



Biosorption of uranium(VI) from aqueous solutions by Ca-pretreated *Cystoseira indica* alga: Breakthrough curves studies and modeling

Morteza Ghasemi^a, Ali Reza Keshtkar^{b,*}, Reza Dabbagh^c, S. Jaber Safdari^b

^a Faculty of Nuclear Engineering, Shahid Beheshti University, Tehran, Iran

^b Nuclear Fuel Cycle School, Nuclear Science and Technology Research Institute, Tehran, Iran

^c Nuclear Science Research School, Nuclear Science and Technology Research Institute, Tehran, Iran

ARTICLE INFO

Article history:

Received 21 October 2010

Received in revised form 16 January 2011

Accepted 6 February 2011

Available online 3 March 2011

Keywords:

Biosorption

Uranium

Packed bed column

Cystoseira indica

Modeling

ABSTRACT

Uranium(VI) biosorption from aqueous solutions containing 60 mg l⁻¹ metal concentration by Ca-pretreated *Cystoseira indica* alga was studied in a packed bed column with 1.5 cm internal diameter. The effect of bed height and flow rate on biosorption process was investigated and the experimental breakthrough curves were obtained. Results showed that by increasing the bed height, the breakthrough and exhaustion times increased and the slope of breakthrough curves decreased. Also, it was observed that the controlled-rate step shifted from external to internal mass transfer limitations, as the flow rate increased. The maximum uptake capacity, 318.15 mg g⁻¹, and total metal removal, 59.32%, were obtained at flow rate of 2.3 ml min⁻¹ and bed height of 6 cm. The column was regenerated using 0.1 M HCl solution and sorption–desorption studies were carried out for three cycles. The obtained results confirmed that reusability of this biosorbent is possible. The results obtained agreed well with the bed depth service time model. In addition, for estimations of the parameters necessary for the design of a large-scale packed bed column, the experimental data were also fitted to the Thomas, Yan and Belter models and were found to agree with the experimental data fairly well.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Uranium is often released into the environment from mining and milling facilities. Excessive amounts of uranium have found their ways into the environment through the activities associated with the nuclear industry. Uranium contamination poses a threat in some surface and ground waters. Hence, the removal of uranium from waste water is important not only for the nuclear industry, but also for environmental remediation [1]. Uranium and any other heavy metal removal from wastewater can be achieved via several chemical (neutralization/precipitation) or physical (evaporation, ion exchange, membrane technology) treatment techniques. These common technologies not only require high capital investment and running costs, but also are ineffective in low strength wastewaters. Hence, environmental engineers and scientists have been trying to find easy, effective, economical, and eco-friendly techniques for removal of heavy metals from wastewater [2–8]. The search for an economical and eco-friendly option has led to the utilization of biological materials (microbial and plant origin) as adsorbents which interact effectively with heavy metals. Biosorption describes the removal of heavy metals by dead biomass from aqueous solutions

and is attributed mainly to the ligands present in their cell wall biomolecules. There are many natural adsorbents such as marine algae, bacteria, fungi, and industrial wastes that have been used for uranium removal from water solutions [1,9–13]. Among these, algal biomass has received much attention due to the cost saving, low sensitivity to environmental and impurity factors, the possible contamination recovery from the biomaterial, and its elevated adsorption capacity. *Cystoseira indica*, brown alga is abundant in the Persian Gulf on the coast of Qeshm, Iran. Pretreated *C. indica* shows high metal loading capacity for the removal of uranium(VI). The pretreatment process enhances biomass surface ions. Since the biosorption of uranium(VI) is largely an ion exchange process, the processed samples of the biomass have higher sorption capacity in comparison with untreated cells [14].

Equilibrium batch tests and dynamic continuous flow studies are two types of investigations that can help examine a biosorption system. The evaluation of equilibrium biosorption performance needs to be supplemented by process-oriented studies of its kinetics and eventually by dynamic continuous flow tests. The sorption rate of the metal uptake, together with the hydrodynamic parameters, determines the size of the contact equipment. These key process parameters could be used for comparison, for process design, and for scale-up purposes. Continuous flow packed bed columns have been used mainly in sorption of heavy metal ions from aqueous solution, due to the efficient utilization of biosorbent

* Corresponding author. Tel.: +98 021 82064399; fax: +98 021 88221127.
E-mail address: akeshtkar@aeoi.org.ir (A.R. Keshtkar).

Nomenclature

a	Yan empirical parameter
C_t	effluent metal concentration at time of t (mg l^{-1})
C_0	influent metal concentration (mg l^{-1})
K_a	rate constant ($\text{l mg}^{-1} \text{ min}^{-1}$)
k_{Th}	Thomas rate constant ($\text{l min}^{-1} \text{ g}^{-1}$)
M	dry weight of biosorbent (g)
m_{ad}	the quantity of metal retained in the column (g)
m_{d}	metal mass desorbed (g)
m_{total}	total amount metal sent to column (g)
N_0	sorption capacity of bed (mg l^{-1})
Q	flow rate (l min^{-1})
q_0	maximum uptake capacity (mg g^{-1})
t	service time (min)
t_b	breakthrough time (min)
t_e	bed exhaustion time (min)
$t_{0.5}$	time at which the effluent concentration is half the influent (min)
V_e	effluent volume (l)
v	linear velocity (cm min^{-1})
Z	bed height of the column (cm)
Z_m	mass transfer zone (cm)

Greek letters

σ	standard deviation
----------	--------------------

capacity. In the column studies, the effectiveness of biomass can be evaluated from the breakthrough curve of the effluent concentration (or the concentration–time profile) and a typical S-shaped breakthrough curve is usually observed [15].

Mathematical modeling of the sorption process offers a very powerful device for a number of tasks on different levels and is necessary for optimal process design and operation. Sorption process modeling is particularly useful for predicting the process performance under different conditions. Then biosorption process modeling can guide experimental research, optimize a given process, provide a basis for process control strategies, and provide a process diagnostic tool [16]. In order to predict the breakthrough curve of an adsorption process in a packed bed column, the Thomas, Yan and Belter models have often been used [5,6,8,15,17–22]. Moreover, the required bed height is an important parameter in designing an adsorption column. This can be determined from the breakthrough curve and the bed depth service time, BDST, model [23,24].

