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Batch and fixed-bed column biosorption of manganese ion by *Sargassum filipendula*

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Abstract

This paper presents experimental data of the biosorption of manganese onto *Sargassum filipendula* in both batch and fixed-bed column systems. Batch equilibrium data were used for nonlinear fittings of the Langmuir and Freundlich isotherms. A mathematical model based on mass balances in the fluid and in the sorbent was applied to represent the experimental fixed-bed column data. The utilization of isotherm parameters from the batch experiments in the breakthrough model implied a significant mismatch in relation to the laboratory data. Alternatively, additional fixed-bed column data provided new parameters for the isotherm evaluation, and the corresponding simulated profile of the breakthrough curve reached better agreement to the experimental results.

Keywords: biosorption, breakthrough curve, equilibrium isotherm, manganese, metal removal

INTRODUCTION

Several important industrial processes are responsible for the generation of large amounts of aqueous wastes that are contaminated with toxic metal elements, which can cause severe environmental problems. Particularly in the case of manganese ions, environmental contamination problems are associated with ore exploiting and dressing, and also with industrial activities such as metallurgy, fertilizer, petrochemical, electroplating and tanneries (Parvathi et al. 2007). Manganese is an essential chemical element that has daily dose requirements between 1.0 mg and 5.0 mg. This element is necessary for bone formation and the metabolism of lipids, glicids and amino acids. Excess consumption of manganese, however, is markedly harmful and causes adverse effects such as neurological dysfunction, with symptoms similar to those of Parkinson's disease (Erikson et al. 2005).

Several methods are used for the removal of heavy metals from liquid wastes when metal ions are present in considerably high concentrations. Such methods include the use of chemical precipitation, evaporation, electrodeposition, ion-exchange and membrane processes (Matheickal and Yu, 1999). However, these processes can be expensive and present numerous technical limitations, such as incomplete metal removal, high sensibility to pH change, moderate selectivity in mixed metal solutions and the production of toxic sludge that also needs to be further discharged. Also, these techniques are markedly inefficient or expensive when used to treat wastewaters contaminated with metal ions at low concentrations (Volesky, 2003).

Biosorption of toxic metals from aqueous wastes can be considered as an alternative treatment for wastewater cleaning. This process is based on the ability of some biological materials to concentrate

heavy metal elements on their surfaces, due to the physico-chemical nature of their chemical constituents, without the involvement of metabolic processes (Kapoor et al. 1999). This innovative process makes use of biomaterials widespread in nature that can be obtained at a low cost, such as seaweeds and biological wastes from fermentation industries and water treatment.

One report found in the literature used *Pseudomonas aeruginosa* cells as manganese biosorbers (Silva et al. 2009). The authors obtained a low uptake capacity from a 60.0 mg/L manganese ion concentration, around 22.3 mg manganese/g biomass. They also mentioned the contribution of the precipitation process due to the slightly high pH values used.

The wide use of *Sargassum* biomass is described in the literature for the biosorption of heavy metal and radionuclide elements, both under batch and continuous conditions. Picardo et al. (2009) evaluated the biosorption of thorium by *Sargassum* biomass in a dynamic system, using different bed depths. The authors observed an increase in thorium biosorption efficiency with increased bed depth, however, without modeling the process.

Luna et al. (2010) investigated the competitive biosorption of cadmium and zinc ions by *Sargassum filipendula* biomass from single and binary systems. The biomass proved to be an efficient biosorption for the removal of both ions with the equilibrium experimental data well represented by Langmuir and Langmuir-Freundlich isotherm models. The authors observed that zinc had a relevant effect on cadmium biosorption, but the interference of cadmium on zinc biosorption was markedly less intense.

Yang et al. (2011) improved the structure of *Sargassum* sp. biomass with epichlorohydrin cross-linked with chitosan for nickel removal from solution. The researchers observed an improvement in nickel biosorption in comparison to the untreated biomass, and also a much reduced leaching of organic material from the biomass after biosorption. Authors also identified the ion-exchange mechanism as well as complexation with carboxyl, amino, alcoholic and ether groups as the predominating sorption mechanisms, as confirmed by FTIR and X-Ray photoelectron spectroscopy.

Kleinübing et al. (2011), recently investigated the equilibrium and continuous biosorption of single and binary copper and nickel solutions by *Sargassum filipendula*. Authors confirmed that data were fitted to distinct equilibrium classical models such as Langmuir, Langmuir with inhibition, Jain and Snowyink and Langmuir-Freundlich. They also observed the preferential biosorption of copper, due to a marked overshoot on the breakthrough curves.

