Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2016.1141324

57 (2016) 24509–24518
November

Taylor & Francis
Taylor & Francis Group

Removal of zinc (II) from synthetic effluent using seaweeds: a review of modeling of fixed-bed columns

Reza Dabbagh[a], Sepideh Sharifipoor[b,*], Alireza Keshtkar[a], Leila Vafajoo[b]

[a]*Nuclear Sciences & Technology Research Institute, Nuclear Fuel Cycle School (NFCS), P.O. Box 11365-8486, Tehran, Iran, Tel. +98 21 88221117; Fax: +98 21 88221116; emails: rdabbagh@aeoi.org.ir (R. Dabbagh), akeshtkar@aeoi.org.ir (A. Keshtkar)*
[b]*Chemical and Environmental Engineering Department, Islamic Azad University, South Tehran Branch, Deh-haqi St. Ahang Blvd, P.O. Box 14569-83974, Iran, Tel. +98 21 88008616; Fax: +98 21 82062539; emails: sepidesharifipoor@yahoo.com (S. Sharifipoor), vafajoo@azad.ac.ir (L. Vafajoo)*

Received 16 June 2015; Accepted 7 January 2016

ABSTRACT

The biosorption of Zn(II) from aqueous solution by algal biomass was carried out in batch and column study. In batch experiments, the effect of the modification on four types of brown algae, *Cystoseira indica*, *Sargassum glaucescens*, *Nizimuddinia zanardini*, and *Padina australis* by Formaldehyde (FA), $CaCl_2$, and HCl was investigated. The results showed that FA-treated *S. glaucescens* has the maximum metal uptake capacity (29.13 mg/g). The ability of *S. glaucescens* to remove Zn(II) was studied in a packed-bed column with 1.6 cm internal diameter. The column experiments were conducted to evaluate the effect of important design parameters such as bed height and flow rate, and the breakthrough curves were obtained. As the bed height increased, the breakthrough and exhaustion time increased, whereas the breakthrough curves slope decreased. The maximum dynamic capacity, 71.17 mg/g, was found in the column with 18 cm height and 4 mL/min flow rate. Several empirical models such as bed depth service time, Thomas, Yoon–Nelson, and modified dose-response were used to obtain the best fit of column data. From the breakthrough curves, the fitness of data to the mentioned models revealed. ANOVA and one-sample *t*-test were performed on experimental data to determine the best desorbent for three sorption–desorption cycles and NaCl performed well in desorption of Zn(II).

Keywords: Biosorption; Zinc; Seaweed; Packed-bed column; Modeling

1. Introduction

The presence of toxic metals such as Cu, Cd, Mg, Mn, and Zn in industrial effluents is an important source of environmental pollution around the world. These heavy metals discharged from various industries such as mining, leather, electroplating, and textile, have inverse effects on human and environment [1,2].

Therefore, the uptake of heavy metal ions from wastewater and investigation of the separation methods has attracted a great attention in recent years [3]. Among all separation methods such as reduction and precipitation, coagulation and flotation, adsorption, ion exchange, membrane technologies, reverse osmosis and filtration, adsorption could be a good technique because of its cost saving. Biosorption, as an alternative method, is more economical and provides

*Corresponding author.

a greater metal sorption capacity, even at very low metal concentration [4,5].

Biomass selectivity is an important activity during the biosorption process. Typical biosorbents could be achieved from three sources as follows: (1) microbial biomass, e.g. bacteria, fungi, and yeast; (2) chitinous materials, e.g. krill, squid, and crab shell; (3) algal biomass, e.g. red, green, and brown algae [6]. Algal biomass as a sorbent has many advantages such as cost saving, the possible contaminant recovery from the biomaterial, low sensitivity to environmental and impurity factors [6,7]. In a category of brown algae, *Sargassum* genus, due to specific construction in its cell wall (carboxylic and sulfate groups in alginic acid and fucoidan) has great ability in heavy metal adsorbing [1,8].

Most of the latest works on algal biosorption have been performed in batch systems [9,10]. Since most treatment systems were changed by time, the recent attempts have been done on the performance of continuous sorption systems (e.g. in packed-bed columns) [1,3,11]. Due to its inherent effectiveness in an adsorption process, the packed-bed column is generally preferred. Packed-bed column has some advantages such as simple operating, high possible packing density of the adsorbent, yielding a high volumetric productivity, and it can be easily scaled up from a laboratory-scale procedure. The stages in the separation protocol can also be automated, and high degrees of purification can often be achieved in a single-step process [12,13].

The aim of this study is the removal of Zn(II) ions by screened alga, *Sargassum glaucescens,* from aqueous solution using a fixed-bed adsorption column. The effects of flow rate and the bed height in the adsorption process were investigated. In this work, mathematical models such as Thomas, bed depth service time (BDST), Yoon–Nelson, and modified dose-response were used to analyze the breakthrough curves.

2. Materials and methods

2.1. Biomass preparation

In this study, samples of brown marine algae as biosorbent, *Cystoseira indica*, *Sargassum glaucescens*, *Nizimuddinia zanardini*, and *Padina australis*, collected from Oman Sea on the coast of Chabahar, Iran. They were washed with tap water followed by sun-drying for 48 h. Then, the samples in the laboratory washed with deionized water and subsequently dried in an oven at 80˚C for 24 h. The dried biomass crushed and sieved (RETSCH AS-200, Germany) to a particle size of 0.5–1.0 mm. Finally, the biomass were pre-treated with calcium chloride ($CaCl_2$) [14], hydrochloric acid (HCl) [13], FA (Formaldehyde) [15], to increase the sorption capacity and to activate the adsorbent binding sites [5].

