ELSEVIER

Chemical Engineering Journal 106 (2005) 177–184

Chemical Engineering Journal
www.elsevier.com/locate/cej

Batch and column removal of copper from aqueous solution using a brown marine alga *Turbinaria ornata*

K. Vijayaraghavan[a], J. Jegan[b], K. Palanivelu[c], M. Velan[a,*]

[a] *Department of Chemical Engineering, Anna University, Chennai 600025, India*
[b] *Department of Chemical Engineering, Sri Venkateswara College of Engineering, Sriperambudur 602105, India*
[c] *Centre for Environmental Studies, Anna University, Chennai 600025, India*

Received 10 August 2004; received in revised form 10 December 2004; accepted 14 December 2004

Abstract

Turbinaria ornata, a brown marine alga, was tested for its ability to remove copper(II) from aqueous solution. Batch equilibrium tests at different pH conditions showed that at pH 6, a maximum copper uptake of 147.06 mg/g was observed according to the Langmuir model. A solution of 0.1 M HCl performed well in eluting copper from copper-loaded biomass and caused no damage to the biosorbent. The ability of *T. ornata* to biosorb copper in a packed column was investigated, as well. The experiments were conducted to study the effect of important design parameters such as bed height and flow rate. The copper uptake remained relatively constant at approximately 68 mg/g irrespective of the bed height, whereas the uptake decreased as the flow rate increased. The bed depth service time model and the Thomas model were used to analyze the experimental data and the model parameters were evaluated. In regeneration experiments, a loss of sorption performance was observed during seven cycles of sorption–desorption indicated by a shortened breakthrough time and a broadened mass transfer zone. The life-factor for *T. ornata* in terms of critical bed length was found to be 0.603 cm/cycle. The elutant, 0.1 M HCl, provided elution efficiencies greater than 98.8% in all the seven cycles. The pH profiles during both sorption and desorption process were also reported.

Keywords: Biosorption; Copper; Packed bed; Regeneration; *Turbinaria ornata*

1. Introduction

Heavy metal pollution represents an important environmental problem due to its toxic effects and accumulation throughout the food chain. The main sources of heavy metal pollution include electroplating, painting, dying, surface treatment industry, etc. These pollutants are toxic and non-biodegradable and probably have health effects. Conventional processes for heavy metal removal often are neither effective nor economical [1]. Biosorption is a promising alternative, which utilizes inactive or dead biomass to bind and concentrate heavy metals from industrial effluents. Various biomaterials have been examined for their biosorptive properties and different types of biomass have shown different levels of metal uptake [2]. Among the most promising biomaterials studied is algal biomass [3–5]. The presence of carboxylic, sulfonic acid and hydroxyl groups in the polysaccharides are believed to be responsible for impressive metal uptake by marine algae [6,7]. It also offers advantages for biosorption because their macroscopic structures present a convenient basis for the production of biosorbent particles suitable for sorption process applications [8]. *Turbinaria ornata* is a very common brown alga found throughout the Pacific and Indian Ocean. It is known for its rigidity but is believed to have no commercial importance.

The most of the earlier investigations on heavy metal biosorption were restricted to batch equilibrium studies. The sorption capacity of biosorbent obtained from batch equilibrium experiments is useful in providing fundamental information about the effectiveness of metal-biosorbent system. However, this data may not applicable to most treatment system (such as column operations) where contact time is not sufficient for the attainment of equilibrium [9]. Hence, there

---

* Corresponding author. Tel.: +91 44 22203506; fax: +91 44 22352642.
E-mail address: velan@annauniv.edu (M. Velan).

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2004.12.039

Nomenclature

a_{RP}	Redlich–Peterson isotherm constant $(l/mg)^{\beta}$
b	Langmuir model constant
C	effluent copper concentration (mg/l)
C_0	initial copper concentration (mg/l)
C_b	breakthrough copper concentration (mg/l)
C_f	final or equilibrium copper concentration (mg/l)
dc/dt	slope of breakthrough curve from t_b to t_e (mg/l h)
E	elution efficiency (%)
F	flow rate (ml/min)
k_L	life-factor (cm/cycle)
k_{Th}	Thomas model constant (l/mg h)
K	Freundlich constant $(l/g)^{1/n}$
K_a	BDST model constant (l/mg h)
K_{RP}	Redlich–Peterson isotherm constant (l/g)
m_{ad}	metal mass adsorbed (mg)
m_d	metal mass desorbed (mg)
m_{total}	total metal mass sent to the column (mg)
M	Sorbent mass (g)
n	Freundlich constant
N_0	sorption capacity of bed (mg/l)
Q	copper uptake (mg/g)
Q_0	Thomas model constant (mg/g)
Q_{max}	maximum copper uptake (mg/g)
t	time (h)
t_b	breakthrough time (h)
t_e	exhaustion time (h)
Δt	mass transfer zone (h)
V_{eff}	effluent volume (l)
x	cycle number
Z	bed height (cm)
Z_m	critical bed length (cm)
$Z_{m,0}$	initial critical bed length (cm)

Greek symbols

β	Redlich–Peterson exponent
υ	linear velocity (cm/h)

is a need to perform biosorption studies using column. Several investigators have identified packed column as the most effective arrangement for cyclic sorption/desorption [10–13], as it makes the best use of concentration difference known to be a driving force for heavy metal sorption.