Two seaweeds, *Sargassum muticum* and *Gracilaria caudata*, were tested by their ability to accumulate nickel. *Sargassum muticum* biomass proved to be better than *Gracilaria caudata*, with a series of process parameters determined: sorption kinetics, metal concentration, sorbent dosage particle size and temperature (Gonzalez Bermudéz et al. 2011).

Thus, due to the lack of information on manganese biosorption by brown seaweeds and on continuous recovery and modeling of such process, the objective of the present work was to study the removal of manganese ions from aqueous effluents by biosorption using the seaweed *Sargassum filipendula*. In the first step, the biosorption was studied under batch conditions, in which the main target was the investigation of the sorption equilibrium between the metal and the algae samples. In the second step, the metal removal in a fixed-bed column system was explored, and a mathematical model was proposed to predict its behavior.

MATERIALS AND METHODS

Biomass

The biomass used in this work was the brown seaweed *Sargassum filipendula* obtained from the Northeastern Coast of Brazil, in the State of Pernambuco (8° 03' 17.48" South - 34° 52' 15.97" West). It was washed with distilled water and dried in an oven for 24 hrs at 343 K. Then it was cut and sieved, and the fraction in the range of 0.3-0.7 mm was used for the batch tests. For the continuous experiments, the dried biomass used was not cut.

Batch biosorption

A manganese stock solution (18.0 mmol/L) was prepared from manganese(II) chloride (Vetec Química Fina Ltda., Brazil) in distilled water. Batch biosorption experiments were performed using 100 mg of dry biomass added to 25 mL of the manganese ion solution in 500 mL polypropylene flasks. The initial manganese concentration was in the range of 0.45-12.9 mmol/L, and the pH equal to 5.5. Flasks were placed on a rotary shaker (Tecnal, Piracicaba, Brasil) at 150 rpm for 120 min. Previous studies on the biosorption of other heavy metals by *Sargassum* sp. (Antunes et al. 2003; Cruz et al. 2004; Martins et al. 2006) indicated that this shaking speed ensures the absence of mass transfer resistances in the bulk of the fluid. Additionally, preliminary kinetic experiments indicated that this shaking time is sufficient to reach the sorption equilibrium.

After shaking, the manganese ion concentration in the solution was determined before and after the tests using a Perkin-Elmer AAnalyst 300 spectrophotometer, equipped with deuterium corrector and air-acetylene flame and controlled by an IBM computer, at 279.5 nm. All tests were performed in duplicate at three different temperatures: 298 K, 313 K and 328 K.

The metal uptake was calculated by mass balance:

$$q_e = \frac{(C_0 - C_e) V}{w 1000}$$

[Equation 1]

where C_0 is the initial metal concentration (mmol/L), C_e is the metal concentration at equilibrium (mmol/L), q_e is the metal uptake at equilibrium (mmol metal ion/g *Sargassum filipendula*), V is the volume of solution (mL) and w is the mass of biomass (g). Preliminary experiments showed that metal adsorption losses to the flasks and filter paper were negligible.

The effect of initial pH on the equilibrium of manganese ions was investigated by repeating the experimental procedure in the range of pH from 2.0 to 7.0. In these experiments, the initial concentration of manganese ions in solution was 0.36 mmol/L, and the temperature was 298 K. The pH of each solution was adjusted with a 0.10 mol/L NaOH solution or a 0.10 mol/L HCl solution.

Fixed-bed column biosorption

For the fixed-bed experiments, an acrylic column (height: 50.0 cm, inner diameter: 7.0 cm) packed with a fixed-bed of *Sargassum filipendula* biomass (100 g) was used. The column void fraction, ε , was determined by the measure of the void volume (volume of distilled water required to fill the bed), as described by da Silva et al. (2002). At the end of each experiment, the solution present inside the column was removed. The exhaustion of the solution was carried out from the bottom of the column using a minimum period of 24 hrs. Afterwards, a peristaltic pump (Milan Model BP-601) fed the column from a reservoir that contained a defined volume of distilled water. The necessary volume of water to fill the bed was determined initially by the difference between the volume contained in the reservoir and the volume remaining after filling the bed. The column void fraction was calculated using the following equation:

$$\varepsilon = \frac{V_v}{V_b}$$

[Equation 2]

where V_v is the bed void volume and V_b is the bed volume. The sorbent density (r_s) was calculated as

$$\rho_s = \frac{w}{(1 - \varepsilon)V_b}$$

[Equation 3]

The bed porosity was 0.86, and the sorbent density was equal to 370 g/L.