2.2. Zinc solution preparation

The stock solution of Zn^{2+} was prepared by dissolving $ZnCl_2$ (Merck, Germany) in distilled water. Batch studies done by other authors indicated that the pH value of Zn^{2+} biosorption using similar seaweeds ranged 4–6, dominantly was about 5 [9,10], so the Zn^{2+} solution pH was maintained on 5 by adding 0.1–1 M NaOH or HCl solution. The pH of column effluent was checked regularly to adjust influent pH.

2.3. Batch biosorption experiments

Batch experiments were performed by adding 0.06 g (2 g/L) of algal biomass into a series of Erlenmeyer flasks containing 30 mL of Zn^{2+} solution having an initial metal concentration of 60.62 mg/L. The flasks were agitated at 150 rpm in a rotary shaker at 25˚C for 1.5 h. The algal biomass was separated from the metal solution by filter paper. The ICP-OES (inductively coupled plasma-optical emission spectrometer, PerkinElmer-optima 2100, USA) was utilized for determining the metal concentration in the solution.

The amount of metal adsorbed by the modified alga was calculated using the following equation [16]:

$$q = \frac{V(C_0 - C_e)}{m} \tag{1}$$

where q is the metal uptake, C_0 and C_e (mg/l) are the initial and equilibrium metal concentrations in the solution, respectively. V (L) is the solution volume, and m (g) is the mass of biosorbent.

The biomass sample's regeneration that performed after their exhaustion is very important due to the economic concepts. The metal-loaded biomass was contacted with three elutants, 0.1 M HCl, 0.1 M EDTA, and 0.1 M NaCl, in 100-ml Erlenmeyer flasks for 6 h on a rotary shaker (150 rpm) to study the elution of biosorbed metal ions. To evaluate the biomass sorption capacity, three cycles of the adsorption–desorption process were performed.

2.4. Column experiments

Continuous-flow sorption experiments were carried out in a glass column of 22 cm length and 1.6 cm internal diameter. Two adjustable polyethylene plungers covered with stainless filter sieves with 0.5 mm pore size at both top and bottom of the column in order to provide a uniform inlet solution flow, a good liquid distribution within the column and to avoid any loss of adsorbent material.

The Zn^{2+} metal solution with 32 mg/L initial solution was pumped upward through the columns of 6, 12, and 18 cm heights, at the distinct flow rate (2, 4, and 8 ml/min) by a peristaltic pump (Watson Marlow). Collected samples from column effluent at different times were analyzed to determine adsorbed metal concentration. The column sorption operation was stopped when the effluent metal concentration reached a constant value ($C/C_0 = 0.95$).

The amount of metal ions adsorbed per unit mass of biosorbent in the column was calculated using the following equation [17]:

$$q = \frac{Q_t}{m} = \frac{\sum v(t_i - t_{i-1})\left(1 - \left(\frac{C}{C_0}\right)_i\right)C_0}{m} \tag{2}$$

where Q_t (mg) is the total amount of Zn^{2+} adsorbed in the biosorbent column; "i" is the number of sampling point; t_i is the ith time point; $(C/C_0)_i$ is the ratio of ith effluent concentration over the initial concentration, v (ml/min) is the flow rate of the influent, and m (g) is the mass of biosorbent packed in the column.

2.5. FT-IR analysis

After metal adsorption and desorption experiments, a sample of biosorbent was washed with distilled water, dried, and used for Fourier transform-infrared spectroscopy (FT-IR) analysis.

FT-IR was carried out to give a qualitative and preliminary characterization of the main functional chemical groups present on the algal biomass, which are responsible for Zn^{2+} biosorption. The KBr-pressed disk technique was used to analyze the FA-treated sample and Zn(II)-loaded biomass.

2.6. Breakthrough curve modeling

The biosorption process modeling is essential and important in designing and optimization of adsorption processes. The performance of a packed-bed is obtained through the concept of the breakthrough curve [17]. The shapes of the breakthrough curve and breakthrough appearance times are two important characteristics for determination of operation and dynamic response of an adsorption column. The prediction of the concentration–time profile from the breakthrough curve for the column effluent is required for a successful design of the column process. In this study, several models such as BDST, Thomas, Yoon–Nelson, and modified dose-response were used to verify the performance of fixed-bed biosorption columns and analyze their breakthrough curves.

2.6.1. BDST model

The BDST model was derived from the equation described by Adams–Bohart, but it was modified By Hutchins [18,19]. It was used to compare the uptake capacity of the adsorption column. BDST is a model for predicting the relationship between service time and bed height in terms of process concentration and biosorption parameters [19,20]. This relation has the term of a straight line, where the biosorption capacity of the bed (N_0) can be evaluated from the line slop, which represents the time required for the adsorption zone to travel a unit length through the adsorbent. The basic assumptions behind this model are that external mass transfer resistance and intraparticle diffusion are negligible, and the adsorption kinetics are controlled by the surface chemical reaction between the solute and the adsorbent [21]. This model can be used for comparing the performance of column under different process variables.

The following equation is the relationship between service time (t) and bed height (z):

$$t = \frac{N_0 Z}{C_0 v} - \frac{1}{K_a C_0}\ln\left(\frac{C_0}{C} - 1\right) \tag{3}$$

where C_0 (mg/L) is the initial metal ion concentration, C (mg/L) is the breakthrough metal ion concentration, N_0 (mg/L) is the biosorption capacity of the bed, v (cm/min) is the linear flow velocity of metal solution through the bed, K_a (L/mg min) is the adsorption rate constant that describes the mass transfer from the liquid to the solid phase, Z (cm) is the bed height, and t (min) is service time.

