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Biosorption of lead(II) and cadmium(II) by protonated *Sargassum glaucescens* biomass in a continuous packed bed column

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Abstract

Biosorption of lead(II) and cadmium(II) from aqueous solutions by protonated *Sargassum glaucescens* biomass was studied in a continuous packed bed column. The selective uptake of Pb^{2+} and Cd^{2+} was investigated in a binary system with initial concentration of 1 mM for each metal ion. The selective uptake capacities of Pb^{2+} and Cd^{2+} at complete exhaustion point were obtained 1.18 and 0.22 mmol/g, respectively; therefore, the biosorbent showed much higher relative affinity for Pb^{2+} than for Cd^{2+}. The optimum range of empty bed contact time (EBCT) was identified as 5–10 min in the packed bed column. The efficiency of biosorbent regeneration by 0.1 M HCl was achieved about 60%, so that the maximum uptake capacity of Pb^{2+} by the regenerated biomass was determined to be 0.75 mmol/g while the same value for the original biomass was 1.24 mmol/g. The Thomas model was found in a suitable fitness with the experimental data ($R^2 > 0.90$ and $\varepsilon\% < 50\%$) at all different operation stages. Monitoring of pH in the effluent of the column presented the simultaneous release of H^+ with the uptake of heavy metals; hence, ion exchange was confirmed to be one of the main biosorption mechanisms.

Keywords: Biosorption; *Sargassum glaucescens*; Heavy metals; Packed bed column; Breakthrough curve

1. Introduction

Contamination of the aqueous environments by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain. Among heavy metals, lead and cadmium have high priority for removal from aqueous environments [1–3]. The conventional technologies for the removal of heavy metals from wastewater include, mainly, chemical precipitation, ion exchange, adsorption, membrane processes and evaporation that require high capital investment and running costs [4–7]. Therefore, there is an urgent need for development of innovative but low cost processes, where metal ions can be removed economically. The search for new treatment technologies has focused on biosorption [8].

Biosorption is a term that describes the removal of heavy metals by the passive binding to nonliving microorganisms (bacteria, fungi and algae) and other biomass (such as peat, rice hull, fruit peel, leave and bark of tree) from an aqueous solution [9–11]. Biosorption has many advantages including low capital and operating costs, the selective removal of metals, biosorbent regeneration and metal recovery potentiality, rapid kinetics of adsorption and desorption and no sludge generation. Biosorption technology has been shown to be a feasible alternative for removing heavy metals from wastewater [12–14]. This technology can utilize naturally abundant biomass such as seaweeds, and of these *Sargassum* has been identified for its high sorption capacity [15].

Most separation and purification processes that employ sorption technology use continuous flow columns. In biosorption applications, a packed bed column is an effective process for continuous wastewater treatment, as it makes the best use of the concentration difference known to be a driving force for heavy metal biosorption and allows more efficient utilization of biosorbent capacity and results in a better quality of the effluent [16–18].

Abbreviations: COD, chemical oxygen demand; EBCT, empty bed contact time; MTZ, mass transfer zone

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Nomenclature

C	effluent metal ion concentration (mM)
C_0	influent metal ion concentration (mM)
H_{MTZ}	length of mass transfer zone (cm)
k_{Th}	Thomas rate constant (m^3/mol h)
M	total mass of the biosorbent loaded in the column (g)
N	number of measurements
q_0	maximum biosorption capacity (mmol/g)
Q	flow rate (L/h)
R	correlation coefficient
V	volume of metal solution passed through the column (L)
V_B	throughput volume to breakthrough (L)
V_E	throughput volume to exhaustion (L)
Z	length of the biosorption bed (cm)

Greek letter

ε%	average percentage errors (%)

The performance of packed bed columns is analyzed using the effluent concentration versus time curves. The plot is usually referred to as the breakthrough curve. Breakthrough curve is a function of the column flow characteristics, sorption equilibrium and mass transfer factors. Typically, breakthrough is said to have occurred when the effluent concentration reaches 5% of the influent value. Exhaustion of biosorption bed is assumed to have occurred when the effluent concentration is equal to 95% of the influent concentration. At complete exhaustion, the effluent concentration is equal to the influent concentration. The area of the biosorption bed in which sorption is occurring is called the mass transfer zone (MTZ). The length of the MTZ is typically a function of empty bed contact time (EBCT) and the characteristics of the biosorbent [19–22].

