorption capacity Q_{max} of the pre-treated biomass was 73.53 mg/g for Cu(II) and 59.52 mg/g for Zn(II). The Q_{max} of the pre-treated biomass of *Oscillatoria planctonica* is considerably high (Cetinkaya et al., 1999; Pairat, 2002; Feng and Aldrich, 2004), however direct comparison of the biosorbents is difficult due to the varying experimental conditions. As seen from Table 1, the Freundlich model exhibited a slightly better fit to the biosorption data than the Langmuir model. However, the Langmuir model also seemed to fit with the experimental data. Similar results were also suggested by Perna et al. (1999), Aksu and Tezer (2000) and Pan et al. (2005). This observation implied that the overall sorption of Cu(II) and Zn(II) on the biomass was complex, monolayer biosorption, as well as heterogenous surface conditions might co-exist under the applied experimental conditions. Furthermore, the magnitudes of K_f and n showed that the pre-treated biomass was more applicable for its higher adsorption capacity and separability than the intact biomass.

Table 1 Comparison of Langmuir and Freundlich parameters and correlation regression coefficients of copper and zinc biosorption by *Oscillatoria planctonica*

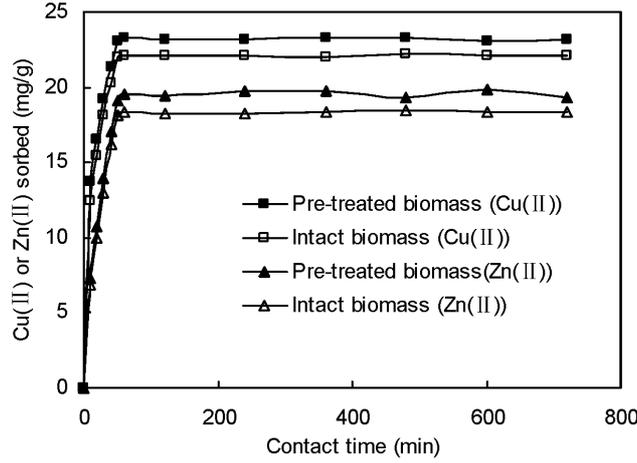
Type of biomass	Cu(II)			Zn(II)		
	q_{eq} (mg/g)	K_2 (g/mg/min)	r^2	q_{eq} (mg/g)	K_2 (g/mg/min)	r^2
Intact	22.22	0.0129	0.9998	18.59	0.0078	0.9994
Pre-treated	23.31	0.0139	0.9999	19.76	0.0079	0.9992

3.4 Biosorption kinetics

The rate of Cu(II) and Zn(II) biosorption by both intact and pre-treated biomass of *Oscillatoria planctonica* are shown in Figure 7. It was observed that about 90% of the total adsorbed Cu(II) or about 80% of the total adsorbed Zn(II) was removed from the solution within 30–40 min of agitation. The amount of biosorption increased with time at slower rates after the rapid biosorption, and no further significant increase was observed beyond 1 h for both kinds of biomass. Heavy metal uptake by non-living biomass, which is metabolism-independent passive binding to external surfaces, is generally considered as a rapid process (Yasemin and Ayten, 2005). Being in accord with biosorption studies with various biosorbents (Akhtar et al., 1996; Kadukova and Vircikova, 2005;

Yasemin and Ayten, 2005; Vitor et al., 2005), the initial rapid metal uptake observed in this study has a practical importance as it will facilitate shorter adsorption columns ensuring efficiency and economy.

Figure 7 Effect of contact time of copper or zinc on its biosorption by *O. planctonica* (Cu(II) or Zn(II) concentration: 50 mg/L; pH: 4.5; biosorbent dose: 1 g/L; temperature: 25°C)



The kinetics of Cu(II) and Zn(II) biosorption were determined with pseudo second-order model, which is expressed as:

$$\frac{dq}{dt} = K_2(q_{eq} - q_t)^2 \quad (7)$$

where q_{eq} (mg/g) and q_t (mg/g) are the amount of metal adsorbed on the biosorbent at equilibrium and at time t , respectively. K_2 (g/mg/min) is pseudo second-order rate constant. After integration and applying the same boundary conditions $t = 0$ and $q_t = 0$ to $t = t$ and $q_t = q_{eq}$ at equilibrium, equation (8) becomes:

$$\frac{t}{q_t} = \frac{1}{K_2 q_{eq}^2} + \frac{t}{q_{eq}} \quad (8)$$

where q_{eq} and K_2 can be determined from the intercept of linearised plot of t/q_t vs. t . The linearised pseudo second-order kinetic plots of Cu(II) and Zn(II) biosorption by *Oscillatoria planctonica* and the values of various kinetic parameters are presented in Figure 8 and Table 2. The correlation coefficients for the pseudo second-order kinetic model obtained were high ($r^2 > 0.999$). Also, the theoretical q_{eq} values for both intact and pre-treated biomass were very close to the experimental data. These suggested that the second-order kinetic model described the experimental data well and the overall adsorption process appeared to be controlled by chemical process (Ho and McKay, 1999).

