Journal of Hazardous Materials 193 (2011) 1–9

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Study of thermodynamics and dynamics of removing Cu(II) by biosorption membrane of *Penicillium* biomass

Xin Zhang, Haijia Su*, Tianwei Tan, Gang Xiao

Beijing Key Laboratory of Bioprocess, Beijing University of Chemical Technology, College of Life Science and Technology, Beijing 100029, China

ARTICLE INFO

Article history:
Received 9 December 2010
Received in revised form 5 March 2011
Accepted 8 March 2011
Available online 12 March 2011

Keywords:
Penicillium
Biosorption
Heavy metals
Thermodynamics
BDST
Regeneration

ABSTRACT

Based on the integration of biosorption and membrane-separation, a novel biosorption membrane with good mechanical property was prepared by immobilizing *Penicillium* biomass with cross-linked chitosan on fabric. The ability of the low cost biosorption membrane to remove Cu(II) ions from a solution was studied through batch and continuous experiments. Langmuir adsorption isotherm models were found to accurately fit the batch experimental data ($R^2 > 0.99$) indicating that sorption was of monolayer-mode. The uptake of Cu(II) could reach 38 mg/g at its initial concentration of 200 mg/L in the solution. Continuous biosorption was investigated in a column and the effects of the height, flow rate and initial concentration of Cu(II) were studied. The Bed Depth Service Time model (BDST) was applied to simulate column adsorption data. The breakthrough time at different flow rates and initial concentrations was accurately predicted by the model (error < 8%). The uptake of Cu(II) could reach 38.3 mg/g at height 30 cm, flow rate 5 mL/min, initial concentration of Cu(II) 200 mg/L. The biosorption membrane was regenerated by washing with 0.05 mol/L solution of HCl, and breakthrough curves remained fairly unchanged after 10 cycles of adsorption–desorption.

1. Introduction

Heavy metal ions existing in wastewaters of various industries such as metal plating, mining operations, battery manufacturing and tannery fabrication are posing serious risks to human health and the environment [1]. The removal of such metals from these effluents is becoming increasingly important as the discharge regulations become more stringent. Among heavy metals in wastewaters, copper has been a major focus in wastewater treatment because it is associated with many health hazards. Conventional technologies for the removal of heavy metals use physical or chemical methods, including the application of chemical reagents, ion exchange, activated carbon sorption and membrane technology [2]. Most of these methods have limits in their applications, for example, very harsh reaction conditions, high cost, and secondary pollution.

Considering the viewpoint of sustainable development and comprehensive utilization of resources, biosorption has a promising prospect and a wide application due to its high removal efficiency, low cost, mild operating conditions, no secondary pollution and good performance over other conventional treatment processes in the removal and recovery of heavy metal ions from wastewater. Biosorbents of metal ions can be obtained by different microorganisms, e.g. algae, yeast and fungi [3,4]. Over the past two decades, the use of mycelia (dead biomass) from the by-product of the fermentation industry as biosorbents has received considerable attention due to its low cost and good performance [5]. Since many fermentation processes, such as penicillin production, produce a large quantity of biomass which has high metal ion adsorption capacity, the use of spent (dead) biomass from these industries also helps to reduce the problem of waste biomass disposal.

However, commercial application of waste biomass in its free form as a biosorbent can suffer from problems associated with the physical characteristics (small particle size, poor mechanical strength and little rigidity) of this material, which would bring about the difficulty in the liquid–solid separation after biosorption, inability to regenerate/reuse and development of high pressure drop in a fixed-bed column mode. Immobilization of the biomass onto a more rigid and open support has been found to be practical to avoid these problems [6].

Chitosan, one of the most abundant polysaccharides, has many $-NH_2$ and –OH groups adsorbing heavy metal ions [7]. The use of many cross-linked chitosans as adsorbents of metal ions has been reported recently. An imprinted chitosan adsorbent prepared by our research group [8] showed good chemical and physical stability and could be reused up to 10 times without loss of adsorption

* Corresponding author at: College of Life Science and Technology, PO Box 53, The Key Laboratory of Bioprocess of Beijing, Beijing University of Chemical Technology, Beijing 100029, China. Tel.: +86 10 64451636; fax: +86 10 64416428.
E-mail address: suhj@mail.buct.edu.cn (H. Su).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.03.014

ability. A modified chitosan transparent thin membrane was prepared by Cheng et al. [9] and used as the adsorbent to removal copper ions from aqueous solution. But the high cost of the imprinted chitosan resin limits the use of chitosan as a biosorbent for the removal of heavy metal ions in large-scale wastewater treatment. A surface imprinted adsorbent (particle) prepared by Su et al. [10] combines the advantages of the mycelium adsorbent with that of the imprinted chitosan adsorbent giving good combined adsorption ability. However, this kind of particles do not overcome the operational problems, showing still low mechanical strength and mechanical breakdown in continuous systems and has failed to lead to industrial development. An economically viable immobilization technology which not only preserves the sorption ability but also improves the mechanical properties would thus be a major step in developing biosorption systems for industrial application.

In the present paper, a novel biosorption membrane was prepared by immobilization of waste *Penicillium* biomass with cross-linked chitosan on a fabric carrier. The biosorption membrane of *Penicillium* biomass has good mechanical properties and was successfully utilized for the removal of copper both in batch as well as in continuous systems, and could be reused in 10 packed-bed column adsorption–desorption cycles without loss of adsorption ability.

2. Materials and methods

2.1. Biomass and reagent

Waste biomass of *Penicillium* was provided by Dongchen Biochemical Engineering Company [Shandong Province, China]. Chitosan with 90% degree of deacetylation was extracted from shrimp shells and procured from Jinan Haidebei Marine Bioengineering Co., Ltd. NaOH, $Cu(NO_3)_2$, HCl, epichlorohydrin and acetic acid were of analytical grade.

2.2. Preparation of biosorption membrane

Penicillium biomass was dried at 80 °C in an air-supplied oven for 12 h, then crushed to powder in a disintegrator and sieved to particle size ≤100 μm for use.

0.2g chitosan was dissolved in acetic acid (2.5% (v/v)), then 2.0 g powder of *Penicillium* was added in the above solution, dispersing with ultrasound for 10 min. Epichlorohydrin as a crosslinking agent of chitosan was added, reacting for 1 h at room temperature. The mixture slurry was spread between two pieces of fabric as a membrane (thickness 0.5–0.7 mm), then soaked into 0.25 mol/L NaOH (as the solidifying solutions) for 3 h. At last, the membrane was washed with distilled water and dried at 80 °C for 12 h.