The system was fed upwards with a peristaltic pump Milan Model BP-601 (Colombo, Brazil). The base case investigated is represented by an initial metal concentration of 10.47 mmol/L at pH 5.5 with a flow rate of 50.0 mL/min. Further experiments were later carried out at same flow rate but exploring different initial metal concentration (2.730 and 1.092 mmol/L). The concentration of the effluent stream was monitored by periodic sampling until saturation of the sorbent.

Modeling

Batch biosorption. The basic description of the equilibrium of metal ions between the solution and the biosorbent usually involves the use of sorption isotherms.

In this paper, two traditional isotherms were used to describe the equilibrium behavior of manganese ions and *Sargassum filipendula*: Langmuir and Freundlich isotherms.

Langmuir isotherm is based on the following hypotheses: (i) the solid surface presents a finite number of identical sites which are energetically uniform; (ii) there are no interactions between adsorbed species; and (iii) a monolayer is formed when the solid surface reaches saturation (Ruthven, 1984). The mathematical expression of the Langmuir isotherm is given by:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$$

[Equation 4]

where Q_0 is the maximum amount of metal ion per unit weight of sorbent and K_L is the equilibrium adsorption constant which is related to the affinity of the binding sites.

The Freundlich isotherm is an empirical equation that considers the heterogeneity of the adsorbent surface:

$$q_e = K_F C_e^{1/n}$$

[Equation 5]

where K_F and n are the Freundlich parameters characteristics of the system. In contrast to the Langmuir isotherm, the Freundlich isotherm does not predict the saturation of adsorbent sites.

The adopted procedure for the parameter estimation of both isotherms corresponds to the minimization of the sum of the squares of the errors:

$$\min \sum_i (q_{e,i}^{calc} - q_{e,i}^{exp})^2$$

[Equation 6]

where $q_{e,i}^{calc}$ and $q_{e,i}^{exp}$ are the calculated value and the measured value of the metal uptake, respectively, for the i -th experimental point. It is important to mention that the isotherms were handled in their original forms, without linearization procedures, *i.e.*, the parameter estimation problem corresponds to a nonlinear optimization.

Fixed-bed column biosorption. The metal concentration in a fixed-bed column biosorption unit can be described by a system of partial differential equations, representing mass balances, applied to the fluid stream and to the sorbent. The hypotheses adopted in the system modeling were: (i) trace system (*i.e.* the sorption does not modify the flow velocity), (ii) axial dispersed plug flow, (iii) the metal concentration along the column is described by a unique spatial coordinate (axial profile), (iv) isothermal bed, and (v) the mass transfer is represented by a linear driving force. According to these premises, the balances assumed the following forms (Ruthven, 1984):

$$\frac{\partial C}{\partial t} + v \frac{\partial C}{\partial z} - D_L \frac{\partial^2 C}{\partial z^2} + \rho_s \frac{1-\varepsilon}{\varepsilon} \frac{\partial q}{\partial t} = 0$$

[Equation 7]

$$\frac{\partial q}{\partial t} = k(q_e - q)$$

[Equation 8]

where C is the cation concentration in the aqueous stream (mmol/L), q is the amount of metal retained in the bed per unit mass of sorbent (mmol/g), t is the flow time (s), z is the bed length (m), v is the interstitial fluid velocity (m/s), D_L is the axial dispersion coefficient (m²/s), ρ_s is the sorbent density (g/L), ε is the bed porosity (dimensionless) and k is the overall effective mass transfer coefficient (1/s). In the above equations, the adsorption isotherms correspond to the variable q_e present in the mass transfer driving force term.

The system of differential equations of the mathematical model is associated to a proper set of initial and boundary conditions:

$$t = 0 \rightarrow q = 0$$

[Equation 9]

$$t = 0 \rightarrow C = 0$$

[Equation 10]

$$z = 0 \rightarrow vC_i = vC - D_L(\partial C / \partial z)$$

[Equation 11]

$$z = L \rightarrow (\partial C / \partial z) = 0$$

[Equation 12]

where C_i is the concentration of the inlet stream.