In this work, we attempted to utilize the potential of *T. ornata* as a biosorbent for the removal of copper from aqueous solution by batch process. The present study also employed an up-flow *T. ornata* biomass packed column for copper removal as a function of bed height and flow rate. The column was regenerated and reused for seven cycles.

2. Materials and methods

2.1. Biomass preparation and chemicals

T. ornata biomass, collected in Mandapam (Tamil Nadu, India), was sun-dried and then grounded to an average particle size of 0.767 mm. The biomass was protonated using 0.1 M HCl for 3 h. The biomass was then washed in distilled water and dried at 60 °C overnight. The weight loss was found to be approximately 20%. All chemicals obtained from Ranbaxy Fine Chemicals Ltd. (India) including $CuSO_4{\cdot}6H_2O$ were of analytical grade.

2.2. Batch experiments

Batch equilibrium experiments were conducted by adding 0.2 g of *T. ornata* biomass to Erlenmeyer flasks containing 100 ml different Cu^{2+} concentrations (50–1000 mg/l) at desired pH conditions. The initial solution pH was adjusted using 0.1 M HCl or 0.1 M NaOH. The flasks were agitated at 150 rpm in a rotary shaker. After 12 h of contact time, the algal biomass was separated from copper solution by centrifugation at 3000 rpm for 10 min. The copper content in the supernatant was determined using Atomic Absorption Spectrophotometer (AAS 6VARIO; Analytik Jena, Germany). Prior to analysis, the equipment was initially calibrated using standard copper solution. When necessary, the samples were diluted with distilled water before analysis. The amount of copper adsorbed by algae was calculated from the differences between the copper quantity added to the biomass and the copper content of the supernatant using the following equation:

$$Q = \frac{V(C_0 - C_f)}{M} \tag{1}$$

where Q is the copper uptake (mg/g), C_0 and C_f are the initial and equilibrium copper concentrations in the solution (mg/l), respectively, V the solution volume (l), and M the mass of biosorbent (g). Copper-free and alga-free blanks were used as controls.

The copper-loaded biomass after biosorption was contacted with 0.1 M HCl in 250 ml Erlenmeyer flasks for 3 h in a rotary shaker (150 rpm) to study the removal of biosorbed copper ions. The remaining procedure was same as that in the biosorption equilibrium experiments. After desorption, the biomass was washed with distilled water then filtered and finally dried overnight at 60 °C. The loss in biomass weight was calculated and the biomass was subsequently used for re-sorption studies.

2.3. Column experiments

Continuous-flow sorption experiments were conducted in a glass column with an i.d. of 2 and 35 cm in length. At the top of the column, an adjustable plunger was attached with a 0.5 mm stainless sieve. At the bottom of the column, a 0.5 mm stainless sieve was attached followed by glass wool. A 2 cm high layer of glass beads (1.5 mm in diameter) was placed at the column base in order to provide a uniform inlet flow of the solution into the column.

A known quantity of *T. ornata* biomass was placed in the column to yield the desired bed height of the sorbent. A relatively low initial copper concentration of 100 mg/l (compared to batch experiments) was used in column experiments, as very high copper concentration was not likely to be present in the industrial effluents [14] and also to obtain gentle breakthrough curves. Copper(II) solution (100 mg/l, pH 6.0) was pumped upward through the column at a desired flow rate by a peristaltic pump (pp40, Miclins). Samples were collected from the exit of the column at different time intervals and analyzed for copper concentration. The pH of the influent and the effluent were recorded. Operation of the column was stopped when the effluent copper concentration exceeded a value of 99.2 mg/l or higher.

After the column reached exhaustion, the loaded biomass with copper ions was regenerated using 0.1 M HCl. The flow rate was adjusted to 5 ml/min. After elution, distilled water was used to wash the bed until the pH of the wash effluent stabilized near 7.0. Then, the column was fed again with copper solution and sorption studies were carried out. After bed exhaustion, elutant was fed into the column and regeneration studies were conducted. These cycles of sorption followed by desorption were repeated for seven times to evaluate the biomass sorption capacity. To determine the weight loss after seven cycles, the biomass was washed with distilled water and dried at 60 °C overnight. All batch and column experiments were carried out in duplicates, and the deviations were within 5%.

2.4. Analysis of column data

The total quantity of metal mass biosorbed in the column (m_{ad}) is calculated from the area above the breakthrough curve (outlet metal concentration versus time) multiplied by the flow rate. Dividing the metal mass (m_{ad}) by the biosorbent mass (M) leads to the uptake capacity (Q) of the biomass [12]. The breakthrough time (t_{b}, the time at which copper concentration in the effluent reached 1 mg/l) and bed exhaustion time (t_{e}, the time at which copper concentration in the effluent exceeded 99.2 mg/l) were used to evaluate the overall sorption zone (Δt) as follows [15]:

$$\Delta t = t_{\mathrm{e}} - t_{\mathrm{b}} \tag{2}$$

The length of the mass transfer zone (Z_{m}), also called as critical bed length, can be calculated from the breakthrough curve as follows [15]:

$$Z_{\mathrm{m}} = Z\left(1 - \frac{t_{\mathrm{b}}}{t_{\mathrm{e}}}\right) \tag{3}$$

where Z is the bed height (cm).