For scanning electron microscopy, samples of biomass of *Penicillium* and biosorption membrane (without fabric) were coated with a thin layer of gold under vacuum and examined using a Hitachi S4700 field emission scanning electron microscope (SEM) (Tokyo, Japan).

The pore characteristic of adsorption membrane (without fabric) was measured by an autopore instrument (IV 9500 V1.09, Micromeritics Instrument Corporation, Atlanta, USA).

2.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of air-dried samples of biosorbents were recorded at room temperature using a Varian 3100 FTIR spectrometer. Chitosan, biomass, immobilized adsorbent or Cu(II)-loaded adsorbent (filtered and dried after contact with an initial Cu(II) concentration of 200 mg/L at pH 5–6) were mixed with KBr and compressed into films for FTIR analysis.

2.4. Batch Cu(II) adsorption experiments

0.2 g of adsorbent was added to each of a series of flasks containing 50 mL of solution with different Cu(II) concentrations at pH 5–6 and constant temperature, agitated in a shaker (model HZQ-X100) for more than 6 h (equilibrium was achieved quickly in less than 2 h). Cu(II) was measured by using a Atomic Absorption Spectrometer (SpectrAA55B). The uptake of Cu(II) by the adsorbents was given by Eq. (1).

$$Q = \frac{(C_o - C_e)V}{W} \tag{1}$$

where Q is uptake of Cu(II) by the adsorbents (mg/g); C_o is the initial Cu(II) concentration (mg/L); C_e is the Cu(II) concentration (mg/L) after the batch adsorption experiment; W is the mass of adsorbent (g) and V is the volume of Cu(II) solution put in contact with the adsorbent. The biosorption membrane was regenerated by washing with a 0.05 mol/L solution of HCl.

2.5. Isotherm models

The Langmuir model [11,12] assumes that uptake occurs on a homogeneous surface by monolayer sorption without interaction between sorbed molecules. The linear form of the Langmuir isotherms is given by Eq. (2), where Q is the uptake of metal ion (mg/g); C_e is equilibrium concentration of metal ion solutions (mg/L); Q_{max} is maximum uptake of metal ion by biosorbent (mg/g); K_L is the Langmuir equilibrium constant (L/g).

$$\frac{C_e}{Q} = \frac{1}{K_L \times Q_{max}} + \frac{C_e}{Q_{max}} \tag{2}$$

The Freundlich equation [13] is an empirical relationship describing the adsorption of solutes from a liquid onto a solid surface. The linear form of this model is given by Eq. (3), where K and n are the Freundlich constants.

$$\ln\ Q = \ln K + n \times \ln C_e \tag{3}$$

2.6. Thermodynamic evaluation

Thermodynamic parameters such as free energy of sorption (ΔG), enthalpy change (ΔH) and entropy change (ΔS) for the adsorption process can be evaluated from Eqs. (4) and (5) [14,15].

$$\Delta G = -RT\ \ln K_L \tag{4}$$

$$\ln K_L = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \tag{5}$$

where R is the ideal gas constant (kJ mol^{-1} K^{-1}) and T is the temperature (K), K_L is Langmuir equilibrium constant (L/g). ΔH and ΔS can be calculated from a plot of $\ln K_L$ versus $1/T$.

2.7. Continuous Cu(II) adsorption experiments

A packed-bed glass column of 1.0 cm diameter and 30 cm in height was used in the continuous system. The biosorption membrane was cut to pieces (2.0–5.0 cm × 0.3 cm) and packed into the column with plastic mesh both at the top and the bottom of the packed-bed to retain the adsorbent in place. Cu(II) aqueous solution was pumped through the bottom of column and the flow rate was regulated with an adjustable peristaltic pump. Column effluent samples were collected from the top regularly until saturation and analyzed for Cu(II) by Atomic Absorption Spectrophotometer (SpectrAA55B). The adsorbent in column was thereafter eluted with 0.05 mol/L solution of HCl for reuse in a new cycle.

The performance of the packed-bed was described through the concept of a breakthrough curve, which was obtained by plot-

Table 1
Comparison on adsorbability of biomass, chitosan and fabric.

	Chitosan	Biomass	Fabric	Adsorbent (except for fabric)
Added mass (g)	0.05	0.5	0.5	0.55
Uptake of Cu(II) (mg)	3.02	19.5	1.01	23.0
Adsorbability per gram (mg/g)	60.6	38.9	2.0	41.9

W = 1.05 g; C_o(Cu(II)) = 200 mg/L; V = 50 mL; t = 8 h.

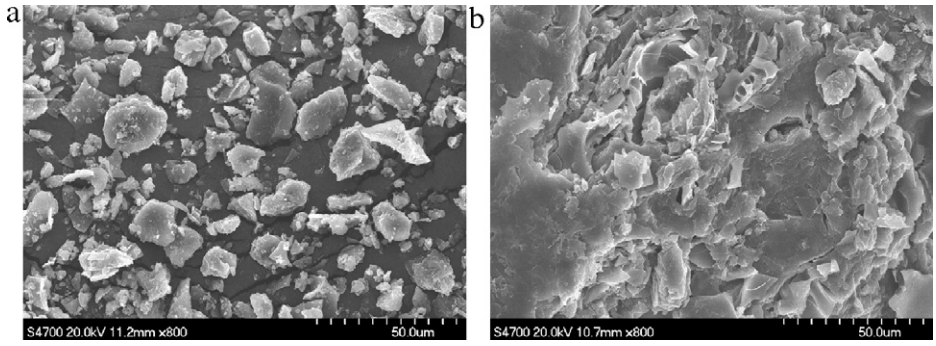

Fig. 1. SEM images of (a) biomass of *Penicillium* and (b) biosorption membrane.

ting the measured concentration divided by the inlet concentration (C/C_o) against outlet volume (V). Breakthrough time (t_b, min) and breakthrough volume (V_b, mL) were obtained when C/C_o reached 0.60; the exhaustion time (t_e, min) and exhaustion volume (V_e, mL) were obtained when C/C_o reached 0.90.

2.8. Bed Depth Service Time model (BDST)

The bed depth for service-time is an important design parameter for a fixed-bed adsorber. The BDST model [16,17] provides a useful relationship between the bed depth (Z) and service time (t), which was proposed by Bohart and Adams in 1920. The BDTS model can be expressed as Eq. (6).

$$t_b = \frac{N_o}{C_o F} Z - \frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \quad (6)$$

where N_o is bed sorption capacity (mg/L), F is the influent linear velocity (cm/min), C_o is the initial concentration in the influent of the column (mg/L), C_t is the effluent concentration of the column at breakthrough (mg/L), K_a is the bed rate constant in the BDST model (L/(min mg)), which represents the rate of solute transfer from the liquid phase to the solid phase, t_b is the service time and Z is the bed height of the column (cm).