The resolution of the model was performed by the method of lines in which the spatial derivatives were discretized by a finite difference approach, and the resultant system of ordinary differential equations was solved by an adequate computational package (ODEPACK, presented in Scilab software).

The transport parameters D_L and k in the model were determined by a parameter estimation procedure based on the experimental breakthrough curve:

$$\min \sum_i (C_{bed,i}^{calc} - C_{bed,i}^{exp})^2$$

[Equation 13]

where $C_{bed,i}^{calc}$ is the value of the ion concentration of the effluent stream evaluated by the mathematical model at the i -th point and $C_{bed,i}^{exp}$ is the corresponding experimental measure at the i -th point.

RESULTS AND DISCUSSION

Batch biosorption

Experimental data of the batch biosorption were used for parameter estimation of the Langmuir and Freundlich isotherms. The values of the parameters along with the standard deviation and the sum of the squares of the errors are presented in Table 1. The experimental data and calculated isotherms are shown in Figure 1, Figure 2, Figure 3. The results indicated that the Freundlich isotherm provides a better description of the equilibrium.

The experimental data for different temperatures does not show any significant difference, indicating that the biosorption of manganese ions is not affected by the temperature in the range investigated (298 K-328 K) (ANOVA with one factor, $p = 0.05$). Similar trends were observed for the removal of copper(II), cadmium(II) and lead(II) by *Sargassum sp.* (Antunes et al. 2003, Cruz et al. 2004, Martins et al. 2006). The comparison of the removal fraction of manganese at different temperatures presented in Table 2 also confirmed that manganese biosorption is virtually independent of temperature.

A comparison of the sorption capacity of *Sargassum filipendula*, according to the Langmuir isotherm, in relation to other biosorbents for manganese uptake is shown in Table 3. It should be noted that the alternative used in this work presents considerably better performance. Biosorption by brown seaweeds is basically mediated by ion-exchange reactions with protonated groups from the surface of the structural polysaccharides in the seaweeds. The high concentration of carboxyl ions as the main chemical group in alginate polysaccharide renders the biomass its natural ability to concentrate heavy metals. On the other hand, if other types of biomass are considered, such as fungal or bacterial microbial cells the outer and cell wall chemical composition is far more complex than the outer structure of *Sargassum* seaweed. In those cases, the ability to concentrate heavy metals by microbial cells is attributed to the presence of particular molecules, characteristic of each species, and also to the high surface area of microbes in comparison to the seaweeds. This information is discussed in a classical paper on the mechanistic aspects of biosorption (Fourest and Volesky, 1995).

The comparison of the sorption capacity of *Sargassum filipendula* obtained in this work in relation to previous results for different toxic elements, employing *Sargassum sp.* under similar experimental conditions, according to the Langmuir model is shown in Table 4. The sorption capacity of manganese is similar to zinc and lower than the other metals, which is similar to the trend found by Vijayaraghavan et al. (2009).

The effect of pH is presented in Figure 4, where it is shown that the biosorption of manganese ions increased from pH 2.0 to pH 3.0, after which the uptake was independent of pH until pH 7.0 (pH values higher than 7.0 were not tested in order to prevent the precipitation of insoluble manganese hydroxide). The pH level is one of the most important parameters on biosorption of metal ions from aqueous solutions. As to *Sargassum sp.*, its high content of ionizable groups (carboxyl groups from mannuronic and guluronic acids) on the cell wall polysaccharides, makes it, at least in theory, very liable to the influence of the medium's pH (Cruz et al. 2004). At pH 2.0, the biosorption of manganese was inhibited, which was probably a result of the competition between hydrogen and manganese ions for the sorption sites on the biomass surface. Apparently hydrogen ions were preferentially recovered, thus preventing manganese biosorption as a consequence of repulsive forces. With increasing pH values, the carboxyl ligand groups from *Sargassum filipendula* become exposed, consequently increasing the negative charge density on the surface of the biomass and contributing to effective manganese biosorption.

Fixed-bed column

The mathematical model of the system was applied to the laboratory data of the fixed-bed column biosorption. Initially, the equilibrium behavior in the breakthrough model was described according to the Freundlich isotherm, in which the values of the parameters were determined in the batch studies (Table 1). The simulated profile of the breakthrough curve and the corresponding experimental data are shown in Figure 5, in which a significant mismatch is evident.