Effluent volume (V_{eff}) can be calculated as follows [12]:

$$V_{\mathrm{eff}} = Ft_{\mathrm{e}} \tag{4}$$

where F is the volumetric flow rate (ml/min).

Total amount of copper ions sent to column (m_{total}) can be calculated as follows [12]:

$$m_{\mathrm{total}} = \frac{C_0 F t_{\mathrm{e}}}{1000} \tag{5}$$

Total copper removal percent with respect to flow volume can be calculated as follows [12]:

$$\text{total copper removal (\%)} = \frac{m_{\mathrm{ad}}}{m_{\mathrm{total}}} \times 100 \tag{6}$$

The metal mass desorbed (m_{d}) can be calculated from the elution curve (C versus t). The elution efficiency (E) can be calculated as follows [15]:

$$E(\%) = \frac{m_{\mathrm{d}}}{m_{\mathrm{ad}}} \times 100 \tag{7}$$

3. Results and discussion

3.1. Batch studies

Fig. 1 shows the experimental copper uptake isotherms for protonated *T. ornata* biomass at different pH conditions. The copper concentrations used were in the range of 50–1000 mg/l to obtain sorption isotherm. This is because to achieve highest possible experimental copper uptake of *T. ornata* biomass (the complete saturation isotherm-curve plateau). Initial pH played a significant role in the biosorption of copper. Since most wastewaters containing heavy metals are acidic [16], experiments were carried out only at acidic pH values (3.0–6.0). Working over pH 6.0 was avoided to prevent the possible precipitation of copper. Little copper uptake at low pH values is an indication of competition of protons for the same binding sites on the algal cell

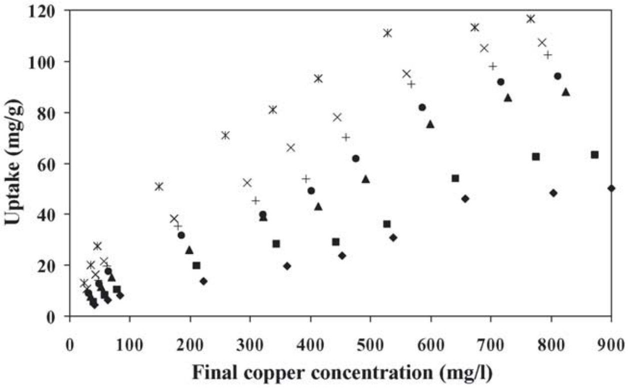

Fig. 1. Effect of pH on copper biosorption by *Turbinaria ornata* (biomass dosage = 2 g/l). Initial solution pH: (◆) pH 3; (■) pH 3.5; (▲) pH 4; (●) pH 4.5; (+) pH 5; (×) pH 5.5; (*) pH 6.

wall. In addition, it was observed that as pH increases, copper uptake also increases and reached a maximum value at pH 6.0.

The equilibrium biosorption data can be modeled by using different simple adsorption models such as Langmuir (Eq. (8)), Freundlich (Eq. (9)) and Redlich–Peterson (Eq. (10)):

$$Q = \frac{Q_{\max} b C_{\mathrm{f}}}{1 + b C_{\mathrm{f}}} \tag{8}$$

$$Q = K C_{\mathrm{f}}^{1/n} \tag{9}$$

$$Q = \frac{K_{\mathrm{RP}} C_{\mathrm{f}}}{1 + a_{\mathrm{RP}} C_{\mathrm{f}}^{\beta}} \tag{10}$$

where $Q_{\max}$ is the maximum metal uptake (mg/g), b the Langmuir equilibrium constant (l/mg), K the Freundlich constant $(\mathrm{l/g})^{1/n}$, n the Freundlich constant, K_{RP} the Redlich–Peterson isotherm constant (l/g), a_{RP} the Redlich–Peterson isotherm constant $(\mathrm{l/mg})^{\beta}$, and β the exponent, which lies between 1 and 0. The main reason for the extended use of these isotherms is that they incorporate constants that are easily interpretable. All the model parameters were evaluated by non-linear regression using MATLAB® software.

Langmuir sorption model [17] served to estimate the maximum metal uptake values where they could not be reached in the experiments. The constant b represents affinity between the sorbent and sorbate. The Langmuir model parameters were largely dependent on the initial solution pH. Both $Q_{\max}$ and b increases with increasing initial solution pH. High values of b are reflected in the steep initial slope of a sorption isotherm, indicating desirable high affinity. Thus, for good biosorbents in general, high $Q_{\max}$ and a steep initial isotherm slope (i.e. high b) are desirable [6]. At pH 6.0, both $Q_{\max}$ and b attained their maximum values of 147.06 mg/g and 0.0043 l/mg, respectively (Table 1). The Freundlich equation [18] is an empirical equation employed to describe the heterogeneous systems. It is worth noting both Freundlich constants (K and n) also reached their maximum values at pH 6.0, this implies that the binding capacity reaches the highest value and the affinity between the biomass and copper ions was also higher than other pH values investigated. The Redlich–Peterson equation [19] is widely used as a compromise between Langmuir and Freundlich systems. The model parameters (K_{RP} and β) increase with increasing pH and reached maximum at pH 6.0 (Table 1). However, the constant a_{RP} decreases with increasing pH. The batch sorption isotherm at pH 6.0, fitted using three examined models is shown in Fig. 2. It was obvious that Langmuir model ($R^2 = 0.991$) fitted the data well, compared to Freundlich ($R^2 = 0.979$) and Redlich–Peterson model ($R^2 = 0.989$).