The objective of this research was to study the biosorption of Pb^{2+} and Cd^{2+} by protonated *Sargassum glaucescens* biomass in a continuous packed bed column. The selective uptake of Pb^{2+} and Cd^{2+} was studied in a binary system. The effect of EBCT on the performance of the packed bed column was investigated. Also the effectiveness of hydrochloric acid in the biosorbent regeneration was studied and the breakthrough curves obtained at different operation stages were analyzed using the Thomas model.

2. Materials and methods

2.1. Biosorbent preparation

The biosorbent used in the experiments was brown macroalga *S. glaucescens* which was harvested from Oman Sea on the coast of Chabahar, Iran. The biomass was washed with tap water and de-ionized water to remove sand and other impurities. The biomass was first sun-dried and then dried in an oven at 70 °C. The dried biomass was ground in a laboratory blender. After this, the biomass was sieved to select particles between 0.3 and 0.8 mm for use. The biomass was subsequently loaded with H^+ in a solution of 0.1 M HCl (biomass concentration of 50 g/L) for 30 min under slow stirring. Then the biomass was washed with de-ionized water to remove excess hydrogen ions. Finally, the biosorbent was again dried at 70 °C for 24 h.

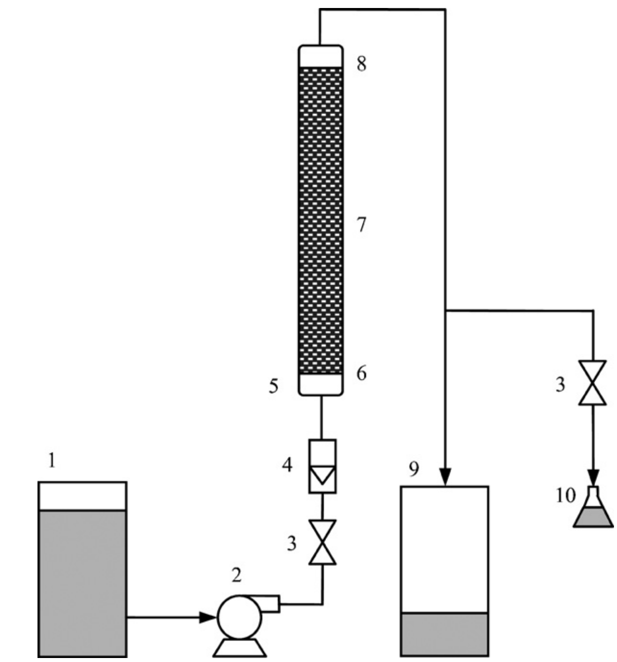

Fig. 1. Experimental arrangement of the biosorption packed bed column: (1) feed storage, (2) peristaltic pump, (3) valve, (4) flowmeter, (5) column, (6) bottom sieve, (7) packed biosorbent, (8) top sieve, (9) effluent storage and (10) sampling vessel.

2.2. Chemicals

The synthetic solutions were all prepared by use of de-ionized water and analytical grade salts of $Pb(NO_3)_2$ and $Cd(NO_3)_2{\cdot}4H_2O$ (Merck supplied). The pH of influent solutions was adjusted to 5 with a pH meter (CAMLAB Ltd, Model CG842) by using 0.1–1 M HCl and/or 0.1–1 M NaOH.

2.3. Continuous flow column system

The column was a simple glass tube with inner diameter of 4 cm, bed depth of 40 cm and bed volume of 503 mL (Fig. 1). Two plastic sieves both with pore size of 0.2 mm were installed at the top and bottom of this column. The experiments were conducted by pumping a metal solution in upflow mode through the packed bed column with a peristaltic pump. As the packing density of the biosorbent was 180.4 kg/m^3, a weight of 90.7 g of the biosorbent was packed within the column. The porosity (bed void volume to bed volume ratio) of the wet biosorption bed was 66% in the packed bed column.