A simplified form of the BDST model is given as:

$$t_b = aZ + b \quad (7)$$

where the slope (a) and the intercept (b) of the equation are given by the expressions below:

$$a = \frac{N_o}{C_o F}, \qquad b = -\frac{1}{K_a C_o} \ln\left(\frac{C_o}{C_t} - 1\right) \quad (8)$$

A plot of t_b versus Z should yield a straight line where N_o and k_a, respectively can be evaluated. The critical bed depth (Z_o), which is defined as the theoretical depth, can prevent the adsorbate concentration from exceeding the breakthrough concentration (C_t) at t = 0. The BDST model parameters can be helpful to scale up the process for other flow rates without further experimental run.

3. Results and discussion

3.1. Characterization of adsorbent

3.1.1. Adsorbability of biomass, chitosan and fabric

In order to distinguish which component is more important for biosorption, adsorption experiments were investigated using chitosan powder, biomass powder, fabric and immobilized adsorbent. The comparison on adsorbability of biomass, chitosan, fabric and immobilized adsorbent is shown in Table 1. Biomass of *Penicillium* and chitosan are also good adsorbent of Cu(II). Due to its quality ratio much more than chitosan, biomass of *Penicillium* still stands as the major contribution of biosorption.

3.1.2. SEM characterization of adsorbent

The surface texture and morphology of the biomass of *Penicillium* and the biosorbent membrane are showed by scanning electro-micrographs (SEM) in Fig. 1. The average size of *Penicillium* biomass particles is 50–150 μm. Fig. 2(b) illustrates the surface porosity of biosorbent membrane, where an uneven surface texture

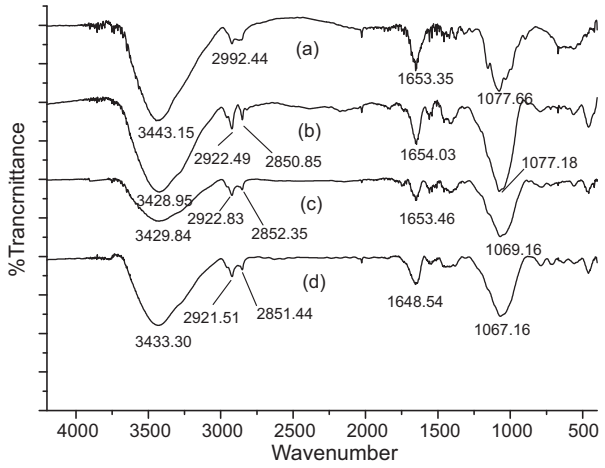

Fig. 2. FTIR spectra of chitosan, biomass, immobilized adsorbent and Cu(II)-loaded adsorbent: (a) chitosan; (b) biomass; (c) adsorbent; (d) adsorbent-Cu.

Table 2
Pore characteristic of adsorbent membrane.

Parameters	Value
Total intrusion volume	0.597 mL/g
Total pore area	7.79 m^2/g
Average pore diameter (4V/A)	306 nm
Apparent (skeletal) density	1.30 g/mL
Porosity	43.7%

along with lot of irregular surface format was observed, thereby increasing the contact area, which facilitates the pore diffusion during adsorption.

3.1.3. Pore characterization of adsorbent

In order to obtain the pore characterization of adsorbent membrane, sample of the adsorbent membrane was measured by using an autopore instrument including total intrusion volume, total pore area, pore diameter, and porosity (shown in Table 2).

3.1.4. FTIR characterization of adsorbent

As can be seen from Fig. 2(a)–(c), chitosan, biomass, immobilized adsorbent have nearly the same peaks which indicate the presence of amino, carboxylic and hydroxyl groups. The wide band at 3700–3000 cm^{-1} is assigned to the stretching vibrations of O–H and N–H bond of macromolecular association. The peaks observed at about 2922 and 2850 cm^{-1} is assigned to the stretching vibrations of C–H bond of methylene groups. The peaks at about 1654 cm^{-1} are caused by the stretching band of carboxyl groups. The bands at 1200–800 cm^{-1} are dominated by C–O and C–N stretching [18,19].

The O–H and N–H absorption peak around 3430 cm^{-1} shifted significantly for protonated peels from 3429 to 3433 cm^{-1} after Cu(II) binding (Fig. 2(c) and (d)). A strong shift was also observed for carboxyl group absorption peak from 1653 to 1648 cm^{-1}. The shift in wave number corresponds to a change in energy of the functional group, indicating that the bonding pattern of O–H, N–H and –COOH groups changes after sorption. This result confirms the involvement of hydroxyl, amino and carboxyl groups in binding of Cu(II).

3.2. Batch Cu(II) adsorption

3.2.1. Effect of temperature and isotherm models

Fig. 3 illustrates the uptake of Cu(II) at 308, 318 and 323 K plotted against the initial concentration of Cu(II). Increase with concentration of Cd(II) from 100 to 2000 mg/L at different temperatures shows an increase in the biosorption capacity. In view of the obtained results, it can be concluded that the temperature strongly affects the metal removal. The maximum uptakes of Cu(II) at 308, 318 and 323 K are 66, 48 and 37 mg/g, respectively (Fig. 3). The biosorption capacity of Cu(II) by adsorbent is decreased with increase in temperature. A similar temperature-effect on the biosorption has previously been reported [20].

Equilibrium data, commonly known as the equilibrium biosorption isotherm, is one of the most important information for the analysis and design of adsorption systems. Isotherm model parameters and the underlying thermodynamic assumptions of the models can provide information on the adsorption mechanisms,

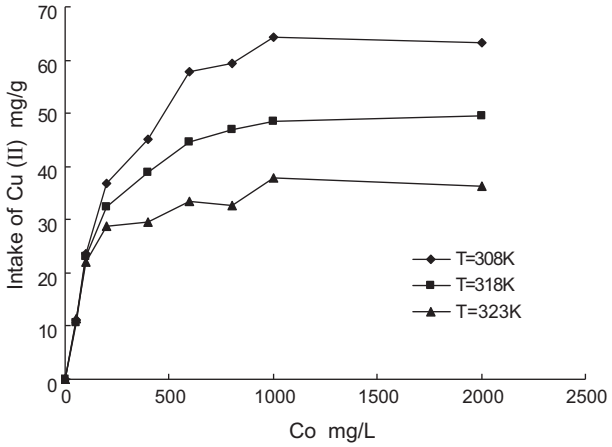

Fig. 3. Adsorption isotherm of Cu(II) at different temperatures. W = 0.2 g, V = 50 mL, pH 5–6, 110 rpm.