2.6.2. The Thomas model

Thomas model is one of the most general and widely used models in describing the column performance [22]. It is also the simplest model for predicting the breakthrough curves of metal sorption by biological and non-biological materials. This model follows the Langmuir kinetics of adsorption, with no axial dispersion as long as the rate-driving force obeys second-order reversible reaction kinetics [11]. Thomas model also assumes a constant separation factor but is applicable to either favorable or unfavorable isotherm. The nonlinear form of the model is given as follows:

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left(\frac{mq_0k_{\mathrm{Th}}}{Q} - \frac{VC_0k_{\mathrm{Th}}}{Q}\right)} \tag{4}$$

where k_{Th} (mL/mg min) is the Thomas rate constant, q_0 is the equilibrium adsorbate uptake, V (l) is the volume of metal solution passed through the column, and m (g) is the mass of adsorbent.

2.6.3. The Yoon–Nelson model

The Yoon–Nelson model is a relatively simple model based on the adsorption of gases on activated charcoal. This model was derived based on the assumption that the rate of decrease in the probability of adsorption for each adsorbate molecule is proportional to the probability of adsorbate adsorption and the probability of adsorbate breakthrough on the adsorbent [23]. The equation of this model is:

$$\frac{C}{C_0} = \frac{\exp(k_{\mathrm{YN}}t - \tau k_{\mathrm{YN}})}{1 + \exp(k_{\mathrm{YN}}t - \tau k_{\mathrm{YN}})} \tag{5}$$

where k_{YN} (min^{-1}) is the Yoon–Nelson rate constant and τ is the time required for 50% adsorbate breakthrough.

2.6.4. The modified dose-response model

This model is also used to analyze the biosorption column data [24]. The empirical equation of this model is:

$$\frac{C}{C_0} = 1 - \frac{1}{1 + \left(\frac{V}{b_{\mathrm{mdr}}}\right)^{a_{\mathrm{mdr}}}} \tag{6}$$

where (l) is the volume of metal solution passed through the column, a_{mdr} and b_{mdr} are the modified dose-response model constants.

3. Results and discussion

3.1. Batch studies

In this research, batch studies were carried out on the comparison between Zn^{2+} biosorption of various species of raw and chemically modified brown algae.

3.1.1. Influence of treatment on biomass

The chemical and physical processes performed on the biosorbent surface, usually increase the adsorption capacity [5]. Surface modification by FA can improve the biosorbent surface and prevent leaching of adsorptive components from biomass. In addition, HCl and $CaCl_2$ act as modifiers and increase the stability of the biosorbent material, reinforce the activate sites and enhance biosorbent properties [14,15].

Four types of brown algae mentioned above were treated by three chemicals, 0.1 M HCl, 0.1 M FA, and $CaCl_2$ at pH of 5. The results indicate that FA-treated *S. glaucescens* have the highest Zn biosorption capacity of 29.13 mg/g. From Fig. 1, it is obvious that modification with FA leads to a significant increase in Zn(II) biosorption.

3.1.2. Batch desorption experiments

Biomass regeneration is essential and necessary because of its economic aspects. For desorption of Zn ions from the algal biomass, three different elutants, namely 0.1 M HCl, 0.1 M NaCl, and 0.1 M EDTA were utilized. To evaluate the sorption capacity, three sorption–desorption cycles were performed at pH of 5. Variance analysis (ANOVA) and one-sample t-test were used to investigate the regeneration experimental results. For Zn^{2+}-loaded biomass, p-value is lower than 0.05 and the values of F are higher than the critical F ($19.61 > 5.14$) (p-value: $0.002 < 0.05$). These values showed that the sorption capacity is affected by the type of desorbent agent solution region of with 0.95 confidence. Furthermore, there is a significant difference

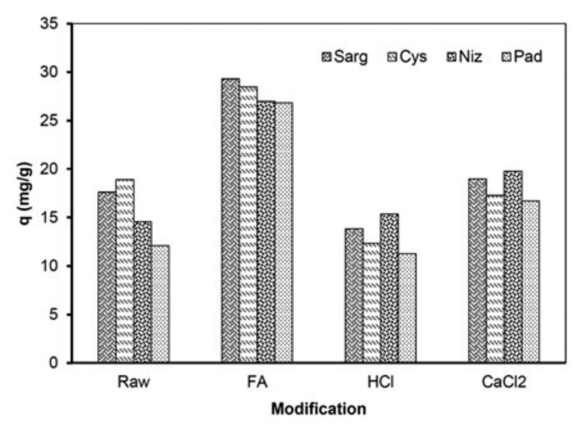

Fig. 1. Comparison between biosorption Zn(II). Various species of raw and chemically modified brown algae ($C_i = 60.62$ mg/l; Time = 1.5 h; T: 25°C; biomass dosage: 2 g/L).

between elutants and biomass sorption capacity after regeneration.

For a 5% level of significance, the critical t is 4.303 and t value for HCl, NaCl, and EDTA were 13.78, 1.70, and 5.01, respectively. For HCl and EDTA, p-values were lower than 0.05 and p-value related to NaCl is high ($0.05 < 0.231$). From the above data, it can be concluded that the t value of NaCl is lower than the critical t. It is obvious from the t-test that the number of elution times does not affect the biosorption process. Therefore, NaCl is the best desorbent for elution and desorption of Zn(II), due to its high desorption capacity. Another advantage of NaCl is its low price, which is an important economic parameter. The MINITAB software was used to carry out the one-way ANOVA and one-sample t-test statistical analysis.