Biosorption equilibrium, kinetic and thermodynamic of binding of uranium(VI) ions to *C. indica* were studied in a batch system with respect to pH, temperature and initial metal ion concentration [11,14]. The present work extended the investigation of the biosorption by the Ca-pretreated *C. indica* alga biomass to the uranium(VI) removal in a packed bed column. In this research, the effect of design parameters, such as bed height and flow rate on uranium(VI) biosorption has been examined. In addition, uranium(VI) biosorption behavior of Ca-pretreated *C. indica* in three consecutive sorption–desorption cycles has been investigated. For a proper design of an adsorption column, an accurate prediction of the breakthrough curve is needed. Therefore, the experimental results obtained from the continuous system were fitted to the abovementioned models for adsorption.

2. Materials and methods

2.1. Preparation of biosorbent

C. indica brown alga (obtained from the Persian Gulf on the coast of Qeshm, Iran) was extensively washed with deionized water, and sun dried and further dried in an oven at 70 °C overnight. Dried biomass was ground in a laboratory blender and sorted by sieving using the standard test sieves. Our previous study showed that the uptake capacity of uranium by calcium pretreated *C. indica* was greater than raw *C. indica* alga [14]. This finding could be due to the exposing of active metal-binding sites embedded in the cell wall and causing availability of more anionic sites. The other reason may be due to removal of surface impurities. Therefore, in this work the biomass treated by calcium solution. For preparation of the calcium pretreated biomass, the batch of biomass with particle size 1–2 mm was selected for subsequent pretreatment. Pretreatment of the biomass was carried out as follows: the sample of biomass was treated with 0.1 M CaCl_2 solution at pH 4 (10 g biomass per liter of solution) for 3 h under slow stirring (150 rpm at 25 °C). Then, pretreated biomass was washed several times with deionized water to remove excess calcium ions. The Ca-pretreated biomass was then dried in an oven at 70 °C overnight.

2.2. Biosorption experiments

All of the experiments were performed at room temperature (25 ± 2 °C). The experiments were carried out in a glass column of 10 cm length and 1.5 cm internal diameter, each filled with different quantities of dried Ca-pretreated biomass. Two plastic sieves both with pore size of 0.5 mm were sealed using cap holders and installed at the top and bottom of this column. The experiments were conducted by pumping a metal solution, prepared by use of deionized water and analytical grade salts of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Merck supplied), in up flow mode through the packed bed column with a peristaltic pump (Watson Marlow Pumps, Model 205U). Uranium(VI) solution had initial concentration of 60 mg l^{-1} and pH 4. This pH value was determined as the optimum pH value for uranium(VI) biosorption [14]. The pH of influent solutions was measured with a pH meter (Metrohm, Model 780) and adjusted by using 0.1 M HCl and/or 0.1 M NaOH. Samples were collected periodically and were analyzed for the remaining uranium(VI) ion concentration by an inductively coupled plasma spectroscopy (ICP, Varian, Model Liberty 150 AX Turbo). Operation of the column was stopped when the effluent metal concentration reached a constant value (equal to the influent concentration). Each analysis was repeated three times and the results given were the average values. The deviation was less than 5%.

3. Modeling and analysis of column data

The performance of packed bed is described through the concept of the breakthrough curve. Breakthrough point is the time that sorbed species are detected in the column effluent at a given concentration and breakthrough curve is the shape of concentration–time profile. Breakthrough point and curve are very important characteristics for process design, dynamic response and operation of a biosorption column because they directly affect the feasibility and economics of the sorption phenomena. Experimental determination of these parameters is very dependent on column operation conditions [16].

The quantity of metal retained in the column, represented by the area above the breakthrough curve (C versus t), was obtained through numerical integration. Dividing the metal mass (m_{ad}) by

the mass of alga in the bed (M), the uptake capacity of the biosorbent was obtained [5,24,25].

The breakthrough time (t_b , the time at which metal concentration in the effluent reached 5% of the influent value) and bed exhaustion time (t_e , the time at which metal concentration in the effluent exceeded 95% of the influent value) were used to evaluate the length of the mass transfer zone (Z_m) as follows [16,24]:

$$Z_m = Z \left(1 - \frac{t_b}{t_e} \right) \quad (1)$$

Effluent volume (V_e) can be calculated as follows [24,26]:

$$V_e = Q \times t_e \quad (2)$$

where Q is the volumetric flow rate ($l \text{ min}^{-1}$). Total amount metal sent to column (m_{total}) can be calculated as follows [24,26]:

$$m_{\text{total}} = \frac{C_0 \times V_e}{1000} \quad (3)$$

Total metal removal percent with respect to flow volume can be calculated as follows [24,26]:

$$\text{Total metal removal (\%)} = \frac{m_{\text{ad}}}{m_{\text{total}}} \times 100 \quad (4)$$

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 [25]:

$$E (\%) = \frac{m_d}{m_{\text{ad}}} \times 100 \quad (5)$$

Among various parameters, the required bed depth for a specific adsorption time (service-time) before the regeneration of the biosorbent is an important design parameter. The bed depth service time (BDST) is a simple model for predicting the relationship between bed height (Z) and service time (t), in terms of process concentrations and adsorption parameters, given by Eq. (6) [27]:

$$\ln \left(\frac{C_0}{C_t} - 1 \right) = \ln \left(e^{(K_a \times N_0 \times Z)/v} - 1 \right) - K_a \times C_0 \times t \quad (6)$$

where C_0 is the influent metal concentration (mg l^{-1}), C_t the effluent metal concentration at time of t (mg l^{-1}), N_0 the sorption capacity of the bed (mg l^{-1}), K_a the rate constant ($l \text{ mg}^{-1} \text{ min}^{-1}$), and v is the linear velocity, calculated by dividing the flow rate by the column section area (cm min^{-1}).

Since the exponential term in this equation is much larger than unity, the expression can be rearranged and reordered, so the following can be obtained [28]:

$$t = \frac{N_0 \times Z}{C_0 \times v} - \frac{1}{K_a \times C_0} \ln \left(\frac{C_0}{C_t} - 1 \right) \quad (7)$$

The sorption capacity (N_0), which represents the time required for the adsorption zone to travel a unit length through the biosorbent, can be determined from the slope of the plot of the service-time versus the bed height. The rate constant (K_a) can be obtained from the intercept of the plot, which represents the rate of solute transfer from the liquid phase to the solid phase. Once the constants of the model have been determined from the experimental data, the model can be used to estimate the service-time for a given bed height and specific solute concentrations at the bed inlet and outlet.