Table 4
Thermodynamic constants for the adsorption of Cu(II) at various temperatures.

T (K)	ΔG (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})
308	−19.5		
318	−20.3	91.3	8.63
323	−21.0		

the surface properties and the uptake capacity of the adsorbent [21]. The widely used Langmuir and Freundlich isotherms are utilized to describe the equilibrium data in this study to describe the adsorption equilibrium.

The plot of C_e vs. C_e/Q of the Langmuir isotherm and the plot of ln Q vs. ln C_e of the Freundlich isotherm are obtained at different temperatures (308, 318 and 323 K), respectively. The parameters of the Langmuir and Freundlich models are listed in Table 3.

The R^2 values in Table 3 suggest that the Langmuir isotherm accurately fits the biosorption process due to the high determination coefficient ($R^2 > 0.99$), whereas the Freundlich model is not a suitable approach for this system ($R^2 < 0.76$). It indicates that the removal process of Cu(II) on a biosorption membrane of *Penicillium* biomass occurred in a monolayer without interaction between sorbed molecules [22]. The maximum monolayer uptake capacities of Cu(II) are found between 36.8 mg/g and 64.5 mg/g at various temperatures in the batch studies.

3.2.2. Thermodynamic evaluation

Using the data in Table 3, the values of free energy of sorption (ΔG) of the Cu(II) biosorption by *Penicillium* membrane at different temperatures were computed. According to Eq. (5), the values of enthalpy change (ΔH) and the entropy change (ΔS) were calculated from a plot of ln K_L (from the Langmuir isotherm) versus $1/T$, respectively (Fig. 4). The results of these thermodynamic calculations are shown in Table 4.

The negative values for ΔG at all temperatures studied (308–323 K) indicate that the adsorption process is spontaneous [23]. A positive value of ΔS indicates increased randomness of adsorbate molecules on the solid surface than in the solution

Table 3
Parameters of the biosorption isotherms obtained at different temperatures.

T (K)	Langmuir				Freundlich			
	Langmuir equation	Q_{max} (mg/g)	K_L (L/g)	R^2	Freundlich equation	n	K	R^2
308	$C_e/Q = 0.016C_e + 0.498$	64.5	32.1	0.997	$\ln Q = 0.447 \ln C_e + 1.33$	0.17	3.79	0.753
318	$C_e/Q = 0.021C_e + 0.628$	46.7	33.4	0.998	$\ln Q = 0.419 \ln C_e + 1.26$	0.24	3.51	0.731
323	$C_e/Q = 0.027C_e + 0.706$	36.8	38.2	0.997	$\ln Q = 0.371 \ln C_e + 1.25$	0.16	3.50	0.700

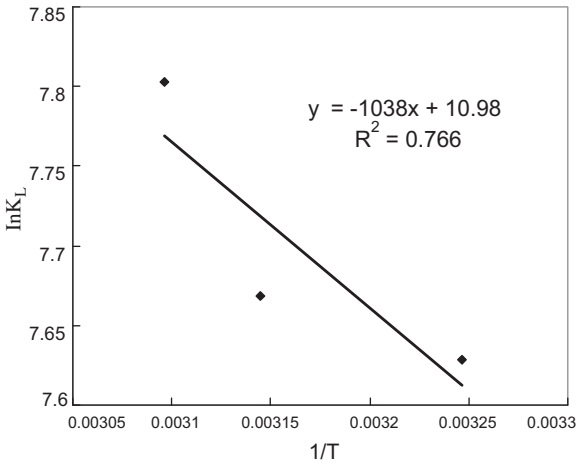

Fig. 4. Plot of the Langmuir isotherm constant ($\ln K_L$) vs. temperature ($1/T$).

[24,25]. The positive value of ΔH shows that Cu(II) biosorption is an endothermic process. The value of ΔH was estimated as 8.63 kJ mol^{-1}. Basically, the heat evolved during physical adsorption generally falls into a range of 8–25 kJ mol^{-1}, while the heat of chemical adsorption generally falls into a range of 80–200 kJ mol^{-1} [26]. Therefore, it seems that Cu(II) biosorption by a membrane of *Penicillium* biomass can be attributed to a physical adsorption process.

3.3. Continuous Cu(II) adsorption

In most industrial wastewater treatment units, a continuous mode of operation is preferred. Therefore, continuous biosorption experiments of Cu(II) were also carried out.

3.3.1. Effect of bed height on biosorption

The effect of the bed height on adsorption of Cu(II) was investigated using various bed heights from 10 to 30 cm. The breakthrough curves obtained from the variation of the metal concentration in the column effluent with volume at different bed heights are represented in Fig. 5. The bed height (Z), breakthrough time (t_b, the position at $C/C_o = 0.6$), adsorbent mass (W), as well as Cu(II) uptake (Q) are tabulated in Table 5.

Table 5
Different experimental parameters of the breakthrough curves at various bed heights.

Z (cm)	t_b (min)	W (g)	Q (mg/g)
10	65	2.15	30.2
15	113.1	3.21	35.2
20	160.2	4.35	36.8
25	196.52	5.13	38.2
30	239.2	6.25	38.3

The typical breakthrough curves are plotted in Fig. 5. Result indicates that the volume treated, breakthrough time and uptake capacity are increased with the rise in bed height from 10 to 30 cm, and the maximum Cu(II) uptake of 38.3 mg/g is obtained in 30 cm of column height. Accumulation of Cu(II) in the packed-bed column is largely dependent on the adsorbent doses inside the column. A taller bed offers more service surface of the adsorbent, which supplies a larger number of active sites and ionic groups of biomass available for the sorption of Cu(II). The result is a delayed breakthrough of the metal ions leads even when the volume of the liquid treated increases [27,28].

As is shown in Table 5, the uptake capacity of Cu(II) increased from 30.2 to 38.3 mg/g when the bed height increased from 10 to 30 cm. This result can be explained by mass transfer phenomena taking place in this process. Higher bed depth results in a longer residence time of the solution in the column, allowing the metal ions to have sufficient time to contact with adsorbent surface and diffuse more deeply inside the adsorbent [29]. When the bed depth is low, the axial dispersion phenomenon predominates in the mass transfer and reduces the diffusion of metallic ions. The metal ions do not have enough time to diffuse into the whole adsorbent mass.

3.3.2. Effect of liquid flow rate on biosorption

The flow rate is an important characteristic in evaluating the performance of biosorption, for continuous treatment of wastewater on industrial scale. Fig. 6 presents the effect of flow rate on breakthrough curves for Cu(II) adsorption at varying the flow rate from 2.0, 5.0, and 7.0 mL/min and keeping the initial Cu(II) concentration (200 mg/L) and bed depth (15 cm) constant.