3.2. Packed-bed column studies

3.2.1. Effect of bed height

Breakthrough curves for Zn(II) biosorption by FA-treated *S. glaucescens* biomass at 4 mL/min flow rate, 32 mg/L initial concentration and different bed heights are shown in Fig. 2. In order to yield various bed heights, 0.95, 1.9, and 2.9 g of the FA-treated biomass were added to the column to produce bed heights of 6, 12, and 18 cm, respectively. It could be observed that the breakthrough time (t_b) and the exhaustion time (t_e) are increased by the bed height increase (Table 1). An expanding in the surface area of the algal sorbent was seen due to the increase in the quantity of biomass and rising column height. The greater number of available sorption sites yielding can be the reason of this event. By increasing the bed heights from 6 to 18 cm, the S-curve slop (dc/dt) is decreased from t_b to t_e, which indicates that the breakthrough curve becomes less steep and the mass transfer zone becomes to more broaden (Fig. 2). Moreover, *S. glaucescens* metal uptake capacity increased by the increase in the bed height, due to the availability of more binding sites for sorption [16].

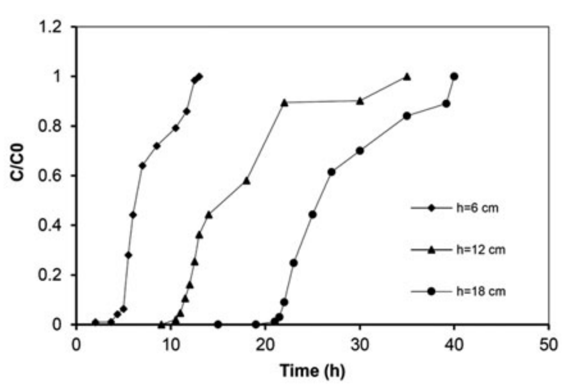

Fig. 2. Breakthrough curves for biosorption of Zn(II) by FA-treated *S. glaucescens* at different bed heights (flow rate = 4 ml/min; C_i = 32 mg/l; pH 5).

3.2.2. Effect of flow rate

The effect of changing flow rate from 2 to 8 mL/min on the biosorption of Zn(II) by FA-treated *S. glaucescens* biomass was studied at 6 cm bed height. The results are shown in the breakthrough curves in Fig. 3. The observed increase at the flow rate leads to a reduction in breakthrough and exhaustion time, so the breakthrough curves become steeper with a shorter mass transfer zone (Table 1). The insufficient residence time of the solute in the column and diffusion limitation of the solute into the pores of the biosorbent at higher flow rates could be the probable reason for this behavior [16]. By increasing the flow rate from 2 to 8 mL/min, a little rise in the FA-treated *S. glaucescens* biosorption capacity was detected and maximum metal uptake was observed at the highest flow rate (8 mL/min) (Table 1).

3.2.3. Model of column data

In this study, four empirical models such as BDST, Thomas, Yoon–Nelson, and modified dose-response have been investigated to obtain the best breakthrough curve fit of data, describing the behavior of a biosorption column. The experimental breakthrough curves have been fitted to the models through the nonlinear regression, using the MATLAB software.

3.2.3.1. BDST model. As shown in Fig. 4, the BDST model confirmed a relationship between the bed depth and the breakthrough time. The column service time was chosen as the time when the effluent Zn(II) concentration reached about 1.6 mg/L ($C/C_0 = 0.05$). A good linearity with 0.98–0.99 regression coefficients for the three flow rates was observed from the plots, indicating the validity for the model. The sorption rates constant (k_a) and the sorption capacity of the bed per unit bed volume (N_0), which shown in Table 2, were evaluated from the intercept and slope of BDST plot, respectively. This model assumes that the initial concentration (C_0) and the linear flow velocity, v (cm/min), are constant during the column operation [25]. The BDST model can be useful to predict the packed-bed column performance with different bed heights and scale up the process for the flow rates without further experimental data and analyses.

Table 1
Adsorption data for fixed-bed column for Zn(II) removal at different process parameters

Bed height (cm)	Flow rate (ml/min)	t_e (min)	t_b (min)	V_e (lit)	q (mg/gr)
6	2	1,350	660	2.7	56.85
6	4	780	260	3.12	56.46
6	8	600	120	4.8	58.71
12	4	2,100	660	8.4	66.29
18	4	2,400	1,290	9.6	71.17

Notes: C_i = 32 mg/l; pH 5.

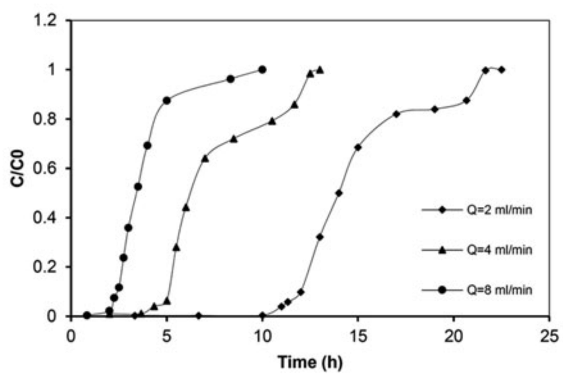

Fig. 3. Breakthrough curves for biosorption of Zn(II) by FA-treated *S. glaucescens* at different flow rates (bed height = 6 cm; C_i = 32 mg/l; pH 5).