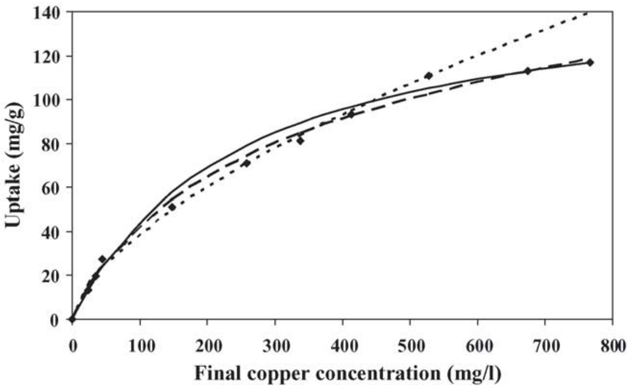

Fig. 2. Application of Langmuir model (—), Freundlich model (- - -) and Redlich–Peterson model (– – –) to experimental isotherm data (♦) at pH 6 and biosorbent dosage = 2 g/l.

The copper-loaded biomass (116.71 mg/g) was eluted using 0.1 M HCl. Elution efficiency (E) was determined by the ratio of the metal mass in the solution after desorption to the metal mass initially bound to the biosorbent [20]. The HCl wash of copper-laden biomass released all the copper ions and no biomass damage was caused by the acid elution. The use of *T. ornata* as a potential biosorbent depends not only on the biosorptive capacity, but also on how well the biomass can be reused. The biomass was used for seven sorption–desorption cycles and regenerated using 0.1 M HCl. The biomass was able to retain its copper uptake capacity for the entire seven cycles examined. The elutant HCl effectively desorbed the biosorbed metal ions and making it ready in its original protonated form for the next cycle. The loss in the dry weight of biomass was less than 3% after seven cycles and no significant reduction in biosorption capacity was observed after seven cycles.

Table 1
Langmuir, Freundlich and Redlich–Peterson model parameters at different pH conditions

pH	Langmuir model			Freundlich model			Redlich–Peterson model			
	$Q_{\max}$ (mg/g)	b (l/mg)	$R^{2\mathrm{a}}$	K $(\mathrm{l/g})^{1/n}$	n	$R^{2\mathrm{a}}$	K_{RP} (l/g)	a_{RP} $(\mathrm{l/mg})^{\beta}$	β	$R^{2\mathrm{a}}$
3.0	57.47	0.0020	0.988	0.235	1.28	0.978	0.248	0.437	0.303	0.981
3.5	71.43	0.0022	0.992	0.361	1.33	0.984	0.324	0.357	0.336	0.985
4.0	96.15	0.0026	0.990	0.596	1.36	0.985	0.444	0.230	0.389	0.987
4.5	104.17	0.0028	0.991	0.787	1.41	0.984	0.478	0.158	0.446	0.985
5.0	119.05	0.0029	0.991	0.947	1.43	0.983	0.483	0.096	0.501	0.986
5.5	125.10	0.0034	0.992	1.266	1.49	0.981	0.498	0.033	0.657	0.992
6.0	147.06	0.0043	0.991	2.287	1.64	0.979	0.754	0.019	0.797	0.989

[a] Correlation coefficient.

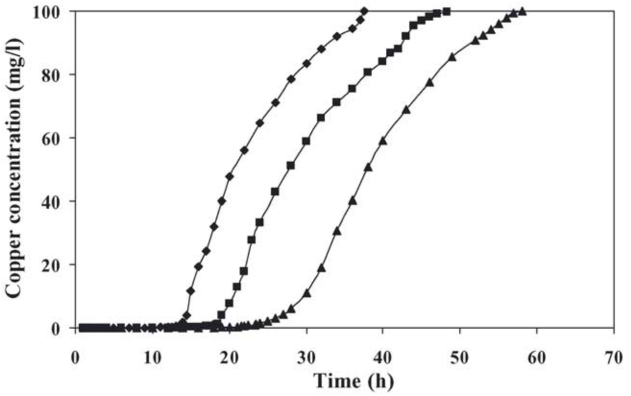

Fig. 3. Breakthrough curves for copper biosorption onto *T. ornata* biomass at different bed heights (flow rate = 5 ml/min, initial copper concentration = 100 mg/l, pH 6.0). Bed heights: (♦) 15 cm; (■) 20 cm; (▲) 25 cm.