Successful design of a column sorption process required prediction of the concentration-time profile or breakthrough curve for the effluent. Various mathematical models can be used to describe packed bed adsorption. Among these, the Thomas model is simple and widely used by several investigators [8,21,26,29]. The Thomas model was derived from equation of mass conservation in a flow system [20]. In addition, the model also assumes that rate driving force obeys second order reversible reaction kinetics, and the adsorption equilibrium follows the Langmuir model with no axial

dispersion [30]. The expression by Thomas for an adsorption column is given as follows:

$$\frac{C_t}{C_0} = \frac{1}{1 + \exp\left(\frac{(M \times q_0 \times k_{\text{Th}})/Q - (C_0 \times k_{\text{Th}} \times t)/1000}{1}\right)} \quad (8)$$

where k_{Th} is the Thomas rate constant ($l \text{ min}^{-1} \text{ g}^{-1}$) and q_0 is the maximum uptake capacity (mg g^{-1}). The model parameters k_{Th} and q_0 can be estimated by non-linear fitting of Eq. (8) to the experimental data of breakthrough curves.

Yan model is based on statistical analysis of experimental data and some simplifications [22]. This model can be represented by:

$$\frac{C_t}{C_0} = 1 - \frac{1}{1 + \left(\frac{((C_0 \times Q)/(q_0 \times M)) \times t}{1} \right)^a} \quad (9)$$

where a is an empirical parameter that decides the slope of the regression function. Yan model has a relative importance because it normally describes the complete breakthrough curves with great accuracy. However, it is difficult to relate the empirical parameter "a" with the experimental conditions, so the scale up of the system is impossible [5]. The model parameters a and q_0 can be estimated by non-linear fitting of Eq. (9) to the experimental data of breakthrough curves.

Belter model which is a simple empirical two parameter model for the modeling of breakthrough curves, takes the form [15]:

$$\frac{C_t}{C_0} = \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{t - t_{0.5}}{\sqrt{2} \times \sigma \times t_{0.5}} \right) \right] \quad (10)$$

where $\operatorname{erf}(x)$ is the error function of x , $t_{0.5}$ the time at which the effluent concentration is half the inlet concentration and σ represents the standard deviation, which is a measure of the slope of the breakthrough curve. The model parameters $t_{0.5}$ and σ can be estimated by non-linear fitting of Eq. (10) to the experimental data of breakthrough curves.

4. Results and discussion

4.1. Chemical and physical characterization of the biosorbent

C. indica alga is a type of brown algae. The cell walls of brown algae, where sorption takes place, generally contain three components: cellulose, the structural support; alginic acid, a polymer of mannuronic and guluronic acids and the corresponding salts of sodium, potassium, magnesium and calcium; and sulphated polysaccharides. As a consequence, carboxyl and sulphate are the predominant active groups in this kind of algae [31].

The spectra of *C. indica* alga were measured by a FTIR spectrometer within the range of 400–4000 cm^{-1} wave number (Fig. 1). In the spectra of this biomass, the peaks which correspond to O–H, C=O and C–O groups as well as C–H and C=C bonds are observed.

The biomass has a high degree of settle ability. The very fast settling observed with the *C. indica* biomass is advantageous for water treatment system operation. The implication is that the material would be suitable for the continuous flow system.

Some chemical and physical characteristics of raw *C. indica* biomass and Ca-pretreated *C. indica* biomass are presented in Table 1. The pretreatment process led to change of density from 1.092 to 1.112 g cm^{-3} . Also, specific area decreased from 2.065 to 1.449 $\text{m}^2 \text{ g}^{-1}$ and porosity increased from 0.504 to 0.585%. These observations indicated that the chemical pretreatment changes the cell wall structure of biomass. These chemical and physical characteristics of this biomass show that it is reasonably good biosorbent.

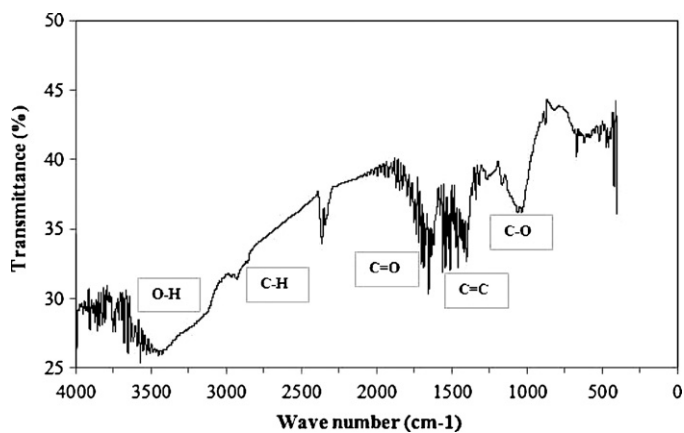


Fig. 1. FTIR analysis of *C. indica* biomass.

Table 1

Chemical and physical properties of raw *C. indica* biomass and Ca-pretreated *C. indica* biomass.

Property	Raw <i>C. indica</i> biomass	Ca-pretreated <i>C. indica</i> biomass
Element analysis	C = 36.98% H = 4.93% N = 2.38%	C = 36.22% H = 5.04% N = 2.26%
Moisture (%)	0.77	0.89
Density (g cm^{-3})	1.092	1.112
Pore volume ($\text{cm}^3 \text{g}^{-1}$)	4.614E-3	5.259E-3
Pore size (nm)	4.635	2.871
Porosity (%)	0.504	0.585
Specific area ($\text{m}^2 \text{g}^{-1}$)	2.065	1.449

4.2. Effect of bed height

The sorption performance of Ca-pretreated *C. indica* biomass was tested at various bed heights at 2.3 ml min^{-1} flow rate and 60 mg l^{-1} initial uranium(VI) concentration. In order to yield different bed heights, 1, 1.25 and 1.75 g of the Ca-pretreated biomass were added to produce bed heights of 3.5, 4.5 and 6 cm, respectively. Fig. 2 shows the breakthrough profiles of uranium(VI) biosorption at different bed heights. The influence of the bed height was prominent in terms of breakthrough time (t_b) and exhaustion time (t_e), as they both increased with increasing the bed height (Table 2). This may be due to an increase in the surface area of the alga as the quantity of biomass packed in the column grows, and