As is shown in Fig. 6, the column performs well at the low flow rate, whereas the breakthrough curve becomes steeper as the flow rate increased. Both a decreasing column breakthrough time

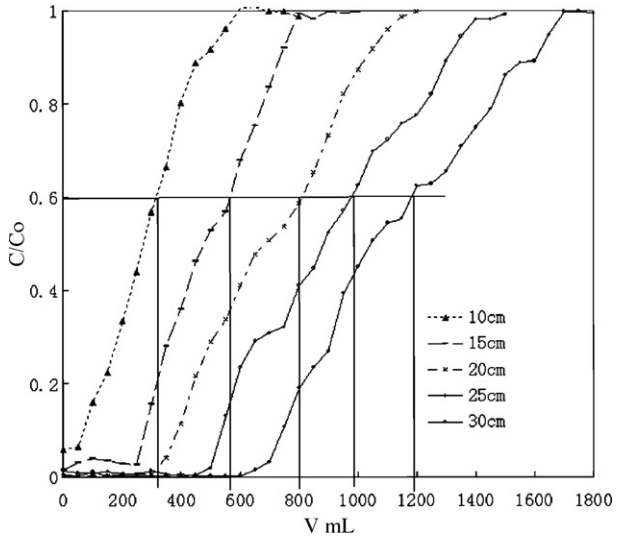

Fig. 5. Effect of bed height on the breakthrough curve. $C_o = 200$ mg/L; $F = 5$ mL/min; pH 6.0–7.0.

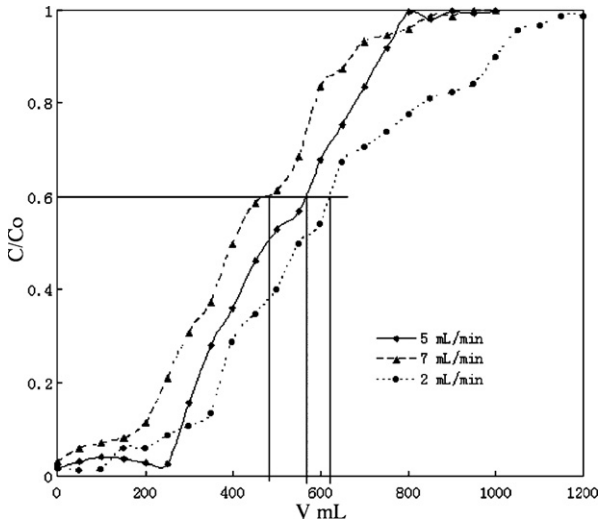

Fig. 6. Effect of flow rate on the breakthrough curve. $C_o = 200$ mg/L; $Z = 15$ cm; pH 6.0–7.0.

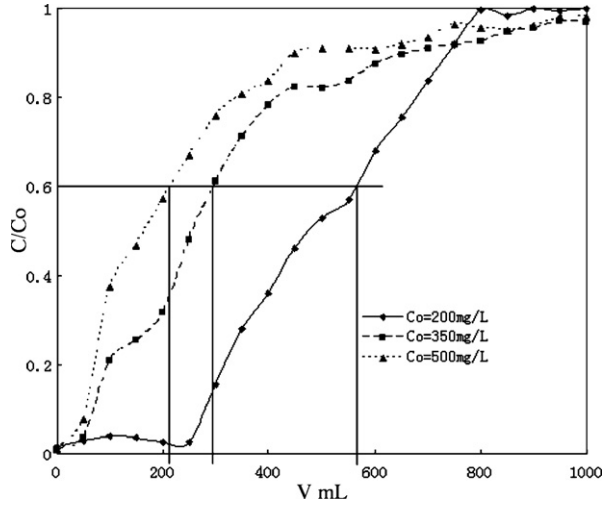

Fig. 7. Effect of initial Cu(II) concentration on the breakthrough curve. Z = 15 cm; F = 5 mL/min; pH 6.0–7.0.

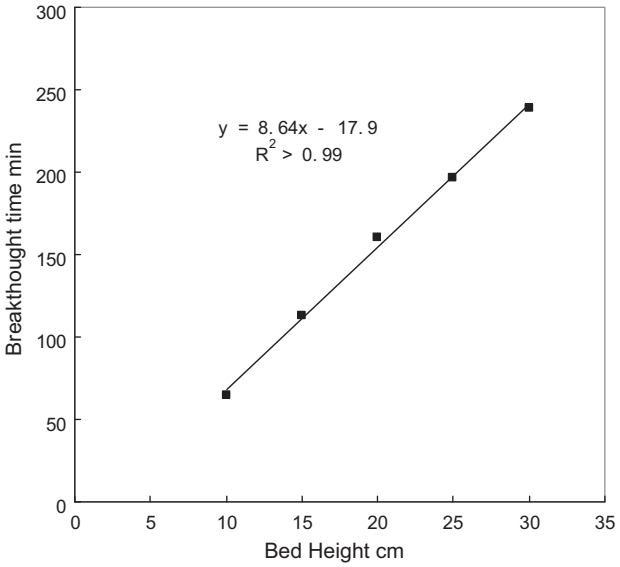

Fig. 8. Determination of BDST model parameters.

(310.8 min, 113.1 min and 69.2 min) and decreasing Cu(II) uptake (38.7 mg/g, 35.7 mg/g and 30.2 mg/g) are noticed when flow rate increases from 2 to 7 mL/min.

This behavior can be explained by the fact that the liquid residence time in the column is critical for the biosorption process [30]. When the flow rate is increased, the liquid residence time in the column is reduced, which restricts the contact between metal solution and active sites on the biosorbent surface. Due to this reason metals ions do not have enough time to diffuse into pores of biosorbent and leave the column before equilibrium is attained. This resulted in shorter breakthrough times and lower metal uptake at higher flow rates [31,32]. Similar results were previously reported [33] in their study of adsorption of reactive dye by metal hydroxide sludge in a fixed-bed column.

Moreover, Doan [34] reported that the overall metal removal process includes two steps: the external mass transfer from the bulk liquid to the solid adsorbent surface, and the intra-particle mass transfer of metal ions into the adsorbent. Since the metal uptake decreased significantly with increasing liquid flow rate, it is believed that the metal removal process is mainly controlled by the step of external mass transfer.

3.3.3. Effect of initial Cu(II) concentration on biosorption

Fig. 7 depicts three breakthrough curves of Cu(II) removal by biosorption membrane of *Penicillium* biomass at different inlet concentrations (200, 350 and 500 mg/L), 15 cm bed-depth, and flow rate of 5.0 mL/min.