2.4. Biosorption experiments

All of the experiments were performed in the packed bed column at room temperature (20 ± 2 °C). Previous study by authors in a batch system indicated that the optimum pH value for Pb^{2+} and Cd^{2+} biosorption by protonated *Sargassum* sp. biomass was about 5 [23]; therefore in this study, the pH of column influent was adjusted to 5 and the pH of column effluent was measured at predetermined time intervals.

2.4.1. Selective biosorption

The selective uptake of Pb^{2+} and Cd^{2+} was studied in a binary system. In this system, the initial concentration of Pb^{2+} and Cd^{2+} was 1 mM for each metal ion and the EBCT was 30 min (Q = 1.0 L/h).

2.4.2. Effect of EBCT

In order to determine the effect of EBCT on the effectiveness of the packed bed column in the removal of Pb^{2+}, the experiments were accomplished at three EBCTs of 5 min (Q = 6.0 L/h), 10 min (Q = 3.0 L/h) and 20 min (Q = 1.5 L/h). At this stage, initial concentration of metal ion was 2 mM.

2.4.3. Biosorbent regeneration

The performance of HCl in the biosorbent regeneration was examined in one cycle. In these experiments, the initial concentration of metal ion (Pb^{2+}) was 2 mM and the EBCT was 10 min. After saturation of the biosorption bed in the first sorption phase, the biosorbent was discharged from the column and regenerated by using HCl. The biomass was contacted with 0.1 M HCl (biosorbent concentration of 50 g/L) for 30 min under slow stirring in a continuous flow reactor with a volume of 2 L at flow rate of 4.0 L/h. Thereafter the biosorbent was washed with deionized water to remove excess hydrogen ions and then loaded in the column. In this study, the regeneration stage was accomplished with discharge and reloading of biosorbent in the column to prevent slight channelization of flow in the biosorption bed; however, in full-scale application of a packed bed column the regeneration stage is performed in column directly. The column supplied with the regenerated bed was then operated in the second sorption phase and the breakthrough curves obtained in the two sorption phases were compared with each other.

2.5. Metal analysis

Liquid samples of the column effluent were collected at predefined time intervals. The samples were passed through 0.45 μm membrane filters (mixed cellulose ester) and filtrates were analyzed for residual heavy metal (Pb^{2+} and/or Cd^{2+}) concentration by a flame atomic absorption spectrophotometer (FAAS, Chem. Tech. Analytical, Model ALPHA4). In each operation phase of the column, metal sampling and analysis were being continued until the breakthrough curve was being formed.

3. Calculation

The breakthrough curves obtained in the experiments need to be examined quantitatively. In this work, the breakthrough and maximum uptake capacities were determined by using the computer program DataStudio. The breakthrough and maximum uptake capacities are presented by the area above the breakthrough curve at breakthrough point ($C = 0.05C_0$) and complete exhaustion point ($C = C_0$), respectively. The height of the MTZ was calculated by using below equation [21]:

$$H_{\mathrm{MTZ}} = Z\left[\frac{V_{\mathrm{E}} - V_{\mathrm{B}}}{V_{\mathrm{E}} - 0.5(V_{\mathrm{E}} - V_{\mathrm{B}})}\right] \quad (1)$$

where H_{MTZ} is the length of mass transfer zone (cm), Z the length of the biosorption bed (cm), V_{E} the throughput volume to exhaustion (L) and V_{B} is the throughput volume to breakthrough (L) [21].