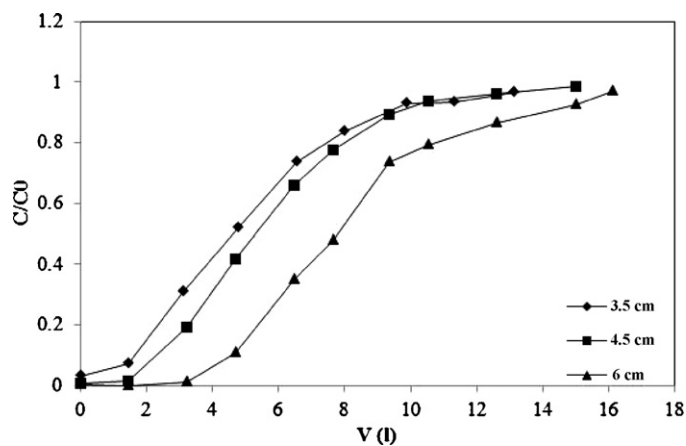


Fig. 2. Breakthrough curves for biosorption of uranium(VI) by Ca-pretreated *C. indica* at different bed heights (flow rate = 2.3 ml min^{-1} ; initial uranium(VI) concentration = 60 mg l^{-1} ; pH 4).

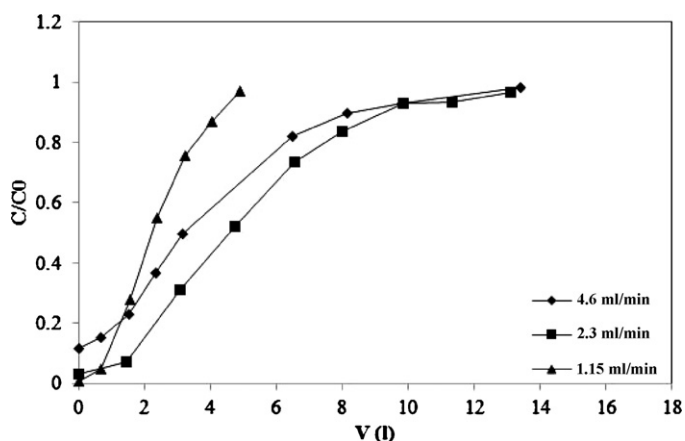


Fig. 3. Breakthrough curves for biosorption of uranium(VI) by Ca-pretreated *C. indica* at different flow rates (bed height = 3.5 cm; initial uranium(VI) concentration = 60 mg l^{-1} ; pH 4).

also, due to the greater number of available sorption sites. In addition, the slope of the S-curve from t_b to t_e decreased when the bed height increased from 3.5 to 6 cm, which implies that the breakthrough curve becomes steeper and the mass transfer zone (Z_m) becomes shorter as the bed height is decreased. This distinctively gradual character of the curves as the bed height increases implies that complete exhaustion of the bed becomes more difficult, as has been shown in the literature [8,24]. For a taller bed, a larger volume of the metal solution could be treated, and a higher percentage metal removal was obtained. However, the metal uptake per unit mass of *C. indica* remained relatively constant for different bed heights. This indicates that the metal uptake amount was directly proportional to the amount of adsorbent available in the bed.

4.3. The effect of flow rate

The effect of flow rate on uranium(VI) biosorption by Ca-pretreated *C. indica* was studied by varying the flow rate from 1.15 to 4.6 ml min^{-1} , while the bed height and initial uranium(VI) concentration were held constant at 3.5 cm and 60 mg l^{-1} , respectively. Fig. 3 shows the breakthrough profile of uranium(VI) biosorption at different flow rates, and the results of the breakthrough curve analysis are given in Table 3. As expected, the breakthrough curves became steeper and the breakthrough time decreased with the increasing flow rate. This behavior may be due to insufficient

Table 2
Column data and parameters obtained at different bed heights.

Bed height (cm)	t_b (min)	t_e (min)	Z_m (cm)	V_e (l)	Uptake capacity (mg g^{-1})	Total metal removal (%)
3.50	283	5313	3.31	12.22	315.43	42.97
4.50	787	5478	3.85	12.60	310.23	51.32
6.00	1661	6804	4.54	15.65	318.15	59.32

Conditions: flow rate = 2.3 ml min^{-1} ; initial uranium(VI) concentration = 60 mg l^{-1} ; pH 4.

residence time of the solute in the column, which causes the uranium(VI) solution to leave the column before equilibrium occurs. On the other hand, the result showed that in the range of low flow rates (high residence times), the overall rate of uranium(VI) ions removal in the packed column was controlled by external mass transfer limitations. In low flow rates (from 1.15 to 2.3 ml min^{-1}), the metal uptake was strongly influenced by increasing the flow rate, so that, its value increased from 168.43 to 315.43 mg g^{-1} . In addition, the results showed that in the range of higher flow rates (lower residence times), the overall rate of metal sorption by *C. indica* biomass was controlled by diffusion limitations of the solute into the pores of sorbent. When the flow rate increased from 2.3 to 4.6 ml min^{-1} , the liquid residence time in the column decreased, resulting in a lesser biosorption of metal ions, and hence, the metal uptake decreased from 315.43 to 308.07 mg g^{-1} . Similar observation was reported by Vijayaraghavan et al. in their study using marine green alga *Ulva reticulata* for biosorption of copper, cobalt and nickel ions in a packed column [21].

The sensitivity of the biosorption to the liquid flow rate can be explained by the fact that the liquid residence time in the column is critical for the biosorption process. When the process is subjected to external mass transfer control, a higher flow rate decreases the liquid film resistance and when the process is subjected to intraparticle mass transfer control, a slower flow rate favors the sorption.

Our previous study showed that the maximum uptake capacity of uranium(VI) by Ca-pretreated *C. indica* biomass in a batch system is 454.5 mg g^{-1} [14]. From comparison of uptake capacity from batch and continuous experiments, we can see less-stirred property in column mode reduced the uranium(VI) biosorption capacity by Ca-pretreated *C. indica* biomass. In the stirred tank (batch system), the particles move freely since a more complete mixture of the biosorbent particles in the uranium(VI) solution exists, which would provide a better interaction between the active sites of the biosorbent and the uranium(VI) ions and, therefore, causing a higher mass transfer rate and a higher uptake capacity of uranium(VI) ions.