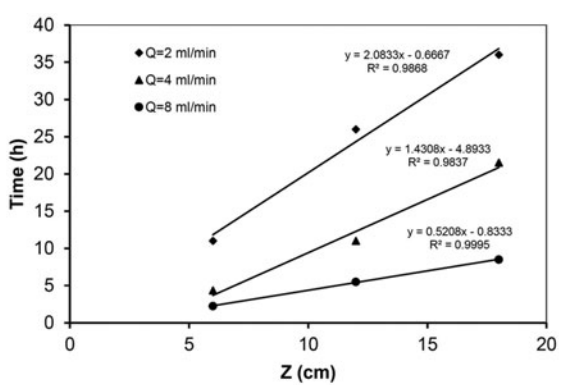

Fig. 4. The plot for Zn(II) biosorption by FA-treated *S. glaucescens* at different flow rates according to the BDST model (C_i = 32 mg/l; pH 5).

3.2.3.2. The Thomas model. To determine the maximum solid-phase concentration (q_0) and Thomas rate constant (k_{Th}), the experimental data were fitted to the Thomas model. The model constants, k_{Th} and q_0, are shown in Table 3. Fig. 5 indicates the predicted values of Zn(II) concentration in the column effluent for different conditions. The regression coefficient (R^2) and other statistical parameters show that the experimental data fitted well to the Thomas model. The model gave a good fit of the experimental data (greater than 0.99 in the column with 6 cm bed height and 8 ml/min flow rate). As the bed height increased at 4 ml/min flow rate, the rate constant k_{Th} values decreased, whereas the maximum uptake capacity (q_0) increased. An increase in the flow rate from 2 to 8 ml/min leads to a little diminution in the maximum uptake capacity. Similarly, researchers reported that the Thomas model overestimated q_0 the value for Zinc (II) sorption by biosorbents [26]. From the good fit of the experimental data on the Thomas model, we can conclude that the internal and external diffusion will not be the limiting step. Furthermore, to study this state and the porous structure role in the biosorption using intraparticle diffusion model, an experimental test has been done, and the results revealed this fact (K_{id} = 29.174 mg/g min$^{-0.5}$, a = 0.130 mg/g, and R^2 = 0.972).

3.2.3.3. The Yoon–Nelson model. The Yoon–Nelson model was applied to investigate the breakthrough behavior of Zn(II) on the algal biomass. The value of the rate constant (k_{YN}) and the time required for 50% adsorbate breakthrough (τ) are given in Table 4. As given on this table, the calculated τ values are quite close to those found experimentally. As the bed height increased from 6 to 18 cm at 4 ml/min flow rate, the values of k_{YN} decreased, whereas the time required reaching 50% of retention, τ, increased. With increasing the flow rate from 2 to 8 ml/min at a constant bed height (6 cm), the k_{YN} value was increased, while the τ values showed a reverse trend. As shown in Fig. 6, the experimental data in the column with 6 cm height and 8 ml/min flow rate, were fitted well (R^2 > 0.99) to the Yoon–Nelson model.

3.2.3.4. The modified dose-response model. The constants of this model (a_{mdr} and b_{mdr}) are shown in Table 5. As the bed height increased from 6 to 18 cm at 4 ml/min flow rate, both a_{mdr} and b_{mdr} increased. For the column with 6 cm height and 8 ml/min flow rate, the

Table 2
BDST model parameters at different flow rates for Zn(II) removal

Flow rate (ml/min)	v (cm/h)	Slope	Intercept	N_0 (mg/l)	K_a (l/mg h)	R^2
2	59.71	2.0833	0.66	3,980.80	0.1414	0.9868
4	119.43	1.4308	4.89	5,468.03	0.0204	0.9837
8	238.85	0.5208	0.83	3,980.64	0.0987	0.9995

Notes: C_i = 32 mg/l; pH 5.

Table 3
Thomas model parameters at different bed heights and flow rates

Bed height (cm)	Flow rate (ml/min)	K_{Th} (l/gr min)	q_{cal} (mg/gr)	q_{exp} (mg/gr)	R^2
6	2	0.393	54.60	56.85	0.98
6	4	0.394	52.83	56.46	0.95
6	8	0.890	53.49	58.71	0.99
12	4	0.188	61.81	66.29	0.95
18	4	0.201	68.06	71.17	0.95

Notes: C_i = 32 mg/l; pH 5.

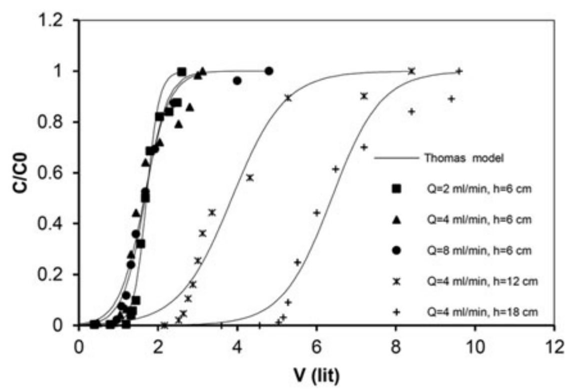

Fig. 5. Comparison of the experimental and predicted breakthrough curves for Zn(II) biosorption by FA-treated *S. glaucescens* at different bed heights and flow rates according to the Thomas model (C_i = 32 mg/l; pH 5).