Figure 8 Linearised pseudo second-order kinetic plots of copper and zinc biosorption by *Oscillatoria planctonica* (Cu(II) or Zn(II) concentration: 50 mg/L; pH: 4.5; biosorbent dose: 1 g/L; temperature: 25°C)

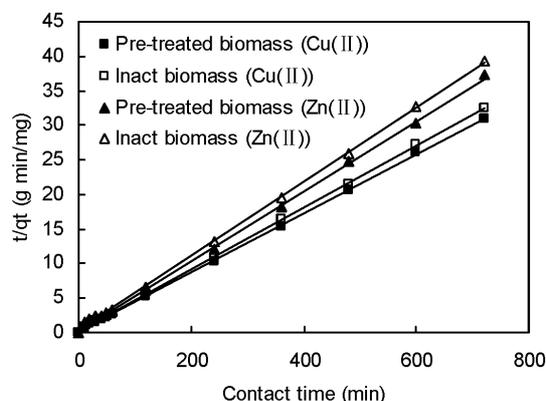


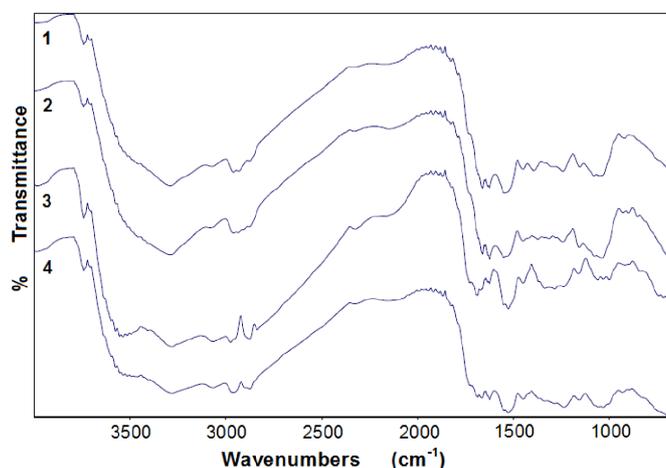
Table 2 Pseudo second-order kinetic parameters and correlation regression coefficients of copper and zinc biosorption by *Oscillatoria planctonica*

Heavy metal	Biomass	Langmuir isotherm			Freundlich isotherm		
		Q_{max} (mg/g)	b (L/mg)	r^2	K_f	n	r^2
Copper	Pre-treated	73.53	0.0173	0.9747	4.09	1.91	0.9981
	Intact	70.92	0.0168	0.9835	3.94	1.89	0.9976
Zinc	Pre-treated	59.52	0.0170	0.9420	4.15	2.14	0.9880
	Intact	58.48	0.0158	0.9372	3.76	2.10	0.9850

3.5 Infrared spectrum analysis

The infrared spectra of intact biomass before and after pre-treatment and biosorption are shown in Figure 9. In general, the FT-IR spectra of the intact and pre-treated biomass before biosorption had an adsorption band at a frequency level of 3300 cm^{-1} representing -OH stretching of carboxylic groups and also representing stretching of -NH groups. The adsorption band at 2960 cm^{-1} was caused by the stretching of -CH groups. The adsorption peaks at 1661 cm^{-1} could be assigned to vibration of C=O and -NH (amide I) peptidic bond of proteins. The adsorption bands at 1550 cm^{-1} and 1051 cm^{-1} were stretching vibrations of C-N and C-O-C of polysaccharides, respectively. The infrared spectra of Cu(II) or Zn(II)-loaded biosorbents showed that, after biosorption, the adsorption intensity of amide I and C-O-C groups decreased obviously. This indicated that these two groups played important role in Cu(II) and Zn(II) biosorption. The stretching vibration of -OH , -CH and C-N groups shifted for a certain extent in addition, which indicated that these three groups possibly involved in the biosorption.

Figure 9 (1) FT-IR spectrum of intact biomass; (2) pre-treated biomass; (3) intact biomass after Zn(II) adsorption and (4) intact biomass after Cu(II) adsorption (see online version for colours)



3.6 Desorption

When considering the choice of a biosorbent in the wastewater treatment it is necessary to evaluate not only the biosorption capacity, but also how well the biomass can be regenerated and used again. For repeated use of a biosorbent in another biosorption cycle, adsorbed metal ions should be easily recovered in the form of concentrated solution under suitable conditions. The results of desorption studies of Cu(II) and Zn(II) in a batch system are shown in Table 3. It was found that HNO₃ (0.1 M) was more efficient in both Cu(II) and Zn(II) desorption, which removed 93% zinc ions and 96% copper ions bound with the pre-treated biomass. Katarzyna et al. (2005) has also reported that nitric acid in the concentration of 0.1 M was the most efficient desorbent of Cu(II), Cd(II) and Cr(III). It removed most of the metal ions bound by the biomass and preserved the biosorptive properties of biomass.