4.4. Biosorbent regeneration

The regeneration and reuse of biosorbent offers an economical method for removal of heavy metals from wastewater streams. The attractiveness of biosorption process is enhanced when a possibility of the recovery of the biosorbed metal exists. The optimal eluent must be effective, non-damaging to the biosorbent, non-polluting, and cheap [7]. The possibility of regeneration of loaded biosorbent is important to keeping the process costs down and

to opening the possibility of recovering the metal(s) extracted from the liquid phase. The potential recovery of the metal from concentrated desorption solutions is another question. It would usually be carried out as an independent metal recovery operation, in a different plant, by an entirely different process or a sequence of operations. It is most often feasible to use electrowinning procedures to recover metals from concentrated solutions [32].

In this study, the saturated biosorbent was regenerated using 0.1 M HCl and the efficiency of biosorbent regeneration, by the desorption agent, was investigated in three sorption–desorption cycles.

The column was packed with 1 g of *C. indica* yielding an initial bed height of 3.5 cm and bed volume of 6.2 ml with packing density of 161.29 g l^{-1} . During the column sorption operation, an aqueous solution containing 60 mg l^{-1} uranium(VI) at pH 4 was pumped upward through the column at a constant flow rate, 2.3 ml min^{-1} , continuously. The samples, collected from the outlet of the column, were analyzed for the uranium(VI) concentration. After the biosorbent in the column became saturated, the column was washed at the same flow rate by deionized water for 30 min , before a subsequent uranium elution with 0.1 M HCl solution. The outlet samples collection and analysis were done the same way as for those used in the sorption uptake run. The biosorption column breakthrough curve and the elution curve for the column acid wash and recovery of uranium during three cycles are shown in Fig. 4. The breakthrough time, exhaustion time and uranium(VI) uptake for all three cycles are summarized in Table 4. The breakthrough time and the uranium(VI) uptake steadily decreased from 283 to 180 min and 315.43 to 248.61 mg g^{-1} as the cycle progressed from 1 to 3, respectively. This behavior is primarily due to gradual deterioration of the biomass because of continuous usage.

The elution curves observed in all the cycles exhibited a similar trend; a gradual decrease of uranium concentration versus effluent volume. As shown in Table 4, high elution efficiencies were obtained for all the three cycles and the elution process resulted in highly concentrated metal solutions, with uranium concentration higher than 5000 mg l^{-1} (Fig. 4). In cycle 3, the elution efficiency was around 104.67% , which may be due to inadequate elution in the previous cycle. The total volume of uranium(VI) bearing solutions treated during this regeneration study was around 29.21 l (in three cycles) and the total volume of 0.1 M HCl utilized for elution process was nearly 0.55 l . Even after three sorption–desorption cycles, *C. indica* exhibited a relatively high percentage of uranium(VI) removal (51.98%) and uranium(VI) uptake of 248.61 mg g^{-1} , indicating the potential of the biomass for the regeneration. A shortened breakthrough time and a decreased

Table 3
Column data and parameters obtained at different flow rates.

Flow rate (ml min^{-1})	t_b (min)	t_e (min)	Z_m (cm)	V_e (l)	Uptake capacity (mg g^{-1})	Total metal removal (%)
4.60	–	4887	–	11.24	308.07	45.70
2.30	283	5313	3.31	12.22	315.43	42.97
1.15	600	2057	2.48	4.73	168.43	59.15

Conditions: bed height = 3.5 cm ; initial uranium(VI) concentration = 60 mg l^{-1} ; pH 4.

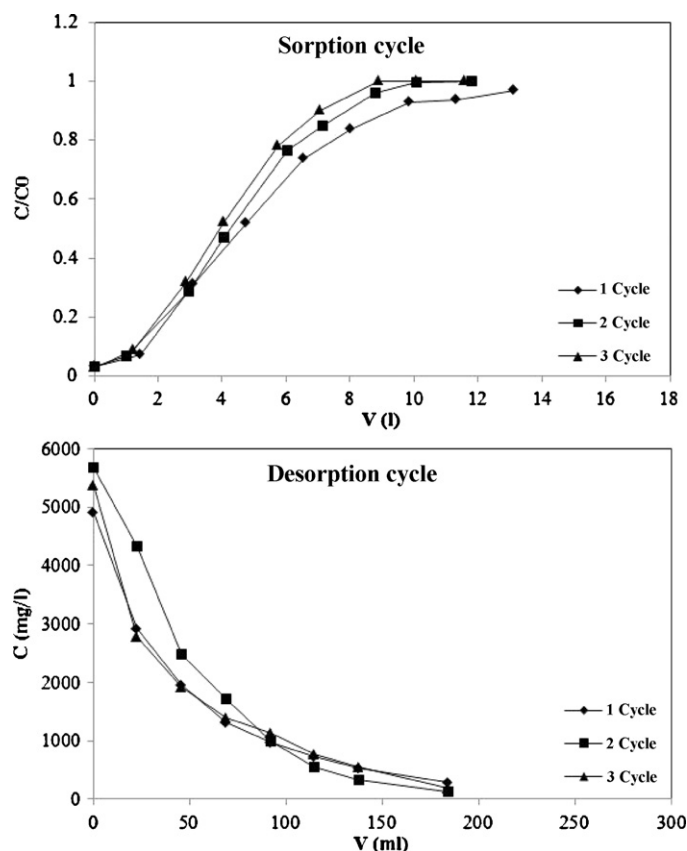


Fig. 4. Sorption and desorption breakthrough curves for uranium(VI) during regeneration cycles (flow rate = 2.3 ml min⁻¹; bed height = 3.5 cm; initial uranium(VI) concentration = 60 mg l⁻¹; pH 4).

metal uptake were observed as the cycles progressed, indicating a loss of sorption performance. However, *C. indica* maintained a good metal sorption capacity in all the cycles examined. This observation clearly pointed out that the loss of sorption performance was not mainly due to biomass damage but rather because of sorbing sites, whose accessibility becomes more difficult as the cycles progress [25].