Successful design of a column biosorption process requires prediction of breakthrough curve and maximum uptake capacity of a biosorbent. Traditionally, the Thomas model is used to fulfill the purpose. In this study, the breakthrough curves were analyzed using the Thomas model. This model has the following form [24,25]:

$$\frac{C}{C_0} = \frac{1}{1 + \exp(k_{\mathrm{Th}}/Q(q_0 M - C_0 V))} \quad (2)$$

where C_0 and C are metal ion concentrations (mM) in the influent and effluent, respectively, k_{Th} the Thomas rate constant (m^3/mol h), Q the flow rate (L/h), q_0 the maximum biosorption capacity (mmol/g), M the total mass of the biosorbent loaded in the column (g) and V is the volume of metal solution passed through the column (L) [24,25]. The linearized form of the Thomas model is as follows:

$$\ln\left(\frac{C_0}{C} - 1\right) = \frac{k_{\mathrm{Th}} q_0 M}{Q} - \frac{k_{\mathrm{Th}} C_0 V}{Q} \quad (3)$$

The kinetic coefficient (k_{Th}) and the maximum biosorption capacity (q_0) were determined from a plot of $\ln[(C_0/C)-1]$ against V at various operation phases. Linear regression coefficient (R^2) and the average percentage errors ($\varepsilon\%$) calculated according to Eq. (4) indicated the fitness between the experimental and predicted breakthrough curves:

$$\varepsilon\% = \frac{\sum_{i=1}^{N}\left|\frac{(C/C_0)_{\mathrm{exp}} - (C/C_0)_{\mathrm{theo}}}{(C/C_0)_{\mathrm{exp}}}\right|}{N} \times 100 \quad (4)$$

where the subscripts 'exp' and 'theo' show the experimental and calculated values and N shows the number of measurements [24].

4. Results and discussion

4.1. Selective biosorption

The selective biosorption of Pb^{2+} and Cd^{2+} was investigated in the packed bed column by use of a solution containing Pb^{2+} and Cd^{2+} with a concentration of 1 mM for each metal ion. The breakthrough curves of Pb^{2+} and Cd^{2+} are shown in Fig. 2. Table 1 represents the results of the breakthrough curve analysis. As shown in Table 1, the breakthrough uptake capacities of Pb^{2+} and Cd^{2+} were obtained 0.97 and 0.15 mmol/g, respectively. Also the maximum uptake capacities of Pb^{2+} and

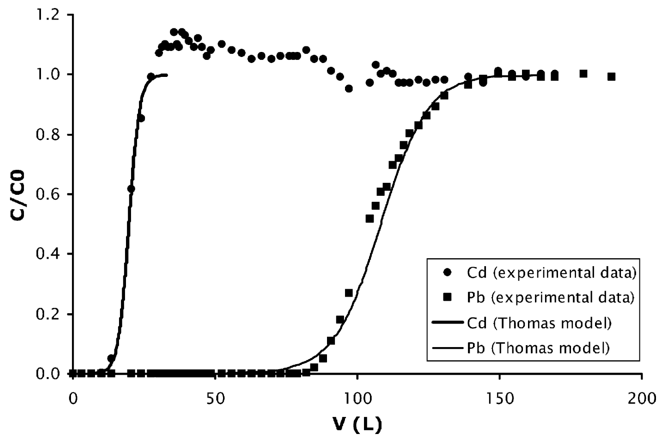

Fig. 2. The experimental and predicted breakthrough curves using the Thomas model at the selective biosorption of Pb^{2+} and Cd^{2+} by *Sargassum glaucescens* biomass.

Cd^{2+} were found to be 1.18 and 0.22 mmol/g, respectively. The breakthrough and exhaustion of Cd^{2+} occurred in the throughput volumes of 13.8 and 26.7 L, respectively, whereas the same values for Pb^{2+} were obtained 88.1 and 134.5 L, respectively. According to Fig. 2, the effluent concentration of Cd^{2+} became more than its influent concentration ($C/C_0 > 1$) in some cases after its complete exhaustion. The phenomenon was as a result of the replacement of some Cd^{2+} ions in the binding sites with Pb^{2+} ions and release of Cd^{2+} ions into the solution. The results showed that the biosorbent had much higher relative affinity for Pb^{2+} than for Cd^{2+}.