Table 3 The desorption efficiency of different desorbents (biomass dose: 1 g/L; Cu(II) or Zn(II) concentration: 50 mg/L; desorption time: 90 min)

Type of biomass	EDTA (0.1 M)		HNO ₃ (0.1 M)	
	Cu(II) (%)	Zn(II) (%)	Cu(II) (%)	Zn(II) (%)
Intact	66	61	94	90
Pre-treated	71	65	96	93

4 Conclusions

The batch experiments conducted with the biosorption demonstrated that both intact and pre-treated biomass of *Oscillatoria planctonica* exhibited the potential for Cu(II) and Zn(II) removal from aqueous solution. The external pH significantly influenced the biosorption, while the biosorption capacity was not affected by temperature.

Optimum pH and temperature for biosorption in studied pH and temperature range were found as 4.5°C and 25°C, respectively. Although the removal of Cu(II) and Zn(II) increased with increase in biosorbent to solution ratio, the sorption capacity of both biosorbents decreased. The biosorption process of both the intact and pre-treated biomass followed both the Freundlich isotherm model and the Langmuir model. The biosorption capacity was found to increase with increasing the solution concentration. The biosorption rate was rapid and equilibrium was reached after 50–60 min. The pseudo second-order kinetics described the experimental data well. HNO₃ (0.1 M) had higher efficiency of both Cu(II) and Zn(II) desorption than EDTA (0.1 M). The analysis of FT-IR spectrum showed the presence of different functional groups in the biomass of *Oscillatoria planctonica*, and their participation in the biosorption of Cu(II) and Zn(II).

Acknowledgements

This research was supported by the National Natural Science Foundation of Hunan (No. 04JJ3013), the Doctoral Foundation of Ministry of Education of China (No. 20050532009) and the National 863 High Technology Research Program of China (No. 2001AA644020, No. 2003AA644010, No. 2004AA649370).

References

- Akhtar, M.N., Sivarama, S.K. and Maruthi, M.P. (1996) 'Mechanism of metal ion biosorption by fungal biomass', *BioMetals*, Vol. 9, No. 1, pp.21–28.
- Aksu, Z. and Tezer, S. (2000) 'Equilibrium and kinetic modelling of biosorption of remazol black B by *Rhizopus arrhizus* in a batch system: effect of temperature', *Process Biochem.*, Vol. 36, pp.431–439.
- Ariff, A.B., Mel, M., Hasan, M.A. and Karim, M.I.A. (1999) 'The kinetics and mechanism of lead(II) biosorption by powderized *Rhizopus oligosporus*', *World J. Microbiol. Biotechnol.*, Vol. 15, No. 2, pp.291–298.
- Bakkaloglu, I., Butter, T.J., Evison, L.M., Holland, F.S. and Hancock, I.C. (1998) 'Screening of various types biomass for removal and recovery of heavy metals (Zn, Cu, Ni) by biosorption, sedimentation and desorption', *Wat. Sci. Tech.*, Vol. 38, No. 6, pp.269–277.
- Cetinkaya, G.D., Aksu, Z., Öztürk, A. and Kutsal, T. (1999) 'A comparative study on heavy metal biosorption characteristics of some algae', *Process Biochem.*, Vol. 34, No. 9, pp.885–892.
- Feng, D. and Aldrich, C. (2004) 'Adsorption of heavy metals by biomaterials derived from the marine alga *Ecklonia maxima*', *Hydrometallurgy*, Vol. 73, Nos. 1–2, pp.1–10.
- Flávia, P.P., Francisca, P.F. and Antonio, C.A.C. (2005) 'The use of waste biomass of *Sargassum sp.* for the biosorption of copper from simulated semiconductor effluents', *Bioresour. Technol.*, Vol. 96, No. 13, pp.1511–1517.
- Harry, E. (1999) 'Treatment of metal-contaminated wastes: why select a biological process', *Trends Biotechnol.*, Vol. 17, No. 12, pp.462–465.
- Ho, Y.S. and McKay, G. (1999) 'Pseudo-second order model for sorption processes', *Process Biochem.*, Vol. 34, No. 5, pp.451–456.
- Kadukova, J. and Vircikova, E. (2005) 'Comparison of differences between copper bioaccumulation and biosorption', *Environment International*, Vol. 31, No. 2, pp.227–232.
- Kapoor, A. and Viraraghavan, T. (1995) 'Fungal biosorption – an alternative treatment option for heavy metal bearing wastewaters: a review', *Bioresour. Technol.*, Vol. 53, No. 3, pp.195–206.