4.5. Mechanism of uranium(VI) biosorption

The knowledge of biosorption mechanism is necessary for understanding of the biosorption process. A number of different metal-binding mechanisms, such as ion exchange, complexation, coordination, chelation, physical adsorption and microprecipitation, has been suggested to be active in biosorption. Also, some of these mechanisms are acting simultaneously to varying degrees depending on the biosorbent and the solution environment. More recent studies with different type of brown algae in particular have indicated a main role of ion exchange metal binding [4,6,7,33]. For example, Naddafi et al. investigated the biosorption of lead(II) and cadmium(II) by protonated *Sargassum glaucescens* biomass and observed that H⁺ simultane-

ously released with the uptake of heavy metals by this biomass [6].

The mechanism of uranium(VI) biosorption by Ca-pretreated *C. indica* biomass was investigated by monitoring of Ca²⁺ ions in the effluent of column (results are not reported). The results showed that the Ca²⁺ ions in the effluent were increasing when the biosorption of uranium(VI) was being performed. These observations confirm that ion exchange is one of the main biosorption mechanisms.

4.6. Model of column data

The BDST model is based on physically measuring the capacity of the bed in different sets of breakthrough values. The column service time was chosen to be the time during which the effluent uranium(VI) concentration reached 3 mg l⁻¹ ($C_t/C_0 = 0.05$). The plot of service time against bed height at a flow rate of 2.3 ml min⁻¹ (graph is not presented) was linear ($R^2 = 0.99$), indicating the validity of BDST model for the present system. The sorption capacity of the bed per unit bed volume (N_0) and the rate constant (K_a) were calculated from the slope and intercept of BDST plot, respectively, assuming initial concentration (C_0) and linear

Table 4
Sorption process parameters for three sorption–desorption cycles.

Cycle no.	t_b (min)	t_e (min)	Uptake capacity (mg g ⁻¹)	Total metal removal (%)	Elution efficiency (%)
1	283	5313	315.43	42.97	83.81
2	220	3918	270.34	49.91	97.51
3	180	3468	248.61	51.98	104.67

Conditions: bed height = 3.5 cm; flow rate = 2.3 ml min⁻¹; initial uranium(VI) concentration = 60 mg l⁻¹; pH 4.

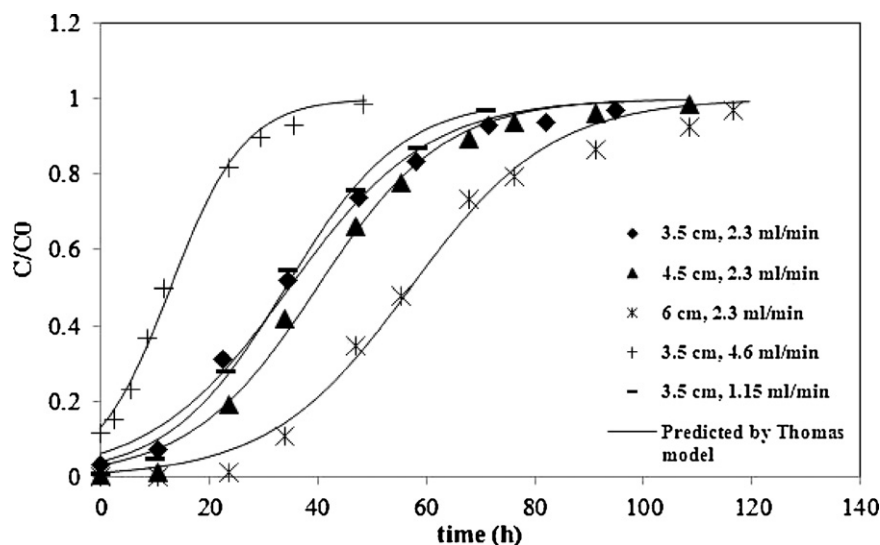


Fig. 5. Comparison of the experimental and predicted breakthrough curves for uranium(VI) biosorption by Ca-pretreated *C. indica* at different bed heights and flow rates according to the Thomas model (initial uranium(VI) concentration = 60 mg l^{-1} ; pH 4).

velocity (v) as constant during the column operation [24]. The computed N_0 and K_a were $43,286 \text{ mg l}^{-1}$ and $2.93 \times 10^{-5} \text{ l mg}^{-1} \text{ min}^{-1}$ ($0.0018 \text{ l mg}^{-1} \text{ h}^{-1}$), respectively. If K_a is large, even a short bed will avoid breakthrough, but as K_a decreases, a progressively longer bed will be required to avoid breakthrough [24]. The BDST model parameters can be useful to scale up the process for other flow rates without further experimental data and analyses.

The column data were fitted to the Thomas model to determine the model constant (k_{Th}) and maximum uptake capacity (q_0) at different flow rates and bed heights. Table 5 illustrates the model constants k_{Th} and q_0 along with correlation coefficients. The predicted values of uranium(VI) concentration in the column effluent for various conditions are plotted in Fig. 5. The metal concentration predicted from the model agrees quite well with the experimental data. The sensitivity of the Thomas model constants with the changes of the liquid flow rates and the existence of a minimum in the k_{Th} values and of a maximum in the q_0 values as the flow rate increases show that the controlled-rate step shifts from external to internal mass transfer limitations. However, the rate constants k_{Th} and the maximum uptake capacity q_0 appear to increase with the bed height at liquid flow rate of 2.3 ml min^{-1} . Only at the liquid flow rate of 4.6 ml min^{-1} , the model underestimates the metal uptake by about 2.5%. Evidently, by comparing the experimental uptake values, that the model overestimated the metal uptake capacity of *C. indica* in the other conditions tested in this study. Similarly, Vijayaraghavan et al. reported that Thomas model overestimated q_0 values of copper, cobalt and nickel biosorption by *U. reticulata* green alga [21].