A careful analysis of the model and its parameters indicated that the source of the problem could be attributed to the equilibrium isotherm. An adequate representation of the behavior of a sorption column is strongly dependent on an accurate evaluation of the equilibrium (Ruthven, 1984).

The description of the partition of a metal ion between a liquid solution and a sorbent by an isotherm in biosorption studies is a widely employed approach. It must be emphasized, however, that the physical phenomenon of the metal-sorbent interactions is not limited to classical adsorption effects, as in the original context where the traditional isotherms were proposed. Thus, the application of isotherms for biosorption studies is useful because it allows mathematical predictions of an assumed equilibrium state, but it is not a real interpretation of the actual phenomenon (Volesky, 2007). Starting from this intrinsic limitation, it should be observed that the difference between batch and continuous conditions may make the utilization of model parameters obtained in one scheme to the other one difficult.

In order to overcome these drawbacks, additional fixed-bed column sorption data were employed to estimate new values for the isotherm parameters. After the bed saturation, the stream concentration can be related to an equilibrium with the total amount of ions retained in the bed. This value can be determined by a mass balance in the bed:

$$q_e = \frac{C_i}{V(1-\varepsilon)\rho_s} F \int_0^{t_f} \left(1 - \frac{C|_{z=L}}{C_i} \right) dt$$

[Equation 14]

where F is the volumetric flow rate in mL/min and the flow time in the integral is also evaluated in min.

Therefore, in order to obtain a new set of isotherm parameters, based on fixed-bed data, two new breakthrough curves were obtained, with initial metal concentrations of 1.092 mmol/L and 2.730 mmol/L. These experimental data together with the first set of data are present in Figure 6. The corresponding new values of the isotherm parameters are shown in Table 5.

In this case, the Langmuir model presented the best fit. A comparison of the isotherms obtained in the batch and the fixed-bed column is depicted in Figure 7, in which it can be seen that the isotherm originated from the fixed-bed column data involves significantly larger uptakes.

This deviation between the batch and the fixed-bed column isotherms was also observed by da Silva et al. (2002) in the removal of copper(II) by *Sargassum* sp., with the same deleterious effect of the batch isotherm in the performance of the predictions of a breakthrough curve model.

The utilization of the new Langmuir parameters in the mathematical model resulted in better fitting, as shown in Figure 8. The estimated values of the transport phenomena parameters were $D_L = 1.09 \cdot 10^{-5}$ m²/s and $k = 8.24 \cdot 10^{-5}$ s⁻¹.

CONCLUDING REMARKS

The current paper presented experimental and simulated data of both the batch and fixed-bed column biosorption of manganese in *S. filipendula*.

The data from the batch experiments described the equilibrium between manganese ions and the sorbent. The corresponding experimental points were analyzed according to the Langmuir and Freundlich isotherms and the parameter estimation procedures indicated that the Freundlich isotherm provided a better fit.

The data from the fixed-bed column studies were employed in an analysis involving a mathematical model of the breakthrough curve. This mathematical model is composed of differential mass balance equations in the fluid and in the sorbent. The fitting of the simulated curve in relation to the experimental points was significantly better when isotherms generated from the fixed-bed column data were employed instead of the isotherms from batch data.

Considering both the experimental and simulated results, it is possible to conclude that *S. filipendula* may be employed to treat wastewaters contaminated with manganese and that simulation tools can be a useful resource in order to complement laboratory data and to help a potential scale-up in the direction of an industrial unit.

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APPENDIX FIGURES

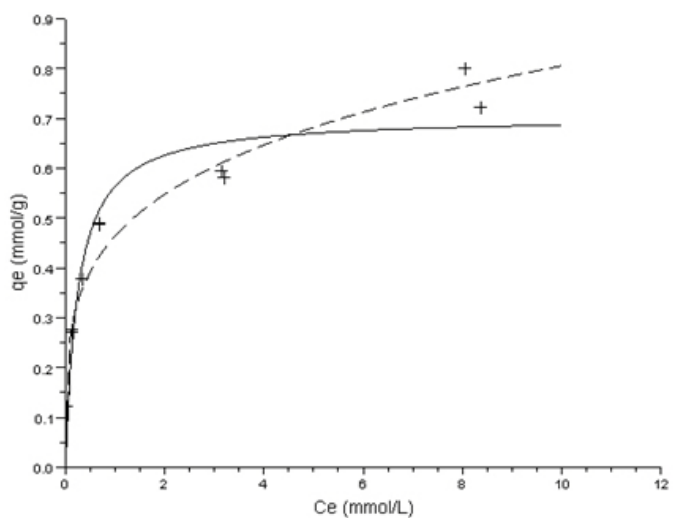


Fig. 1 Isotherms: Experimental data (+), Langmuir (solid line) and Freundlich (dashed line) -298 K.