4.2. *Effect of EBCT*

In the application of a fixed bed column, a short EBCT has significant practical importance as it will facilitate smaller reactor volumes ensuring efficiency and economy [21]. Besides, the height of the MTZ varies with the EBCT because dispersion, diffusion and channeling in a granular medium are directly related to the EBCT, so in very short EBCTs, the height of the MTZ becomes longer than the column bed depth and the adsorbate is observed in the column effluent in the beginning of the column operation. Therefore, the optimum EBCT must be established for full-scale application of a biosorbent. The optimum value of EBCT is related to biosorption kinetic and the characteristics of the biosorbent [21].

The breakthrough curves of Pb^{2+} biosorption at different EBCTs (20, 10 and 5 min) are shown in Fig. 3. The results of the breakthrough curve analysis are given in Table 1. According to Table 1, as the EBCT decreased from 20 to 5 min, the V_B decreased from 43.8 to 41.8 L and the V_E increased from 68.7 to 74.2 L, but the maximum uptake capacity was remained constant (about 1.2 mmol/g). The height values of the MTZ at the EBCTs of 20, 10 and 5 min were calculated as 17.8, 21.3 and 22.4 cm, respectively. Alteration of EBCT in the range of 5–20 min had not significant influence on the height of the MTZ; therefore the optimum range of EBCT was specified at 5–10 min in the biosorption system. The short optimum EBCT is advantageous for the process and it results from the rapid kinetics of the Pb^{2+} uptake by the biosorbent.

4.3. *Biosorbent regeneration*

The regeneration and reuse of biosorbent offers an economical method for removal of heavy metals from wastewater streams. In this study, the saturated biomass was regenerated using 0.1 M HCl and the efficiency of biosorbent regeneration by the desorption agent was investigated in one cycle. Fig. 4 shows the breakthrough curves obtained in the two sorption cycles with the original and regenerated biosorbent as the biosorption bed. The results of the breakthrough curve analysis are shown in Table 1. According to Table 1, the breakthrough and maximum uptake capacities of the regenerated biosorbent were determined to be 0.54 and 0.75 mmol/g, respectively, whereas the breakthrough and maximum uptake capacities of the original biosorbent were 0.92 and 1.24 mmol/g, respectively. Thus, the efficiency of regeneration by the eluent was found to be about 60%.

The result indicated that the desorption agent (0.1 M HCl) had not suitable efficiency in the biosorbent recovery. In addition to inefficiency of the eluent, also the leaching of alginate and other polymers containing various functional groups as binding sites for metal ions out of the biosorbent might lead to a loss of adsorption capacity of the biomass, because the dissolved organic matter was observed in the effluent of the packed bed column at the concentration range of 2–5 mg/L as COD (data

Table 1
Analysis of the breakthrough curves obtained at the various operation stages of the packed bed column for Pb^{2+} and Cd^{2+} biosorption by *Sargassum glaucescens* biomass

Operation stage	Metal ion	V_B (L)	V_E (L)	H_{MTZ} (cm)	Breakthrough uptake capacity (mmol/g)	Maximum uptake capacity (mmol/g)
Selective biosorption	Pb^{2+}	88.10	134.53	16.7	0.97	1.18
	Cd^{2+}	13.75	26.73	25.7	0.15	0.22
Effect of EBCT						
EBCT = 20 min	Pb^{2+}	43.73	68.72	17.8	0.96	1.16
EBCT = 10 min	Pb^{2+}	41.77	72.10	21.3	0.92	1.24
EBCT = 5 min	Pb^{2+}	41.80	74.22	22.4	0.92	1.20
Biosorbent regeneration						
Original biosorbent	Pb^{2+}	41.77	72.10	21.3	0.92	1.24
Regenerated biosorbent	Pb^{2+}	24.55	44.90	23.4	0.54	0.75