Yan model allowed us to describe with great precision the tendency of experimental curves in the whole range of effluent concentration (Fig. 6). The parameters obtained by non-linear fit

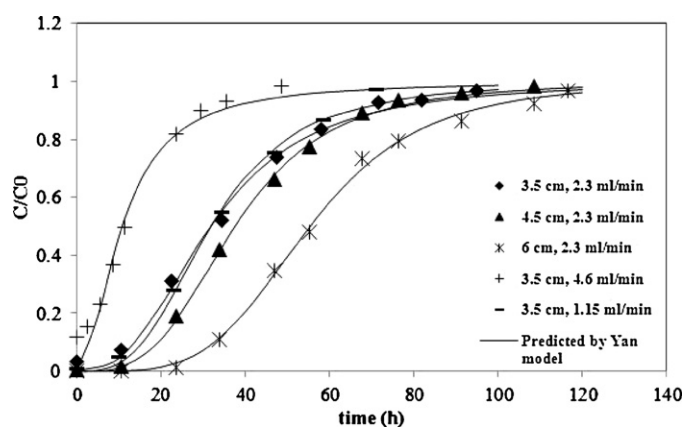


Fig. 6. Comparison of the experimental and predicted breakthrough curves for uranium(VI) biosorption by Ca-pretreated *C. indica* at different bed heights and flow rates according to the Yan model (initial uranium(VI) concentration = 60 mg l^{-1} ; pH 4).

of the data, q_0 , and a along with correlation coefficients are listed in Table 5. The inconvenience of this model is that the q_0 values and the measurement of curve slope (a) show no apparent dependence on the flow rate and bed depth variables. Then, it is impossible to correlate these parameters with any variable employed in the process and therefore, only a very good description of the breakthrough curve is attained [5].

The Belter model parameters $t_{0.5}$ and σ for the biosorption of uranium(VI) on Ca-pretreated *C. indica* are found by fitting Eq. (10) to the experimental data. Breakthrough curves calculated using these fit values for $t_{0.5}$ and σ are shown in Fig. 7, in comparison with

Table 5

Parameters obtained from the non-linear fit of breakthrough data to the Thomas, Yan and Belter models.

Q (ml min^{-1})	Z (cm)	Thomas model			Yan model			Belter model		
		k_{Th} ($\text{l g}^{-1} \text{ min}^{-1}$)	q_0 (mg g^{-1})	R^2	a	q_0 (mg g^{-1})	R^2	σ	$t_{0.5}$ (min)	R^2
4.60	3.50	0.0316	273.09	0.99	1.907	229.32	0.97	0.8864	780	0.99
2.30	3.50	0.0209	297.79	0.99	2.652	272.36	0.99	0.6186	2092	0.99
1.15	3.50	0.0222	164.06	0.99	3.098	153.74	0.99	0.5337	2045	0.99
2.30	4.50	0.0212	295.53	0.99	3.337	278.42	0.99	0.4938	2393	0.99
2.30	6.00	0.0191	302.42	0.98	4.175	293.42	0.99	0.3824	3430	0.98

Conditions: initial uranium concentration(VI) = 60 mg l^{-1} ; pH 4.

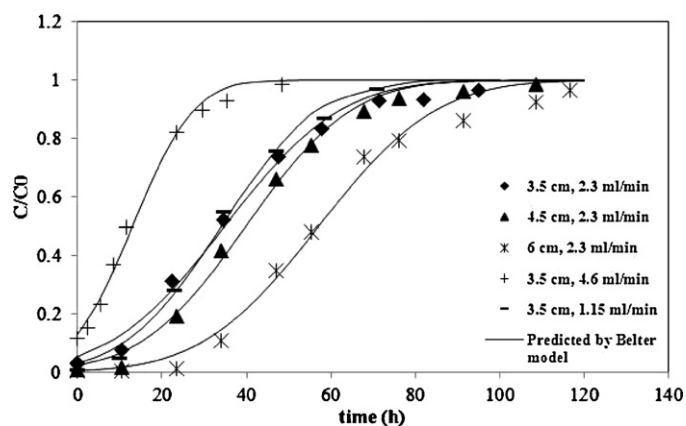


Fig. 7. Comparison of the experimental and predicted breakthrough curves for uranium(VI) biosorption by Ca-pretreated *C. indica* at different bed heights and flow rates according to the Belter model (initial uranium(VI) concentration = 60 mg l^{-1} ; pH 4).

the experimental data. Table 5 listed the Belter model parameters $t_{0.5}$ and σ along with correlation coefficients. The model showed a good fit to most of the obtained column data. It must be pointed out that, particularly at the highest bed depth, this model overestimates the metal effluent concentration. Similar to the Yan model, the model parameters of the Belter show no apparent dependence on the flow rate and bed depth variables. It must be taken into account that these empirical model parameters lack any physical significance and are only valid under the same conditions employed to obtain the breakthrough curves, because they can change with variables such as flow rate, bed depth, column dimensions, or algae packed. Nevertheless, this shortcoming is also present when simplified mechanistic models are used. To summarize, it can be said that the Yan and the Belter models are able to describe the complete breakthrough curve, suggesting that the features of the dynamics of sorption column have been taken into account by the mathematical form of the model equation.

5. Conclusions

Uranium(VI) biosorption by Ca-pretreated *C. indica* biomass was studied, using a continuous packed bed column. Breakthrough curves were obtained at different bed heights and liquid flow rates. The metal uptake capacity was found to remain constant with the rise in bed height, while the breakthrough and the exhaustion times increased. Moreover, the decrease in the column bed height resulted in a steeper breakthrough curve, a shorter mass transfer zone, and a lower percentage metal removal. It was found that the adsorption breakthrough was strongly dependent on the liquid flow rate, as expected. In addition, it was observed that the controlled-rate step shifted from external to internal mass transfer limitations, as the flow rate increased.

A successful biosorption process operation requires the multiple reuses of the sorbent, which greatly reduces the process cost as well as decreasing the dependency of the process on continuous supply of the sorbent. The results on column regeneration for three cycles indicate that the usability of *C. indica* biomass for uranium(VI) removal and recovery is viable.

The bed depth service time model well correlated the relationship between service time and bed height for uranium(VI) biosorption in a packed bed of *C. indica*, which is essential in column process design. The application of other mathematical models such as the Thomas, Yan and Belter models to a packed bed adsorbent was also investigated. The constants of these models were obtained with high regression coefficients greater than 0.97.

Thus, high biosorption efficiency of the algae, low biomass cost, less dependency on the biomass (due to reuse), and high efficient elutant make this process an effective, cheap, and alternative technique for treatment of uranium(VI) bearing solutions.