As expected, a decreased initial Cu(II) concentration yields a later breakthrough time (from 41.8 min to 113.1 min) and the treated volume is increased from 209.0 mL to 565.5 mL with decreasing concentration from 500 to 200 mg/L. This indicates that a better column performance is obtained at lower initial Cu(II) concentration and the reason for this behaviors is that the lower solute concentration difference (between the sorbent and the solution) causes a slower diffusion and a decreased mass transfer coefficient [35]. A high concentration difference provides a high driving force for the adsorption process. With increasing inlet Cu(II) concentration, the binding sites became more quickly saturated in the system [36].

3.3.4. Bed Depth Service Time model (BDST)

The plot of breakthrough time against bed height at a flow rate of 5 mL/min and initial Cu(II) concentration of 200 mg/L (Fig. 8) was linear (R^2 = 0.9974) indicating the suitability of BDST model for the present system. Parameters in the BDST model and breakthrough time error (ε) are shown in Table 6, where the sorption capacity per unit bed volume (N_o) was calculated from the slope of BDST plot, and the rate constant (K_a) calculated from the intercept of BDST plot.

The BDST model constants can be helpful to analyze the process for new flow rates and concentration without further experimental run, which is significant for application in treatment of practical wastewater.

The slope constant for a different flow rate can be directly calculated from Eq. (9) given below [37,38]:

$$a' = a\frac{F}{F'} \tag{9}$$

where a and F are the old slope and influent linear velocity, respectively; a' and F' are the new slope and new influent linear velocity, respectively.

For other influent concentrations, the desired equation is given by a new slope and new intercept given by Eqs. (10) and (11):

$$a' = a\frac{C_o}{C_o'} \tag{10}$$

$$b' = b\frac{C_o}{C_o'}\frac{\ln(C_o' - 1)}{\ln(C_o - 1)} \tag{11}$$

where b' and b are the new and old intercepts, respectively; C_o' and C_o are the new and old effluent concentrations, respectively.

The predicted values, $(t_b)_{\text{theor}}$, experimental values, $(t_b)_{\text{exp}}$ of breakthrough time and error (ε) for new flow rates and effluent concentrations are shown in Tables 7 and 8, respectively. The low value of the relative error (ε < 8%) (shown in Tables 6–8) proves that breakthrough time at different bed heights, flow rates and initial concentrations were accurately predicted by the BDST model.

3.3.5. Regeneration and reuse of biosorbent

The regeneration of the biosorbents is one of the key factors in assessing their potential for commercial applications. The multiple reuses of the biosorbent can reduce the process cost as well as decreased the process on continuous supply of the biosorbent [39]. The sorption performance of biosorption membrane of *Penicillium* biomass was evaluated in 10 sorption–desorption cycles. The column was packed with 3.0 g (bed height 15 cm) of biosorbent and the flow rate was adjusted to 5 mL/min. The breakthrough curve for all sorption cycles is presented in

Table 6
Parameters in the BDST model and breakthrough time error.

Z (cm)	N_o (mg/L)	K_a (L/(min mg))	Z_o (cm)	t_b (min)		ε (%)
				$(t_b)_{theor}$	$(t_b)_{exp}$	
10	10,996.5	1.131×10^{-4}	2.08	68.4	65	5.03
15				111.6	113.1	1.32
20				154.8	160.2	3.49
25				198.0	196.5	0.74
30				241.2	239.2	0.82

Table 7
Predicted breakthrough time based on BDST constants for new flow rates.

a (min/cm)	b (min)	Z (cm)	F (mL/min)	F (mL/min)	a' (min/cm)	t_b (min)		ε (%)
						$(t_b)_{theor}$	$(t_b)_{exp}$	
8.64	17.9	15	5	2	21.6	306.1	310.8	1.54
				5	–	111.6	113.1	1.32
				7	6.17	74.7	69.2	7.33

Table 8
Predicted breakthrough time based on BDST constants for new effluent concentrations.

a (min/cm)	b (min)	Z (cm)	C_o (mg/L)	C'_o (mg/L)	a' (min/cm)	b' (min)	t_b (min)		ε (%)
							$(t_b)_{theor}$	$(t_b)_{exp}$	
8.64	17.9	15	200	200	–	–	111.6	113.1	1.32
				350	4.94	11.3	62.7	58.6	6.60
				500	3.46	8.4	43.4	41.8	3.77

Table 9
Sorption–desorption process parameter for ten sorption–desorption cycles.

Cycle no.	C_o (mg/L)	Z (cm)	Uptake (mg/g)	Desorption (%)	V_b (mL)	V_e (mL)	t_b (min)
1	200	15	36.0	94.1	578	747	115.6
2			31.4	90.8	504	721	100.8
3			28.9	96.0	464	652	92.8
4			29.5	98.7	474	630	94.8
5			29.2	98.9	468	612	93.6
6			28.8	93.3	463	628	92.6
7			26.9	92.8	432	622	86.4
8			25.0	92.8	401	600	80.2
9			23.2	90.3	372	541	74.4
10			20.9	–	336	519	67.2

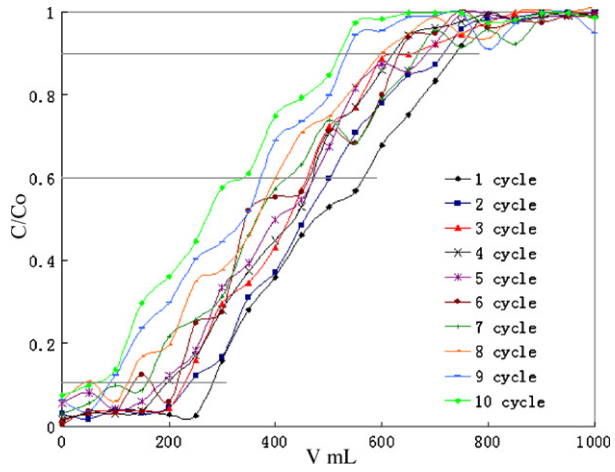

Fig. 9. Sorption breakthrough curve during ten sorption cycles. C_o = 200 mg/L; Z = 15 cm; F = 5 mL/min; pH 6.0–7.0.

Fig. 9. The metal uptake capacity, desorption efficiency (%), breakthrough volume, exhaustion volume and breakthrough time for all the 10 sorption cycles were calculated and are presented in Table 9.

It can be seen from Fig. 9 that with the progress of sorption cycle, the breakthrough curve became flat as a result of the decrease of breakthrough time (from 115.6 to 67.2 min) with the cycle extended, as well as the Cu(II) uptake capacity decrease from 36.0 to 20.9 mg/g; however, it is very satisfactory that the biosorption membrane of *Penicillium* biomass offers the potential to be used repeatedly in Cu(II) biosorption studies without significant loss in the total biosorption capacity in the forthcoming cycle. This is due to previous elution processes, which affect the biomass binding sites.