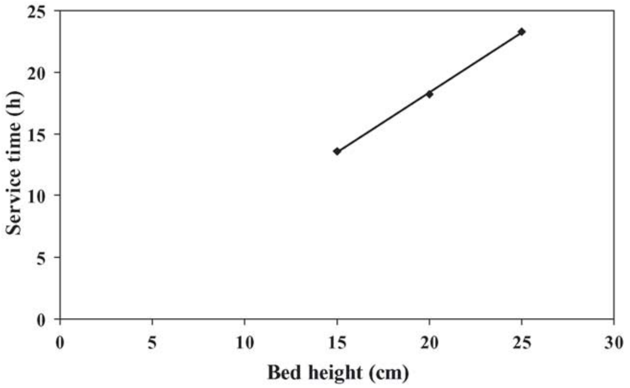

Fig. 4. BDST model plot for copper biosorption by *T. ornata* (flow rate = 5 ml/min, initial copper concentration = 100 mg/l, pH 6.0).

3.2. Column studies

3.2.1. Effect of bed height

Accumulation of metals in the packed bed column is largely dependent on the quantity of sorbent inside the column. In order to yield different bed heights, 9.75, 12.99 and 16.21 g of biomass were added to produce 15, 20 and 25 cm, respectively. The sorption breakthrough curves obtained by varying the bed heights from 15 to 25 cm at 5 ml/min flow rate and 100 mg/l initial copper concentration for *T. ornata* biomass are given in Fig. 3. Both breakthrough time and exhaustion time increased with increasing bed height, as more binding sites available for sorption, also resulted in a broadened mass transfer zone. The copper uptake capacity of the biomass remained relatively constant at 67.96, 68.46 and 68.76 mg/g for 15, 20 and 25 cm, respectively. This trend was expected because uptake capacity usually depends on the amount of sorbent available for sorption. Also, a significant increasing trend was observed for total copper removal percentages as 58.89, 61.37 and 63.94% for 15, 20 and 25 cm, respectively.

BDST is a simple model, which states that bed height (Z) and service time (t) of a column bears a linear relationship. The equation can be expressed as [21] follows:

$$t = \frac{N_0 Z}{C_0 \upsilon} - \frac{1}{K_a C_0} \ln\left(\frac{C_0}{C_b} - 1\right) \tag{11}$$

where C_b is the breakthrough metal ion concentration (mg/l), N_0 the sorption capacity of bed (mg/l), υ the linear velocity (cm/h), and K_a the rate constant (l/mg h). The column service time was selected as time when the effluent copper concentration reached 1 mg/l. The plot of service time against bed height at a flow rate of 5 ml/min (Fig. 4) was linear ($R^2 = 0.999$) indicating the validity of BDST model for the present system. The sorption capacity of the bed per unit bed volume, N_0, was calculated from the slope of BDST plot, assuming initial concentration, C_0, and linear velocity, υ, as constant during the column operation. The rate constant, K_a, calculated from the intercept of BDST plot, characterizes the rate of solute transfer from the fluid phase to the solid phase [22]. The computed N_0 and K_a were 9267 mg/l and 0.044 l/mg h, respectively. If K_a is large, even a short bed will avoid breakthrough, but as K_a decreases a progressively longer bed is required to avoid breakthrough [22]. The BDST model parameters can be useful to scale up the process for other flow rates without further experimental run.

3.2.2. Effect of flow rate

Flow rate is one of the important characteristics in evaluating sorbents for continuous-treatment of metal-laden effluents on an industrial scale [23]. The effect of flow rate on copper biosorption by *T. ornata* was studied by varying the flow rate from 5 to 20 ml/min, while the bed height and initial copper concentration were held constant at 25 cm and 100 mg/l, respectively. The plots of effluent copper concentration versus time at different flow rates are shown in Fig. 5. An earlier breakthrough and exhaustion time were observed in the profile, when the flow rate was increased to 20 ml/min. The flow rate also strongly influenced the copper uptake capacity of *T. ornata* as 68.76, 63.52 and 50.61 mg/g, which were recorded at 5, 10 and 20 ml/min, respectively. This be-

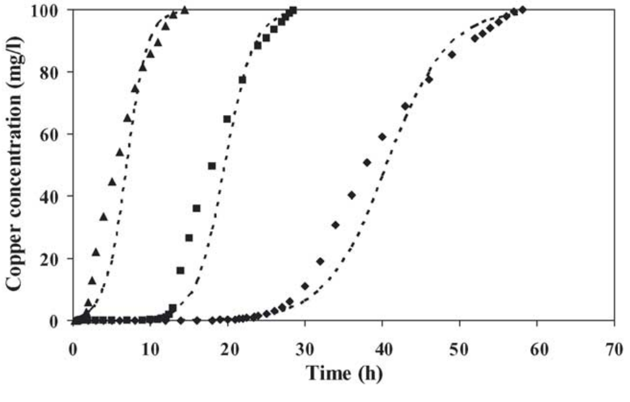

Fig. 5. Breakthrough curves for copper biosorption onto *T. ornata* biomass at different flow rates (bed height = 25 cm, initial copper concentration = 100 mg/l, pH 6.0). Flow rates: (♦) 5 ml/min; (■) 10 ml/min; (▲) 20 ml/min. (- - -) Predicted from Thomas model.

havior may be due to insufficient time for the solute inside the column and the diffusion limitations of the solute into the pores of the sorbent at higher flow rates [24]. Even though more shortened mass transfer zone (usually preferable) was observed at higher flow rates, the total copper removal percentage (a reflective of system performance) was actually recorded as 63.95, 60.22 and 47.47% at 5, 10 and 20 ml/min, respectively.