References

- [1] C. Gok, S. Aytas, Biosorption of uranium(VI) from aqueous solution using calcium alginate beads, *J. Hazard. Mater.* 168 (2009) 369–375.
- [2] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, *Bioresour. Technol.* 98 (2007) 2243–2257.
- [3] R. Apiratikul, P. Pavasant, Batch and column studies of biosorption of heavy metals by *Caulerpa lentillifera*, *Bioresour. Technol.* 99 (2008) 2766–2777.
- [4] C.E. Borba, R. Guirardello, E.A. Silva, M.T. Veit, C.R.G. Tavares, Removal of nickel(II) ions from aqueous solution by biosorption in a fixed bed column: experimental and theoretical breakthrough curves, *Biochem. Eng. J.* 30 (2006) 184–191.
- [5] P. Lodeiro, R. Herrero, M.E. de Vicente, The use of protonated *Sargassum muticum* as biosorbent for cadmium removal in a fixed-bed column, *J. Hazard. Mater.* 137 (2006) 244–253.
- [6] K. Naddafi, R. Nabizadeh, R. Saeeadi, 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 (2007) 785–791.
- [7] K. Vijayaraghavan, K. Palanivelu, M. Velan, Treatment of nickel containing electroplating effluents with *Sargassum wightii* biomass, *Process Biochem.* 41 (2006) 853–859.
- [8] 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.
- [9] G. Bayramoglu, G. Celik, M.Y. Arica, Studies on accumulation of uranium by fungus *Lentinus sajor-caju*, *J. Hazard. Mater.* 136 (2006) 345–353.
- [10] M. Kalin, W.N. Wheeler, G. Meinrath, The removal of uranium from mining waste water using algal/microbial biomass, *J. Environ. Radioact.* 78 (2005) 151–177.
- [11] M.H. Khani, A.R. Keshtkar, M. Ghannadi, H. Pahlavanzadeh, Equilibrium, kinetic and thermodynamic study of the biosorption of uranium onto *Cystoseira indica* algae, *J. Hazard. Mater.* 150 (2008) 612–618.
- [12] P.F. Li, Z.Y. Mao, X.J. Rao, X.M. Wang, M.Z. Min, L.W. Qiu, Z.L. Liu, Biosorption of uranium by lake-harvested biomass from a cyanobacterium bloom, *Bioresour. Technol.* 94 (2004) 193–195.
- [13] H. Parab, S. Joshi, N. Shenoy, R. Verma, A. Lali, M. Sudersanan, Uranium removal from aqueous solution by coir pith: equilibrium and kinetic studies, *Bioresour. Technol.* 96 (2005) 1241–1248.
- [14] M.H. Khani, A.R. Keshtkar, B. Meysami, M.F. Zarea, R. Jalali, Biosorption of uranium from aqueous solutions by nonliving biomass of marine algae *Cystoseira indica*, *Elect. J. Biotechnol.* 9 (2006) 100–106.
- [15] K.H. Chu, Improved fixed bed models for metal biosorption, *Chem. Eng. J.* 97 (2004) 233–239.
- [16] B. Volesky, Sorption and Biosorption, BV Sorbex, St. Lambert, Que., Inc., Canada, 2003.
- [17] R. Han, Y. Wang, W. Zou, J. Shi, Comparison of linear and nonlinear analysis in estimating the Thomas model parameters for methylene blue adsorption onto natural zeolite in fixed-bed column, *J. Hazard. Mater.* 145 (2007) 331–335.
- [18] L. Lin, J. Li, R. Juang, Removal of Cu(II) and Ni(II) from aqueous solutions using batch and fixed-bed ion exchange processes, *Desalination* 225 (2008) 249–259.
- [19] L.C. Stanley, K.L. Ogden, Biosorption of copper (II) from chemical mechanical planarization wastewaters, *J. Environ. Manage.* 69 (2003) 289–297.
- [20] H.C. Thomas, Chromatography; a problem in kinetics, *Ann. N.Y. Acad. Sci.* 49 (1948) 161–182.
- [21] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Biosorption of copper, cobalt and nickel by marine green alga *Ulva reticulata* in a packed column, *Chemosphere* 60 (2005) 419–426.
- [22] G. Yan, T. Viraraghavan, M. Chen, A new model for heavy metal removal in a biosorption column, *Adsorption Sci. Technol.* 19 (2001) 25–43.
- [23] 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.
- [24] K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Removal of nickel(II) ions from aqueous solution using crab shell particles in a packed bed up-flow column, *J. Hazard. Mater.* 113 (2004) 223–230.
- [25] B. Volesky, J. Weber, J.M. Park, Continuous-flow metal biosorption in a regenerable *Sargassum* column, *Water Res.* 37 (2003) 297–306.
- [26] Z. Aksu, F. Gönen, Biosorption of phenol by immobilized activated sludge in a continuous packed bed: prediction of breakthrough curves, *Process Biochem.* 39 (2003) 599–613.
- [27] Z. Zulfadhly, M.D. Mashitah, S. Bhatia, Heavy metals removal in fixed-bed column by the macro fungus *Pycnoporus sanguineus*, *Environ. Pollut.* 112 (2001) 463–470.

- [28] R.A. Hutchings, New method simplifies design of activated carbon system, *Chem. Eng.* 80 (1973) 133–138.
- [29] G. Yan, T. Viraraghavan, Heavy metal removal in a biosorption column by immobilized *M. rouxii* biomass, *Bioresour. Technol.* 78 (2001) 243–249.
- [30] S.S. Baral, N. Das, T.S. Ramulu, S.K. Sahoo, S.N. Das, G.R. Chaudhury, Removal of Cr(VI) by thermally activated weed *Salvinia cucullata* in a fixed-bed column, *J. Hazard. Mater.* 161 (2009) 1427–1435.
- [31] E. Romera, F. Gonzalez, A. Ballester, M.L. Blazquez, J.A. Munoz, Comparative study of biosorption of heavy metals using different types of algae, *Bioresour. Technol.* 98 (2007) 3344–3353.
- [32] B. Volesky, Detoxification of metal-bearing effluents: biosorption for the next century, *Hydrometallurgy* 59 (2001) 203–216.
- [33] V.J. Vilar, C.M. Botelho, J.M. Loureiro, R.A. Boaventura, Biosorption of copper by marine algae *Gelidium* and algal composite material in a packed bed column, *Bioresour. Technol.* 99 (2008) 5830–5838.