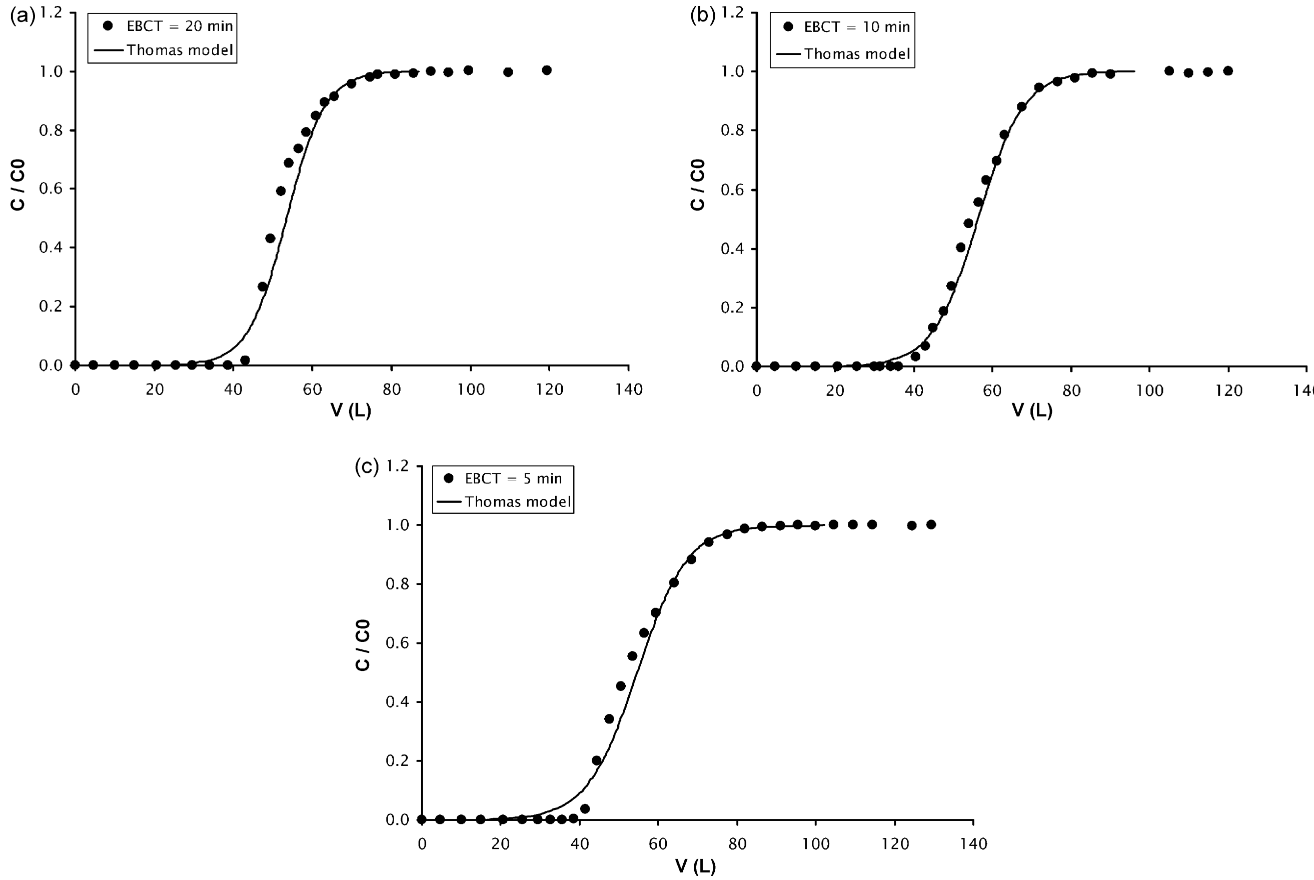

Fig. 3. The experimental and predicted breakthrough curves using the Thomas model for Pb^{2+} biosorption by *S. glaucescens* biomass at different EBCTs: (a) EBCT = 20 min, (b) EBCT = 10 min and (c) EBCT = 5 min.

not shown). Hence, the other eluents and chemical modifiers of the biosorbent to increase the stability of the biomass materials should be studied in the next research.