Successful design of a column sorption process required prediction of the concentration–time profile or breakthrough curve for the effluent [11]. Various mathematical models can be used to describe fixed bed adsorption. Among these, the Thomas model is simple and widely used by several investigators [11,12]. The linearized form of Thomas model is expressed as follows:

$$\ln\left(\frac{C_0}{C}-1\right)=\frac{k_{\mathrm{Th}}Q_0M}{F}-\frac{k_{\mathrm{Th}}C_0}{F}V \qquad (12)$$

where k_{Th} is the Thomas model constant (l/mg h), Q_0 the maximum solid-phase concentration of solute (mg/g), V the throughput volume (l). The model constants k_{Th} and Q_0 can be determined from a plot of $\ln[(C_0/C)-1]$ against t at a given flow rate [12]. It is clear from Fig. 5 that the model gave a good fit of the experimental data at all flow rates examined with high correlation coefficients greater than 0.978. The values of k_{Th} obtained from Thomas model were 0.0025, 0.0053 and 0.0073 l/mg h at 5, 10 and 20 ml/min, respectively. The values of Q_0 obtained from the Thomas model were 75.07, 72.64 and 51.06 mg/g at 5, 10 and 20 ml/min, respectively.

3.2.3. Regeneration

Reusability of sorbent is of crucial importance in industrial practice for metal removal from wastewater. This can be evaluated by comparing the sorption performance of regenerated biomass with the original biomass [23]. The column regeneration studies were carried out for seven sorption–desorption cycles at 5 ml/min. The column was packed with 16.21 g of *T. ornata* biomass yielding an initial bed height of 25 cm and bed volume of 78.5 ml with a packing density of 206.5 g/l. The breakthrough time, exhaustion time and copper uptake for all seven cycles are summarized in Table 2. At the end of seventh cycle, 11.78 g of dry biomass was left in the column indicating a weight loss of 27.33%. The bed height was dropped from 25 to 22.8 cm, whereas bed volume decreased to 71.6 ml and packing density decreased to 164.5 g/l after seven sorption–desorption cycles.

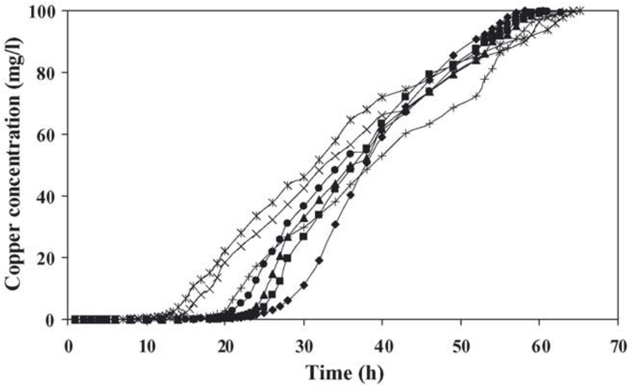

Fig. 6. Breakthrough curves for copper biosorption onto *T. ornata* biomass during regeneration cycles (initial bed height = 25 cm, flow rate = 5 ml/min, initial copper concentration = 100 mg/l, pH 6.0). Sorption cycles: (◆) 1 cycle; (■) 2 cycle; (▲) 3 cycle; (●) 4 cycle; (+) 5 cycle; (×) 6 cycle; (*) 7 cycle.

A decreased breakthrough time and an increased exhaustion time were observed as the regeneration cycles progressed, which also resulted in a broadened mass transfer zone. This behavior is primarily due to gradual deterioration of biomass because of continuous usage. The bed exhaustive limit was selected as 99.2 mg Cu/l in order to avoid the time delay that normally occurs for full bed saturation. The breakthrough curves for all the seven cycles are presented in Fig. 6. The actual length of the bed was not constant during the seven regeneration cycles. It showed a similar trend as that of the slope of subsequent breakthrough curves, which also decreased as the cycles progressed. It was interesting to note that the loss of sorption performance was not reflected in the biosorption capacity, as it remained reasonably consistent irrespective of the number of cycles. This observation clearly pointed out that the loss of sorption performance is not mainly due to biomass damage but rather because of sorbing sites, whose accessibility becomes difficult as the cycles progressed [15]. The uptake also strongly depended on the previous elution step, since prolonged elution may destroy the binding sites or inadequate elution may allow metal ions to remain in the sites.