The desorption curves obtained for all cycles are presented in Fig. 10. The flow rate was maintained at 5.0 mL/min to avoid over contact of the desorbent with the biosorbent. The desorption curves observed in all the cycles exhibit a similar trend: a sharp increase in the beginning followed by a gradual decrease. Similar result was observed by S.H. Hasan and P. Srivastava [40]. The desorption efficiency exceeds 90.2% in all 10 desorption cycles. The total volume of Cu(II) bearing solution (200 mg/L) treated during this regeneration study was around 6.3 L in 10 cycles by 3.0 g biosorbents and highly concentrated Cu(II) solutions are present in only a small volume of desorbent. For instance, in the first cycle at V = 100 mL, the effluent Cu(II) concentration was 1589.2 mg/L. This result shows that the biosorption membrane of *Penicillium* biomass is a good adsorbent that can be regenerated

Table 10
Comparison of biosorption capacity for Cu(II) ions from the literature.

Biosorbent material	C_o (mg/L)	Flow rate (mL/min)	Uptake (mg/g)	Regeneration (cycles)	Reference
Immobilized *Arthrobacter* sp.	50	3.5	32.6	6	[40]
Fennel biomass	50	1.0	16.7	–	[41]
Wheat straw	100	18.3	0.736	–	[34]
Sargassum	35	15	38.0	10	[42]
Membrane of *Penicillium*	200	5.0	38.3	10	Present study

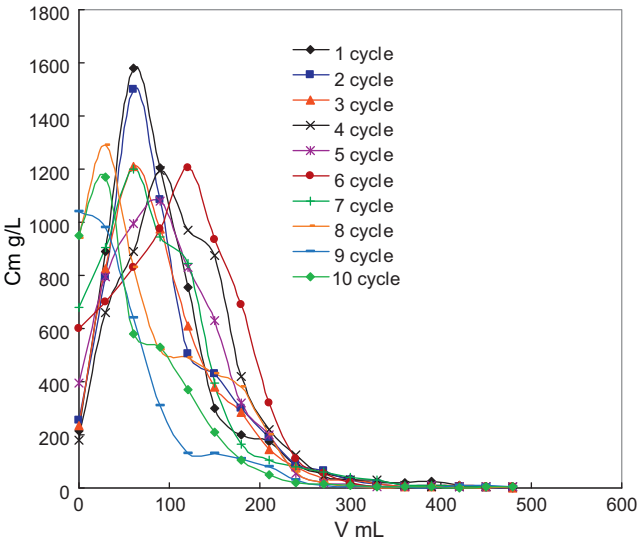

Fig. 10. Column desorption curve during ten desorption cycles. C(HCl) = 0.05 mol/L; Z = 15 cm; F = 5 mL/min.

and reused for the efficient removal of Cu(II) from aqueous solutions.

A comparison of adsorption capacity of some other low cost adsorbents to uptake Cu(II) from aqueous solutions is shown in Table 10. From Table 10, it was observed that Cu(II) sorption capacity and ability of being reused by the biosorption membrane of *Penicillium* biomass are found to be relatively higher than the other low cost adsorbents.

4. Conclusion

The low cost biosorption membrane of *Penicillium* biomass was successfully utilized for the removal of copper in a batch system. The Langmuir isotherm model fitted the sorption data ($R^2 > 0.996$) indicating that sorption was monolayer and the maximum uptake of Cu(II) was 66 mg/g at 308 K. The adsorption process was also endothermic and thermodynamically spontaneous under natural conditions.

In fixed-bed, continuous experiments, a taller bed, lower flow rate and lower initial Cu(II) concentration were favourable for the biosorption and the maximum uptake capacity (38.3 mg/g) was obtained at height 30 cm, flow rate 5 mL/min, initial concentration of Cu(II) 200 mg/L. The breakthrough time at different bed heights, flow rates and initial concentrations was accurately predicted (relative error < 8%) by the BDST model.

The biosorption membrane of *Penicillium* biomass with good mechanical property was successfully utilized for the continuous removal of copper and could be reused in 10 adsorption–desorption cycles without loss of adsorption ability in a packed-bed column. The Cu(II) sorption capacity and ability of reused biosorption membrane of *Penicillium* biomass was found to be relatively higher than other low cost adsorbents.

Acknowledgements

The authors gratefully acknowledge the following institutions for their support: the National Natural Science Foundation of China (20876008, 21076009), the National Basic Research Program (973 Program) of China (2007CB714305), the (863) High Technology Project (2006AA020101) and the Chinese Universities Scientific Fund (ZZ1024).