- Katarzyna, C., Andrzej, C. and Helena, G. (2005) 'Biosorption of Cr^{3+} , Cd^{2+} and Cu^{2+} ions by blue-green algae *Spirulina sp.*: kinetics, equilibrium and the mechanism of the process', *Chemosphere*, Vol. 59, No.1, pp.75–84.
- Márcia, T.V., Célia, R.G.T., Sandra, M. and Terezinha, A.G. (2005) 'Adsorption isotherms of copper(II) for two species of dead fungi biomasses', *Process Biochem.*, Vol. 40, No. 10, pp.3303–3308.
- Neetu, T., Vasudevan, P. and Guha, B.K. (2005) 'Study on biosorption of Cr(VI) by *Mucor hiemalis*', *Biochemical Eng. J.*, Vol. 23, No. 2, pp.185–192.
- Nuhoglu, Y. (2002) 'The removal of Cu(II) from aqueous solutions by *Ulothrix zonata*', *Bioresour. Technol.*, Vol. 85, No. 3, pp.331–333.
- Osman, G., Saadet, S. and Erdal, K. (2005) 'Study of Cu(II) biosorption by dried activated sludge: effect of physico-chemical environment and kinetics study', *J. Hazardous Materials*, Vol. 120, Nos. 1–3, pp.193–200.
- Özer, D., Aksu, Z., Kutsal, T. and Caglar, A. (1994) 'Adsorption Isotherms of Lead(II) and Chromium(VI) on *Cladophora Crispata*', *Environ. Technol.*, Vol. 15, No. 5, pp.439–448.
- Pairat, K. (2002) 'Biosorption of copper(II) from aqueous solutions by pre-treated biomass of marine algae *Padina sp.*', *Chemosphere*, Vol. 47, No. 10, pp.1081–1085.
- Pairat, K. and Qiming, Y. (2001) 'Cadmium(II) removal from aqueous solutions by pre-treated biomass of marine alga *Padina sp.*', *Environmental pollution*, Vol. 112, No. 2, pp.209–213.
- Palmieri, M.C., Volesky, B. and Garcia J.O. (2002) 'Biosorption of lanthanum using *Sargassum fluitans* in batch system', *Hydrometallurgy*, Vol. 67, No. 1, pp.31–36.
- Pan, X.L., P., Wang, J.L. and Daoyong, Z. (2005) 'Biosorption of Pb(II) by *Pleurotus ostreatus* immobilized in calcium alginate gel', *Process Biochem.*, Vol. 40, No. 8, pp.2799–2803.
- Prerna, A., Rani, G. and Saxena, R.K. (1999) ' Zn^{2+} biosorption by *Oscillatoria angustissima*', *Process Biochem.*, Vol. 34, No. 1, pp.77–85.
- Renmin, G., Yi, D., Huijun, L., Qiuyi, C. and Zhili, L. (2005) 'Lead biosorption and desorption by intact and pretreated *spirulina maxima* biomass', *Chemosphere*, Vol. 58, No. 1, pp.125–130.
- Sánchez, A. (1999) 'Biosorption of copper and zinc by *Cymodocea nodosa*', *FEMS Microbiol. Rev.*, Vol. 23, No. 5, pp.527–536.
- Schiewer, S. and Volesky, B. (1995) 'Modeling of the proton-metal ion exchange in biosorption', *Environ. Sci. Technol.*, Vol. 29, No. 12, pp.3049–3058.
- Thomas, A.D., Bohumil, V. and Alfonso, M. (2003) 'A review of the biochemistry of heavy metal biosorption by brown algae', *Water Res.*, Vol. 37, No. 18, pp.4311–4330.
- Veglio, F. and Beolchini, F. (1997) 'Removal of metals by biosorption: a review', *Hydrometallurgy*, Vol. 44, No. 3, pp.301–316.
- Vitor, J.P.V., Cidália, M.S.B. and Rui, A.R.B. (2005) 'Influence of pH, ionic strength and temperature on lead biosorption by *Gelidium* and agar extraction algal waste', *Process Biochem.*, Vol. 40, No. 10, pp.3267–3275.
- Wallace, M.A., Aderval, S.L., Cristiane, A.H. and Costa, A.C.A. (2003) 'An evaluation of copper biosorption by a brown seaweed under optimized conditions', *Electronic J. Biotech.*, Vol. 6, No. 3, pp.174–184.
- Yasemin, S. and Ayten Ö. (2005) 'Biosorption of chromium(VI) ions from aqueous solution by the bacterium *Bacillus thuringiensis*', *Process Biochem.*, Vol. 40, No. 5, pp.1895–1901.