The minimum bed length (Z_{m}) required to obtain the breakthrough time t_{b} at $t = 0$ (also called critical bed length) was uniformly increased as the cycle progressed, indicating

Table 2
Sorption and elution process parameters for seven sorption–desorption cycles

Cycle no.	Uptake (mg/g)	t_{b} (h)	t_{e} (h)	Δt (h)	dc/dt (mg/l h)	Z (cm)	Z_{m} (cm)	V_{eff} (l)	Copper removal (%)	Elution efficiency (%)
1	68.76	23.3	58.1	34.8	3.174	25.0	15.0	17.4	63.95	99.6
2	69.97	22.2	60.4	38.2	2.786	24.5	15.5	18.1	62.59	100.0
3	69.87	21.5	60.4	38.9	2.599	24.1	15.5	18.1	62.50	98.9
4	66.10	19.9	62.7	42.8	2.446	23.8	16.2	18.8	56.96	99.8
5	72.21	18.2	63.9	45.7	2.232	23.4	16.7	19.2	61.06	98.8
6	64.97	14.5	64.3	49.8	2.010	23.1	17.9	19.3	54.59	100.5
7	63.18	12.0	65.1	53.1	1.924	22.8	18.6	19.5	52.44	99.2

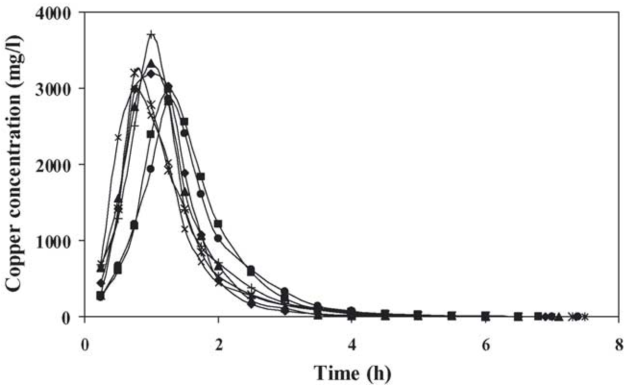

Fig. 7. Elution curves for desorption of copper during regeneration cycles (flow rate = 5 ml/min, elutant = 0.1 M HCl). Elution cycles: (♦) 1 cycle; (■) 2 cycle; (▲) 3 cycle; (●) 4 cycle; (+) 5 cycle; (×) 6 cycle; (*) 7 cycle.

the broadening of mass transfer zone. For biosorption, the activity-indicator can be calculated as “life-factors” based on the minimum bed length [15].

In order to calculate life-factor in terms of critical bed length, a linear regression was used:

$$Z_\mathrm{m} = Z_{\mathrm{m},0} + k_\mathrm{L}x \tag{13}$$

where x is the cycle number, $Z_{\mathrm{m},0}$ the initial critical bed length (cm), and k_L the corresponding life-factor (cm/cycle). From the plot of Z_m versus x (graph not presented), $Z_{\mathrm{m},0}$ and k_L values were found to be 14.08 cm and 0.603 cm/cycle, respectively.

For a system of continuous operation to work successfully, the desorption process and agents must be effective and should not cause much damage to the sorbent. The elution curves obtained for all the seven cycles are presented in Fig. 7. The elution curves observed in all the cycles exhibited a similar trend, a sharp increase in the beginning followed by a gradual decrease. The elution efficiencies were always greater than 98.8% throughout the experiment. In cycle 6, the elution efficiency was around 100.5%, this may be due to inadequate elution in the previous cycle. The elution process was carried out at an average of 7.2 h cycles and stopped when the effluent copper concentration reached less than 5 mg/l. In cycle 5 at $t = 60$ min, 3705 mg Cu/l was present and this value was not reached in any of the other cycles.

The pH profile during the course of sorption and elution process for cycles 1, 4 and 7 are presented in Fig. 8. The major mechanism responsible for metal binding in brown algae is ion-exchange [6]. Several researchers have identified that in brown algae, carboxylic and sulfonic groups are the two key functional groups for the ion-exchange [6,25]. In the present study, biomass was protonated and when it was contacted with copper solution, Cu^{2+} ions exchanged with H^+ ions and occupied the binding sites and therefore pH tended to decrease. In all the sorption cycles effluent pH continuously decreased as the saturation of the bed progressed and finally stabilized near 3.0. The pH profiles during the course of elution process showed a trend similar that of the elution curves. In all the elution cycles, it was observed that the pH increased in initial stages followed by a gradual decrease in pH. The H^+ ions provided by the elutant (0.1 M HCl) is exchanged with Cu^{2+} ions in occupying the sites, which results in increasing the pH of the solution up to the point where the copper concentration peaked in the effluent. Thereafter as the effluent copper concentration decreased, the effluent pH also decreased and eventually reached the influent pH. Thus, the pH profiles obtained during sorption and elution cycles supports the fact that ion exchange may be the major mechanism responsible for copper biosorption by *T. ornata*.

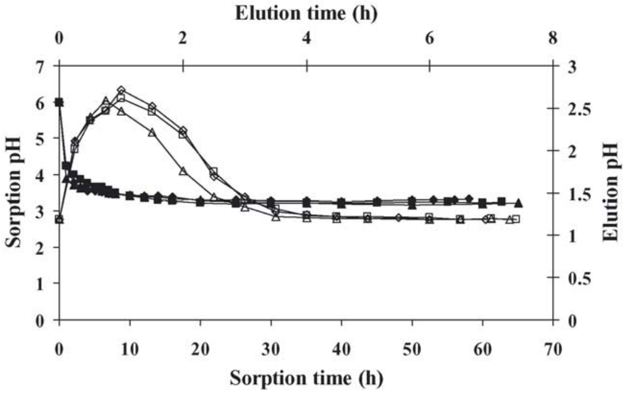

Fig. 8. Sorption and elution pH profiles during regeneration cycles (initial bed height = 25 cm, flow rate = 5 ml/min, initial copper concentration = 100 mg/l, elutant = 0.1 M HCl). Sorption cycles: (♦) 1 cycle; (■) 4 cycle; (▲) 7 cycle. Elution cycles: (◊) 1 cycle; (□) 4 cycle; (△) 7 cycle.