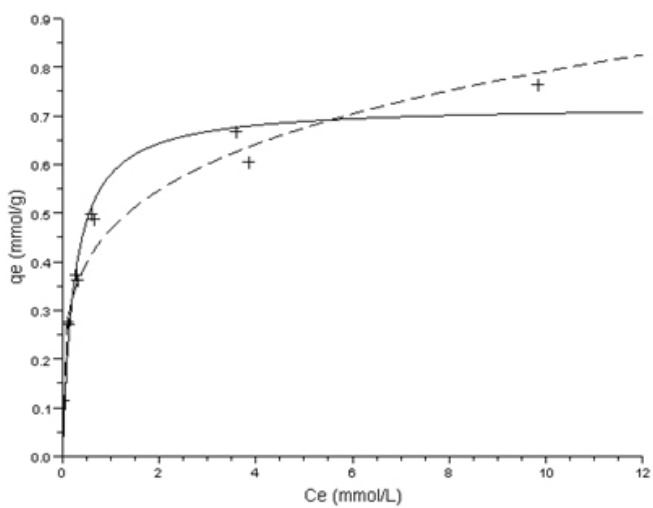


Fig. 2 Isotherms: Experimental data (+), Langmuir (solid line) and Freundlich (dashed line) -313 K.

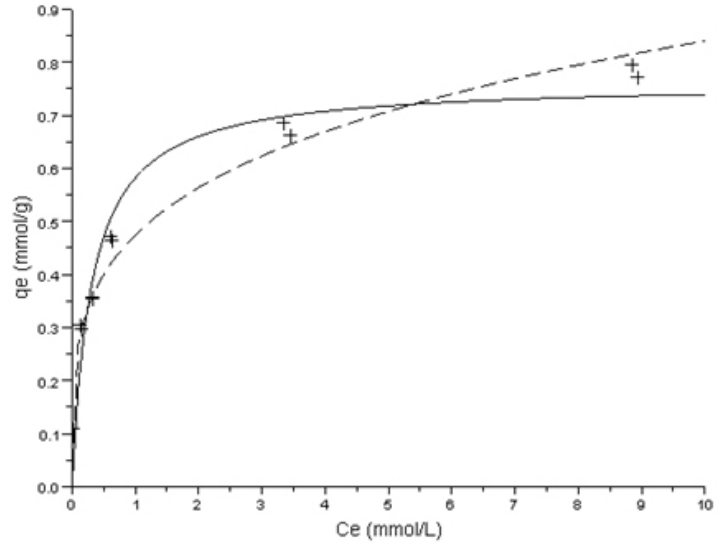


Fig. 3 Isotherms: Experimental data (+), Langmuir (solid line) and Freundlich (dashed line) -298 K.

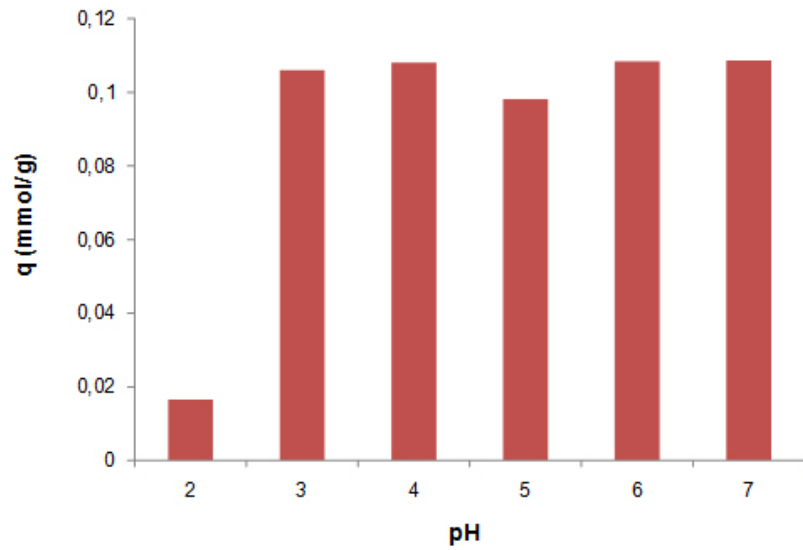


Fig. 4 Effect of initial pH on the biosorption of manganese ions by the seaweed *Sargassum filipendula* ($T = 298$ K, $C_0 = 0.36$ mmol/L).