4.4. Application of the Thomas model

The breakthrough curves were analyzed using the Thomas model to determine the Thomas rate constant (k_{Th}) and maximum uptake capacity (q_0). The Thomas or reaction model, which assumes Langmuir kinetics of adsorption–desorption and no axial dispersion is derived with the assumption that the rate driving force obeys second-order reversible reaction kinetics. Thomas solution also assumes a constant separation factor but it is applicable to either favorable or unfavorable isotherms [24,25].

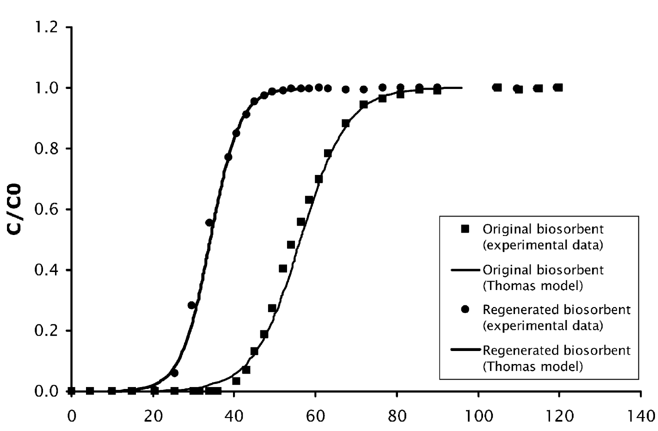

Fig. 4. The experimental and predicted breakthrough curves using the Thomas model for Pb^{2+} biosorption by the original and regenerated biosorbent.

Application of the Thomas model to the data at C/C_0 ratios higher than 0.01 and lower than 0.99 enabled the determination of the kinetic coefficients and maximum uptake capacities in the system. A linear regression was then performed on each set of transformed data to determine the parameters from slope and intercept. Figs. 2–4 illustrate both experimental breakthrough curves and predicted breakthrough curves from the Thomas model at all operation stages of the packed bed column. Table 2 shows that the coefficients of the model differed for each experiment (also see Figs. 2–4). As indicated in Table 2, the Thomas model was found in a suitable fitness with the experimental data ($R^2 > 0.90$ and $\varepsilon\% < 50\%$). In the Pb^{2+} biosorption at different EBCTs, as the EBCT decreased from 20 to 5 min, the values of k_{Th} increased from 0.155 to 0.472 m^3/mol min, but the value of q_0 (maximum uptake capacity) was remained about 1.2 mmol/g and did not changed significantly. The data in Tables 1 and 2 also showed a negligible difference between the experimental and predicted values of q_0. The Thomas model had an appropriate performance in the description of breakthrough curves obtained at different operation stages.

Table 2
Parameters predicted from the Thomas model and model deviations for Pb^{2+} and Cd^{2+} biosorption by *S. glaucescens* biomass at the various operation stages of the packed bed column

Operation stage	Metal ion	q_0 (mmol/g)	k_{Th} (m^3/mol h)	R^2	ε%
Selective biosorption	Pb^{2+}	1.19	0.121	0.963	21.0
	Cd^{2+}	0.22	0.534	0.975	7.3
Effect of EBCT					
EBCT = 20 min	Pb^{2+}	1.18	0.155	0.908	49.6
EBCT = 10 min	Pb^{2+}	1.24	0.260	0.986	12.7
EBCT = 5 min	Pb^{2+}	1.21	0.472	0.954	26.7
Biosorbent regeneration					
Original biosorbent	Pb^{2+}	1.24	0.260	0.986	12.7
Regenerated biosorbent	Pb^{2+}	0.75	0.414	0.991	8.6

The Thomas model has been used for analysis of breakthrough curves in other biosorption studies. According to Addour et al. [26], the Thomas equation adequately described the breakthrough data ($R^2 = 0.94$) obtained from biosorption of Zn^{2+} by *Streptomyces rimosus* and the Thomas parameter q_0 was determined to be 0.04 mmol/g. The Thomas model was found in a relatively good fitness ($R^2 \geq 0.85$) with breakthrough curves for biosorption of Pb^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} by immobilized *Mucor rouxii*. Also the q_0 values of immobilized *M. rouxii* for Pb^{2+}, Zn^{2+}, Cd^{2+} and Ni^{2+} were 0.03, 0.09, 0.02 and 0.01 mmol/g, respectively [25]. Although due to the various experimental conditions employed in different studies, comparison of their results is difficult, but the maximum uptake capacity of *S. glaucescens* biomass for Pb^{2+} obtained in this study far exceeded those of the biosorbents mentioned above; thus, brown macroalga *S. glaucescens* could be classified as a good biosorbent.