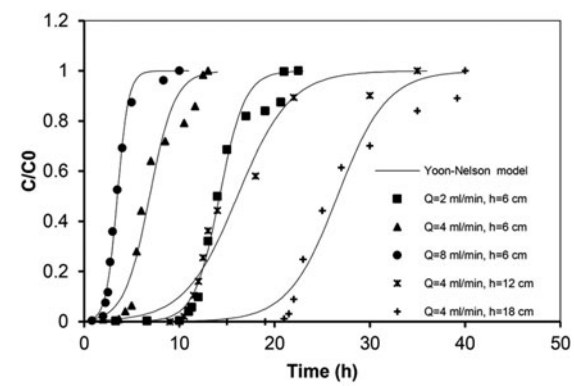

Fig. 6. Comparison of the experimental and predicted breakthrough curves for Zn(II) biosorption by FA-treated *S. glaucescens* at different bed heights and flow rates according to the Yoon–Nelson model (C_i = 32 mg/l; pH 5).

Table 4
Yoon–Nelson model parameters at different bed heights and flow rates

Bed height (cm)	Flow rate (ml/min)	K_{YN} (1/h)	τ_{cal} (h)	τ_{exp} (h)	R^2
6	2	0.754	14.22	14	0.97
6	4	0.757	6.88	6.5	0.95
6	8	1.709	3.48	3.5	0.99
12	4	0.361	16.1	16	0.95
18	4	0.385	26.6	26.2	0.96

Notes: C_i = 32 mg/l; pH 5.

Table 5
Modified dose-response model parameters at different bed heights and flow rates

Bed height (cm)	Flow rate (ml/min)	a	b	R^2
6	2	9.88	1.704	0.98
6	4	4.97	1.616	0.97
6	8	5.51	1.647	0.99
12	4	5.44	3.774	0.96
18	4	9.55	6.635	0.97

Notes: C_i = 32 mg/l; pH 5.

experimental data fitted well to the modified dose-response model ($R^2 > 0.99$) as it has shown in Fig. 7.

3.3. *Biosorbent characterization*

The chemically functional groups such as carboxylic acids, amide, amine, amino, and sulfonate in the adsorbent cell wall could be identified with FT-IR analysis. The results from this analysis for FA-treated and Zn-loaded *S. glaucescens* biomass are shown in Fig. 8. Comparing FA-treated biomass and Zn-loaded biomass revealed that two peaks were observed at 3,437 cm^{-1} (FA-treated biomass) and 3,429 cm^{-1} (Zn-loaded biomass), characterizing N–H and O–H stretching (amine and hydroxyl groups, respectively) [27,28]. Although, amine functional groups were not the main group within the cell wall structure of the brown alga, their contribution at Zn(II) biosorption was confirmed with FT-IR analysis [29].

The shift from 2,930 cm^{-1} (FA-treated biomass) to 2,922 cm^{-1} wavenumbers in Zn-loaded biomass attributed to O–H stretching vibration of the carboxyl group [27,30]. The observed peaks at 2,866 cm^{-1} (FA-treated biomass) are related to the normal stretch of carboxylic acid groups and the peak at 2,082 cm^{-1} (in both biomass) representing amine groups (N–H) [30,31,32]. The shift stretch and peak at 1,629 cm^{-1} (FA-treated biomass) and 1,637 cm^{-1} (Zn-loaded biomass) are related to COOH stretch vibration of carboxylic acid groups. The peaks at 1,438 and 1,383 cm^{-1} (FA-treated and Zn-loaded biomass) may be attributed to $-CH_3$ unsymmetrical bending vibration and C(=O)–O^- symmetrical stretching vibration in carboxylate, respectively [24,31]. The shift from 1,094 cm^{-1} (FA-treated biomass) to 1,054 cm^{-1} (Zn-loaded biomass) could be related to the organic phosphate groups and P–O stretch [24,32]. Some functional groups such as sulfate (S–O and S=O stretches) had less influence on the adsorption [29].

From the Fig. 8, it can be seen the considerable shift in the analysis spectrum before and after Zn sorption at 2,343 cm^{-1} wave number, representing C–H functional group [27,33]. From the above, it can be concluded that the functional groups such as carboxyl, amine, and carboxylic acid have the most influence on Zn^{2+} biosorption.

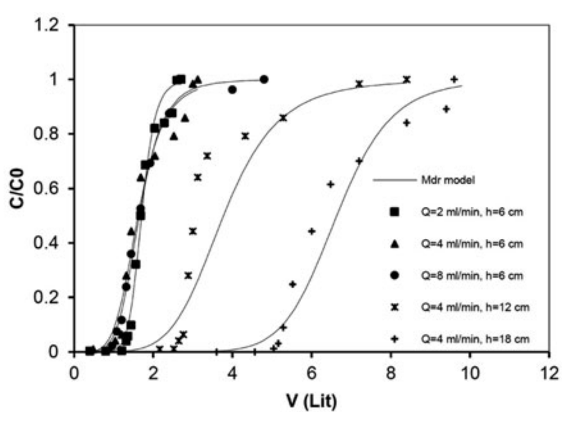

Fig. 7. Comparison of the experimental and predicted breakthrough curves for Zn(II) biosorption by FA-treated *S. glaucescens* at different bed heights and flow rates according to the modified dose-response model (C_i = 32 mg/l; pH 5).