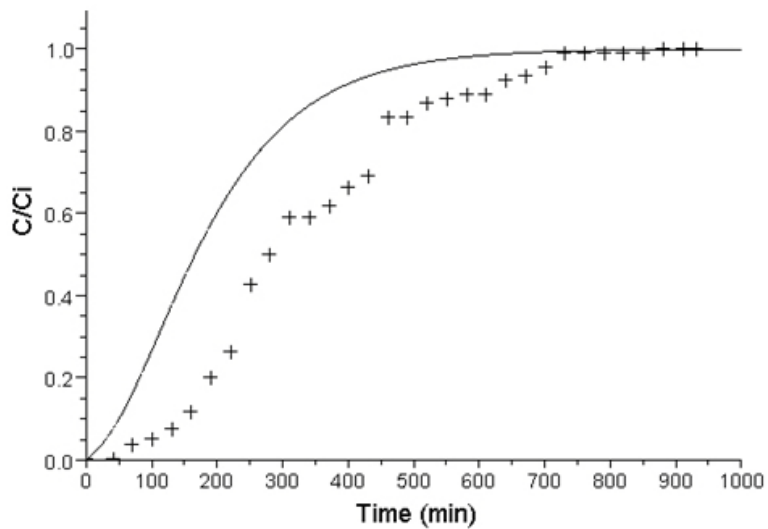


Fig. 5 Breakthrough curve-Freundlich parameters from batch data.

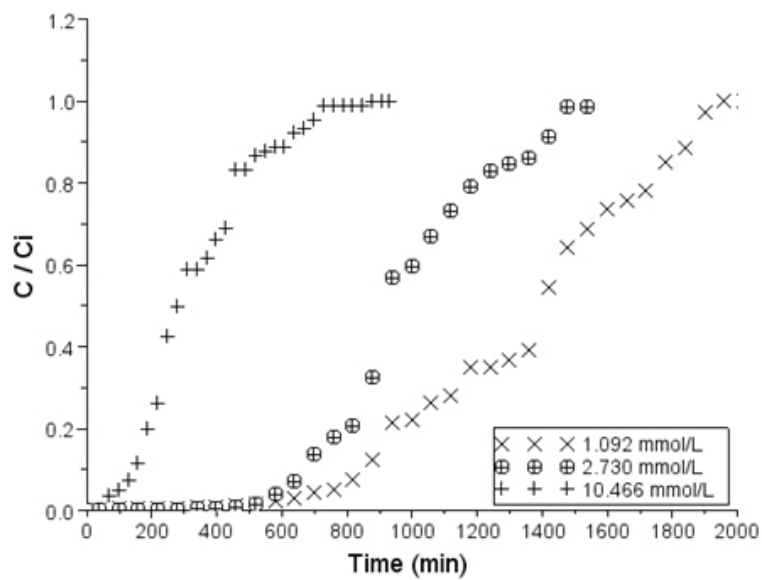


Fig. 6 Set of breakthrough curves.

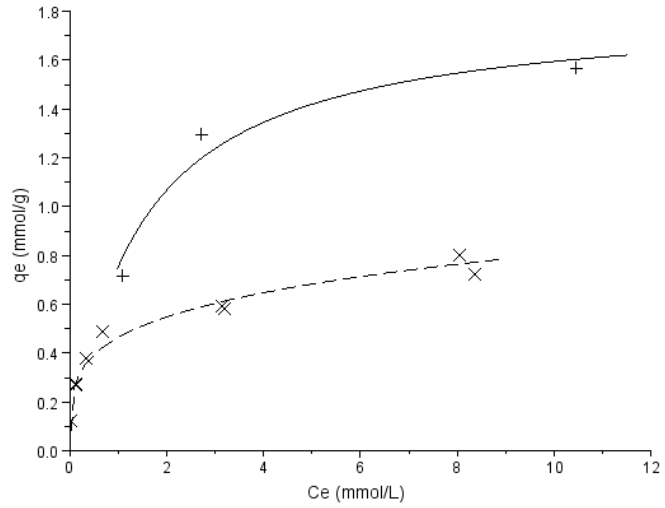


Fig. 7 Comparison between isotherms originated from batch data (dashed line) and fixed-bed column data (continuous line).