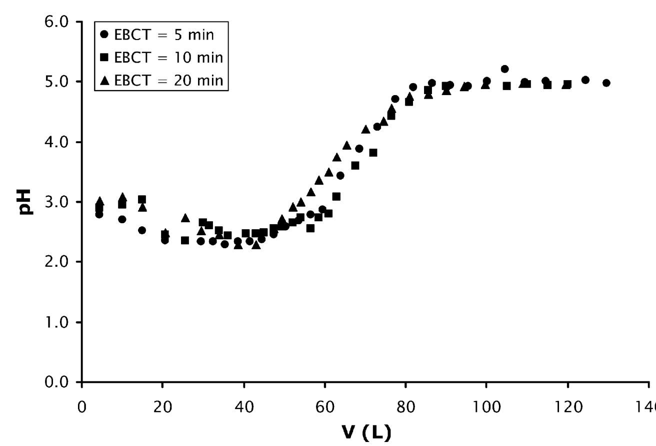

Fig. 5. Effluent pH vs. effluent volume for Pb^{2+} biosorption at different operation phases of the packed bed column.

4.5. Monitoring of pH

Monitoring of pH in the column effluent at different operation phases presented the simultaneous release of H^+ with the uptake of heavy metals, because the pH of effluent was decreasing when the biosorption of Pb^{2+} and Cd^{2+} was being performed. The plots of effluent pH versus effluent volume for Pb^{2+} biosorption at different EBCTs are given in Fig. 5. As indicated in Fig. 5, the plots of effluent pH versus effluent volume were similar to breakthrough curves. In the beginning of the column operation, the effluent pH decreased to about 2.3 by the most replacement of hydrogen ions in the binding sites with Pb^{2+} and then by reduction of protonated binding sites as well as decrease of Pb^{2+} biosorption rate, the effluent pH increased gradually until the effluent pH became equal to the influent pH (about 5) at complete exhaustion of the biosorption bed, so the rate of metal ion biosorption was proportionate to release of hydrogen ions. This observation confirmed that ion exchange was one of the main biosorption mechanisms.

Other studies with seaweed biomass have indicated ion exchange to be the dominant mechanism of biosorption. Diniz and Volesky [27] observed that ion exchange was the main mechanism of lanthanum, europium and ytterbium biosorption by *Sargassum polycystum*. The biosorption of Zn^{2+} by *Oscillatoria anguistissima* was an ion exchange phenomenon as a large amount of Mg^{2+} were released during Zn^{2+} uptake [28].

5. Conclusions

Biosorption performance of the locally derived brown macroalga *S. glaucescens* was investigated for the removal of lead(II) and cadmium(II) from aqueous solutions in a continuous packed bed column. The selective biosorption capacities of Pb^{2+} and Cd^{2+} at complete exhaustion point were determined to be 1.18 and 0.22 mmol/g, respectively; therefore, the biosorbent exhibited much higher relative affinity for Pb^{2+} than for Cd^{2+}. Because of rapid kinetics of biosorption by *S. glaucescens*, the optimum range of EBCT was very short in the packed bed column. The efficiency of biosorbent regeneration by 0.1 M HCl was found to be about 60%. The Thomas model had an appropriate performance in the description of breakthrough curves obtained at different operation stages. Ion exchange was confirmed to be one of the main mechanisms responsible for biosorption. The study indicated that the protonated *S. glaucescens* biomass could be used as an efficient biosorption bed in the packed bed columns for the treatment of Pb^{2+} or Cd^{2+} ions bearing wastewater streams.

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