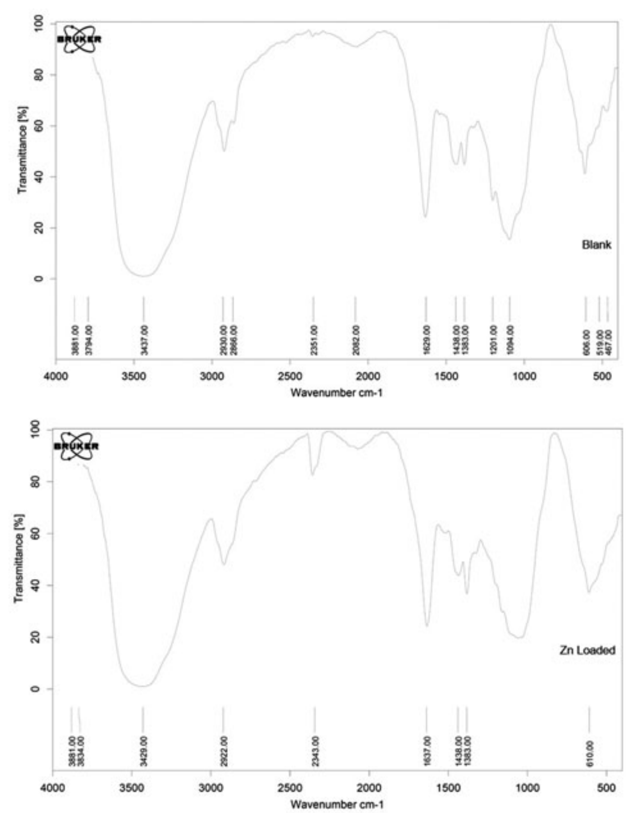

Fig. 8. FT-IR spectra of FA-treated *S. glaucescens* before (up) and after (down) Zn(II) biosorption.

Table 6
A comparison between zinc ion sorption by some sorbents

Biosorbent	Class	Operating conditions	q_{max} (mg/g)	Type of reactor and operation mode	Refs.
Palm tree leaves	Agricultural wastes	pH 5.5	14.70	BSR	[34]
Rice bran	Agricultural wastes	pH 5.0	21.07	BSR	[35]
Activated carbon	Agricultural wastes	pH 5.0	6.65	PBR	[36]
Wheat bran	Agricultural wastes	pH 6.5	16.40	BSR and PBR	[37]
Fucus spiralis	Green microalgae	pH 4.5	34.30	BSR	[38]
Sargassum glaucescens	Brown alga	pH 5.0	29.07	BSR and PBR	Current research

Notes: BSR, Batch stirred reactor; PBR, Packed-bed reactor.

4. Conclusions

A lot of studies carried out to remove zinc ions (or heavy metals) from aqueous solutions using biosorbents in the batch systems. Results showed biosorbents having a good potential to removal Zn^{2+} ion from aqueous solutions. A comparison between some sorbents and their sorption capacities reported by researchers is summarized in Table 6. In this research, the biosorption of Zn^{2+} by dried brown algal biomass was studied in both batch and column system. Batch experiments were performed on four types of brown algae, namely *Cystoseira indica*, *Sargassum glaucescens*, *Nizimuddinia zanardini*, and *Padina australis*, to evaluate their Zn(II) biosorption capacity. Comparison of Zn(II) biosorption capacity between four brown algae in raw, and chemically modified forms indicated that the maximum uptake capacity occurs in the Zn(II) biosorption by FA-treated *S. glaucescens* at pH of 5. This value measured to be 29.13 mg/g. Desorption experiments were carried out with three elutants, namely NaCl, HCl, and EDTA and statistical analysis results showed that NaCl is the best deosrbent.

FA-treated *S. glaucescens* was utilized in a packed-bed column for biosorption Zn(II), due to its high sorption capacity. Breakthrough curves were obtained at different bed heights and liquid flow rates. The metal uptake capacity was increased by the rise in bed height, and the breakthrough time (t_b) and exhaustion time (t_e) were increased as well. Flow rate changing had no significant effect on metal uptake capacity. The bed depth service time model was used to predict the relationship between service time and bed height, which is essential in column process design. The behavior of breakthrough curves for the packing bed column was also investigated with other models such as Thomas, Yoon–Nelson, and modified dose-response. The constants of these models were obtained with high regression coefficients to be ranged from 0.95 to 0.99. Among all models that were investigated in this paper, the BDST model gives the best fit of the breakthrough curves to experimental data.

References

[1] 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. B137 (2006) 244–253.
[2] C.C. Liu, Y.S. Li, Y.M. Chen, M.K. Wang, C.S. Chiou, C.Y. Yang, Y.A. Lin, Biosorption of chromium, copper and zinc on rice wine processing waste sludge in fixed bed, Desalination 267(1) (February 2011) 20–24.
[3] E. Oguz, M. Ersoy, Removal of Cu^{2+} from aqueous solution by adsorption in a fixed bed column and neural network modelling, Chem. Eng. J. 164 (2010) 56–62.
[4] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.
[5] B. Volesky, Sorption and Biosorption, BV Sorbex, St. Lambert, Que., Inc., Canada, 2003.
[6] R. Apiratikul, P. Pavasant, Batch and column studies of biosorption of heavy metals by *Caulerpa lentillifera*, Bioresour. Technol. 99 (2007) 2766–2777.
[7] H.D. Doana, A. Lohia, V.B.H. Dang, T. Dang-Vu, Removal of Zn^{+2} and Ni^{2+} by adsorption in a fixed bed of wheat straw, Process Saf. Environ. Prot. 86 (2008) 259–267.
[8] S.J. Kleinubing, E. Guibal, E.A. da Silva, M.G.C. da Silva, Copper and nickel competitive biosorption simulation from single and binary systems by *Sargassum filipendula*, Chem. Eng. J. 184 (2012) 16–22.
[9] Y. Liu, Q. Cao, F. Luo, J. Chen, Biosorption of Cd^{2+}, Cu^{2+}, Ni^{2+} and Zn^{2+} ions from aqueous solutions by pretreated biomass of brown algae, J. Hazard. Mater. 163 (2009) 931–938.
[10] S. Kam, D. Lee, M. Lee, Biosorption of copper and zinc by biomass of marine brown algae in Cheju Island, Environ. Eng. Res. 2(3) (1997) 181–190.
[11] M. Ghasemi, A.R. Keshtkar, R. Dabbagh, J. Safdari, Biosorption of uranium (VI) from aqueous solutions by Ca-pretreated *Cystoseira indica* alga: Breakthrough curves studies and modeling, J. Hazard. Mater. 189 (2011) 141–149.
[12] B. Volesky, J. Weber, J.M. Park, Continuous-flow metal biosorption in a regenerable *Sargassum* column, Water Res. 37 (2003) 297–306.