References

[1] D. Nilanjana, Recovery of precious metals through biosorption—a review, J. Hydrometallurgy 103 (2010) 180–189.
[2] A.T. Davisa, B. Voleskya, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, J. Water Res. 37 (2003) 4311–4330.
[3] Z. Aksu, Application of biosorption for the removal of organic pollutants: a review, Process Biochem. 40 (2005) 997–1026.
[4] J. Wang, C. Chen, Biosorption of heavy metals by *Saccharomyces cerevisiae*: a review, Biotechnol. Adv. 24 (2006) 427–451.
[5] K. Vijayaraghavan, Y. Yun, Bacterial biosorbents and biosorption, J. Biotechnol. Adv. 26 (2008) 266–291.
[6] T.J. Beveridge, G.E. Murray, Uptake and retention of metals by cell walls of *Bacillus subtilis*, J. Bacteriol. 127 (1976) 15–18.
[7] T.J. Beveridge, G.E. Murray, Sites of metal deposition in the cell wall of *Bacillus subtilis*, J. Bacteriol. 141 (1980) 876–879.
[8] H. Huo, H. Su, T. Tan, Adsorption of Ag^+ by a surface molecular-imprinted biosorbent, Chem. Eng. J. 150 (2009) 139–144.
[9] Z. Cheng, X. Liu, M. Han, W. Ma, Adsorption kinetic character of copper ions onto a modified chitosan transparent thin membrane from aqueous solution, J. Hazard. Mater. 182 (2010) 408–415.
[10] H. Su, J. Li, T. Tan, Adsorption mechanism for imprinted ion (Ni^{2+}) of the surface molecular imprinting adsorbent (SMIA), Biochem. Eng. J. 39 (2008) 503–509.
[11] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024–1029.
[12] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[13] M.F. Freundlich, Uber die adsorption in Losungen, Z. Phys. Chem. 57 (1906) 385–470.
[14] V.S. Munagapati, V. Yarramuthi, S.K. Nadavala, S.R. Alla, K. Abburi, Biosorption of Cu(II), Cd(II) and Pb(II) by *Acacia leucocephala* bark powder: kinetics, equilibrium and thermodynamics, Chem. Eng. J. 157 (2010) 357–365.
[15] Y. Liu, H. Xu, Equilibrium, thermodynamics and mechanisms of Ni^{2+} biosorption by aerobic granules, Biochem. Eng. J. 35 (2007) 174–182.
[16] R. Han, Y. Wang, W. Yu, W. Zou, J. Shi, H. Liu, Biosorption of methylene blue from aqueous solution by rice husk in a fixed bed column, J. Hazard. Mater. 141 (2007) 713–718.
[17] D. Kratochvil, B. Volesky, Advances in heavy metal biosorption, Trends Biotechnol. 16 (1998) 291–300.
[18] S. Schiewer, A. Balaria, Biosorption of Pb^{2+} by original and protonated citrus peels: equilibrium, kinetics, and mechanism, Chem. Eng. J. 146 (2009) 211–219.
[19] N. Chubar, T. Behrends, P.V. Cappellen, Biosorption of metals (Cu^{2+},Zn^{2+}) and anions ($F^-H_2PO_4^-$) by viable and autoclaved cells of the Gram-negative bacterium *Shewanella putrefaciens*, J. Colloids Surf. B: Biointerfaces 65 (2008) 126–133.
[20] S. Qaiser, A.R. Saleemi, M. Umar, Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: batch and column study, J. Hazard. Mater. 166 (2009) 998–1005.
[21] A. Gundogdu, D. Ozdes, C. Duran, V.N. Bulut, M. Soylak, H.B. Senturk, Biosorption of Pb(II) ions fromaqueous solution by pine bark, Chem. Eng. J. 153 (2009) 62–69.
[22] X.C. Chen, Y.P. Wang, Q. Lin, J.Y. Shi, W.X. Wu, Y.X. Chen, Biosorption of copper(II) and zinc(II) from aqueous solution by *Pseudomonas putida* CZ1, Colloids Surf. B. Biointerfaces 46 (2005) 101–107.
[23] M. Nadeem, A. Mahmood, S.A. Shahid, S.S. Shah, A.M. Khalid, G. Mckay, Sorption of lead from aqueous solution by chemically modified carbon adsorbents, J. Hazard. Mater. B 138 (2006) 604–613.
[24] S.Q. Memon, N. Memon, S.W. Shah, M.Y. Khuhawar, M.I. Bhanger, Sawdust—a green and economical sorbent for the removal of cadmium(II) ions, J. Hazard. Mater. B139 (2007) 116–121.

[25] N. Bektas, B.A. Agim, S. Kara, Kinetic and equilibrium studies in removing lead ions from aqueous solution by natural sepiolite, J. Hazard. Mater. B112 (2004) 115–122.
[26] Z. Aksu, G. Karabayır, Comparison of biosorption properties of different kinds of fungi for the removal of Gryfalan Black RL metal-complex dye, J. Bioresour. Technol. 99 (2008) 7730–7741.
[27] S. Netpradit, P. Thiravetyan, S. Towprayoon, Evaluation of metal hydroxide sludge for reactive dye adsorption in a fixed-bed column system, Water Res. 38 (1) (2004) 71–78.
[28] S.S. Baral, N. Das, T.S. Ramulu, S.K. Sahoo, S.N. Das, G. Roy Chaudhury, Removal of Cr(VI) by thermally activated weed *Salvinia cucullata* in a fixed-bed column, J. Hazard. Mater. 161 (2–3) (2009) 1427–1435.
[29] K. Naddafi, R. Nabizadeh, R. Saeedi, A.H. Mahvi, F. Vaezi, K. Yaghmaeian, A. Ghasri, S. Nazmara, Biosorption of lead (II) and cadmium(II) by protonated *Sargassum glaucescens* biomass in a continuous packed bed column, J. Hazard. Mater. 147 (3) (2007) 785–791.
[30] W. Mendenhall, T. Sincich, Statistics for Engineering and the Sciences, 4th ed., Prentice-Hall, Inc., Upper Saddle River, NJ, 1995, pp. 452–459.
[31] K.H. Chu, Improved fixed bed models for metal biosorption, Chem. Eng. J. 97 (2–3) (2004) 233–239.
[32] Z. Zulfadhly, M.D. Mashitah, S. Bhatia, Heavy metals removal in fixed-bed column by macro fungus *Pycnoporus sanguineus*, Environ. Pollut. 112 (2001) 463–470.
[33] B. Volesky, Sorption and Biosorption, BV Sorbex Inc., Montreal-St. Lambert, Quebec, Canada, 2003, ISBN 0-9732983-0-8.
[34] H. Muhamad, H. Doan, A. Lohi, Batch and continuous fixed-bed column biosorption of Cd^{2+} and Cu^{2+}, Chem. Eng. J. 158 (2010) 369–377.
[35] E. Valdman, L. Erijman, L.P. Pessoa, G.F. Leite, Continuous biosorption of Cu and Zn by immobilized waste biomass *Sargassum* sp., J. Process Biochem. 36 (2001) 869–873.
[36] G. Palma, J. Freer, J. Baeza, Removal of metal ions by modified *Pinus radiate* bark and tannins from water solutions, Water Res. 37 (2003) 4974–4980.
[37] J. Goel, K. Kadirvelu, C. Wang, Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies, J. Hazard. Mater. 125 (2005) 211–220.
[38] M.Z. Othman, F.A. Roddick, R. Snow, Removal of dissolved organic compounds in fixed-bed columns: evaluation of low-rank coal adsorbents, Water Res. 35 (2001) 2943–2949.
[39] G. Yan, T. Viraraghvan, Heavy metal removal in a biosorption column by immobilized *Mucor rouxii* biomass, Bioresour. Technol. 78 (2001) 248–249.
[40] S.H. Hasan, P. Srivastava, Batch and continuous biosorption of Cu^{2+} by immobilized biomass of *Arthrobacter* sp., J. Environ. Manage. 90 (2009) 3313–3321.
[41] R.A. Rao, M.A. Khan, F. Rehman, Utilization of Fennel biomass (*Foeniculum vulgari*) a medicinal herb for the biosorption of Cd(II) from aqueous phase, Chem. Eng. J. 156 (2010) 106–113.
[42] B. Voleskya, J. Weber, J.M. Parkb, Continuous-flow metal biosorption in a regenerable Sargassum column, J. Water Res. 37 (2003) 297–306.