The total volume of the copper bearing solution (100 mg/l) treated during this regeneration study was around 130.47 l (in seven cycles) and the total volume of 0.1 M HCl utilized for elution process was nearly 15.15 l, which corresponded to approximately 21 days of continuous operation. Even after seven sorption–desorption cycles, *T. ornata* biomass exhibited a relatively high copper uptake of 63.18 mg/g, indicating the potential of *T. ornata* to withstand extreme conditions at the same time retaining its copper biosorption capacity.

4. Conclusions

This study identified *T. ornata* as a suitable biosorbent to be utilized for continuous removal of copper(II) ions from aqueous solution. The dried biomass of *T. ornata* shows good mechanical stability, flow permeability and copper uptake capacity in repeated column operations. In addition to this, easy availability and low cost make this biomass an attractive option for the treatment of copper-laden effluents.

References

[1] B. Volesky, Z.R. Holan, Biosorption of heavy metals, Biotechnol. Prog. 11 (1995) 235–250.
[2] Z.R. Holan, B. Volesky, Biosorption of lead and nickel by biomass of marine algae, Biotechnol. Bioeng. 43 (1994) 1001–1009.

[3] N. Kuyucak, B. Volesky, Accumulation of cobalt by marine alga, Biotechnol. Bioeng. 33 (1989) 809–814.
[4] Q. Yu, J.T. Matheickal, P. Yin, P. Kaewsarn, Heavy metal uptake capacities of common marine macro algal biomass, Water Res. 33 (1999) 1534–1537.
[5] M.A. Hashim, K.H. Chu, Biosorption of cadmium by brown, green, and red seaweeds, Chem. Eng. J. 97 (2004) 249–255.
[6] T.A. Davis, B. Volesky, A. Mucci, A review of the biochemistry of heavy metal biosorption by brown algae, Water Res. 37 (2003) 4311–4330.
[7] G. McKay, Y.S. Ho, J.C.Y. Ng, Biosorption of copper from waste waters: a review, Sep. Purif. Meth. 28 (1999) 87–125.
[8] R.H.S.F. Vieira, B. Volesky, Biosorption: a solution to pollution? Int. Microbiol. 3 (2000) 17–24.
[9] Z. Zulfadhly, M.D. Mashitah, S. Bhatia, Heavy metals removal in fixed-bed column by the macro fungus *Pycnoporus sanguineus*, Environ. Poll. 112 (2001) 463–470.
[10] D. Kratochvil, B. Volesky, G. Demopoulos, Optimizing Cu removal/recovery in a biosorption column, Water Res. 31 (1997) 2327–2339.
[11] G. Yan, T. Viraraghavan, Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass, Biores. Technol. 78 (2001) 243–249.
[12] Z. Aksu, F. Gonen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, Proc. Biochem. 39 (2003) 599–613.
[13] K.H. Chu, Improved fixed bed models for metal biosorption, Chem. Eng. J. 97 (2004) 233–239.
[14] Z. Aksu, T. Kutsal, Determination of kinetic parameters in the biosorption of copper(II) on *Cladophora* sp. in a packed bed column reactor, Proc. Biochem. 33 (1998) 7–13.
[15] B. Volesky, J. Weber, J.M. Park, Continuous-flow metal biosorption in a regenerable *Sargassum* column, Water Res. 37 (2003) 297–306.
[16] M.Y. Lee, S.H. Lee, H.J. Shin, T. Kajiuchi, J.W. Yang, Characteristics of lead removal by crab shell particles, Proc. Biochem. 33 (1998) 749–753.
[17] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[18] H. Freundlich, Ueber die adsorption in loesungen, Z. Phys. Chem. 57 (1907) 385–470.
[19] O. Redlich, D.L. Peterson, A useful adsorption isotherm, J. Phys. Chem. 63 (1959) 1024–1029.
[20] T.A. Davis, B. Volesky, R.H.S.F. Vieira, *Sargassum* seaweed as biosorbent for heavy metals, Water Res. 34 (2000) 4270–4278.
[21] R.A. Hutchins, New method simplifies design of activated carbon systems, Chem. Eng. 80 (1973) 133–138.
[22] D.O. Cooney, Adsorption Design for Wastewater Treatment, CRC Press, Boca Raton, 1999.
[23] M. Zhao, J.R. Duncan, R.P. Van Hille, Removal and recovery of zinc from solution and electroplating effluent using *Azolla filiculoides*, Water Res. 33 (1999) 1516–1522.
[24] D.C.K. Ko, J.F. Porter, G. McKay, Optimised correlations for the fixed-bed adsorption of metal ions on bone char, Chem. Eng. Sci. 55 (2000) 5819–5829.
[25] D. Kratochvil, B. Volesky, Advances in the biosorption of heavy metals, Trends Biotechnol. 16 (1998) 291–300.