[13] Z. Aksu, T. Kutsal, Determination of kinetic parameters in the biosorption of copper (II) on Cladophora sp in a packed bed column reactor, Process Biochem. 33 (1998) 7–13.

[14] L. Yang, P. Chen, Biosorption of hexavalent chromium onto intact and chemically modified *Sargassum* sp. Bioresour. Technol. 99 (2008) 297–307.

[15] A. Leusch, Z.R. Holan, B. Volesky, Biosorption of heavy metals (Cd, Cu, Ni, Pb, Zn) by chemically-reinforced biomass of marine algae, J. Chem. Technol. Biotechnol. 62 (1995) 279–288.

[16] K. Vijayaraghavan, K. Palanivelu, M. Velan, Biosorption of cobalt (II) and nickel (II) by seaweeds: Batch and column studies, Sep. Purif. Technol. 44 (2005) 53–59.

[17] 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 (2009) 1427–1435.

[18] R.A. Hutchins, New method simplexes design of activated carbon system, Chem. Eng. J. 80 (1973) 133–138.

[19] V.C. Taty-Costodes, H. Fauduet, C. Porte, Y.S. Ho, Removal of lead(II) ions from synthetic and real effluents using immobilized *Pinus sylvestris* sawdust: Adsorption on a fixed-bed column, J. Hazard. Mater. 123 (2005) 135–144.

[20] 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.

[21] 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.

[22] H.C. Thomas, Heterogeneous ion exchange in a flowing system, J. Am. Chem. Soc. 66 (1944) 1664–1666.

[23] Y.H. Yoon, J.H. Nelson, Application of gas adsorption kinetics I. A theoretical model for respirator cartridge service life, Am. Ind. Hyg. Assoc. J. 45 (1984) 509–516.

[24] S.V. Gokhale, K.K. Jyoti, S.S. Lele, Modeling of chromium (VI) biosorption by immobilized *Spirulina platensis* in packed column, J. Hazard. Mater. 170 (2009) 735–743.

[25] 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.

[26] R. Senthilkumar, K. Vijayaraghavan, M. Thilakavathi, P.V.R. Iyer, M. Velan, Seaweeds for the remediation of wastewaters contaminated with zinc(II) ions, J. Hazard. Mater. 136 (2006) 791–799.

[27] J. Pan, R. Liu, H. Tang, Surface reaction of *Bacillus cereus* biomass and its biosorption for lead and copper ions, J. Environ. Sci. 19 (2007) 403–408.

[28] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, John Wiley & Sons, Inc., Hoboken, NJ, 2009.

[29] J. Plaza Cazon, C. Bernardelli, M. Viera, E. Donati, E. Guibal, Zinc and cadmium biosorption by untreated and calcium-treated *Macrocystis pyrifera* in a batch system, Bioresour. Technol. 116 (2012) 195–203.

[30] R.M. Silverstein, Spectrometric Identification of Organic Compounds, John Wiley & Sons, Inc., Hoboken, NJ, 1991.

[31] L. Ramrakhiani, S. Khowala, Effect of prettreatment on hexavalent chromium biosorption and multimetal biosorption efficiency of Termitomyces *Clypeatus* biomass, I, J. Integr. Sci. Innov. Technol. 1(1) (2012) 7–15.

[32] L.G. Wade, Organic Chemistry, eighth ed., Pearson Pub., USA, 2013.

[33] J.H. Joo, H.A. Sedky, S.E. Oh, Comparative study of biosorption of Zn^{2+} by pseudomonas aeruginosa and bacillus cereus, Int. Biodeterior. Biodegrad. 64 (2010) 734–741.

[34] F.A.A. Al-Rub, Biosorption of zinc on palm tree leaves: Equilibrium, kinetics, and thermodynamics studies, Sep. Purif. Technol. 41 (2006) 3499–3515.

[35] X.S. Wang, Y. Qin, Z.F. Li, Biosorption of zinc from aqueous solutions by rice bran: Kinetics and equilibrium studies, Sep. Sci. Technol. 41 (2006) 747–756.

[36] M.A. Ferro-Garcia, J. Rivera-Utrilla, J. Rodriguez-Gordillo, I. Bautista-Toledo, Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products, Carbon 26(3) (2008) 363–373.

[37] D. Dupont, J. Bouanda, J. Dumonceau, M. Aplincourt, Biosorption of Cu(II) and Zn(II) onto a lignocellulosic substrate extracted from wheat bran, Environ. Chem. Lett. 2 (2005) 165–168.

[38] O.M.M. Freitas, R.J.E. Martins, C.M. Delerue-Matos, R.A.R. Boaventura, Removal of Cd(II), Zn(II) and Pb (II) from aqueous solutions by brown marine macro algae: Kinetic modelling, J. Hazard. Mater. 153 (2008) 493–501.