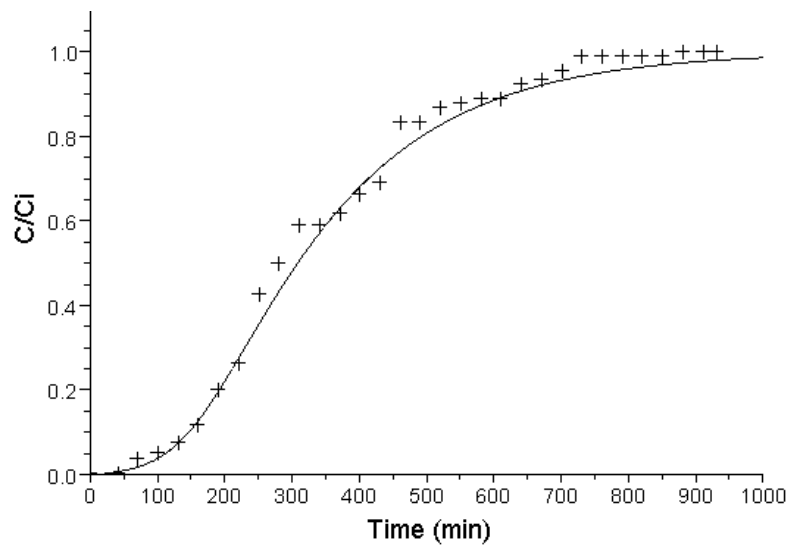


Fig. 8 Breakthrough curve-Langmuir parameters from fixed-bed column data.

APPENDIX

TABLES

Table 1. Adjusted isotherm parameters and corresponding standard deviation-Batch studies.

	Temperature (K)	Q_0 (mmol/g)	K_L (L/mmol)	Sum of the squares of the errors
Langmuir isotherm	298	0.704 ± 0.029	4.02 ± 1.49	0.037
	313	0.722 ± 0.018	4.06 ± 1.23	0.028
	328	0.762 ± 0.015	3.22 ± 0.68	0.031
	Temperature (K)	K_F	N	SSE
Freundlich isotherm	298	0.464 ± 0.042	4.17 ± 0.30	0.024
	313	0.467 ± 0.048	4.37 ± 0.30	0.027
	328	0.474 ± 0.046	4.03 ± 0.30	0.021

Table 2. Removal fraction of manganese at different temperatures*.

298 K	Initial concentration (mmol/L)	0.49	1.22	1.84	2.63	5.52	11.2
	Removal fraction (%)	95.7	89.5	82.3	74.3	42.5	27.1
313 K	Initial concentration (mmol/L)	0.48	1.20	1.77	2.59	6.25	12.9
	Removal fraction (%)	95.8	90.6	82.3	75.9	40.6	23.7
323 K	Initial concentration (mmol/L)	0.45	1.34	1.75	2.49	6.27	12.0
	Removal fraction (%)	95.3	90.0	81.3	75.0	44.2	26.0

*Removal fraction = $1 - (\text{equilibrium concentration} / \text{initial concentration}) \times 100$.

Table 3. Sorption capacity of manganese in different biosorbents.

Biosorbent	Q_0 (mmol/g)	Reference
<i>Sargassum filipendula</i>	0.70	This work
<i>Bacillus</i> sp.	0.24	Hasan et al. (2010)
<i>Sargassum</i> sp.	0.37	Vijayaraghavan et al. (2009)
<i>Pseudomonas aeruginosa</i>	0.41	Silva et al. (2009)
<i>Pythium torulosum</i>	0.07	de Souza et al. (2008)
<i>Saccharomyces cerevisiae</i>	0.36	Parvathi et al. (2007)
<i>Aspergillus niger</i>	0.35	Parvathi et al. (2007)

Table 4. Sorption capacity for different metal ions in *Sargassum* sp.

Metal	Q_0 (mmol/g)	Reference
Mn ²⁺	0.70	This work
Cu ²⁺	1.32	Kleinübing et al. (2011)
Ni ²⁺	1.07	Kleinübing et al. (2011)
Cd ²⁺	1.03	Luna et al. (2010)
Zn ²⁺	0.69	Luna et al. (2010)
Th ²⁺	2.59 x 10 ⁻³	Picardo et al. (2009)
Zn ²⁺	0.70	Britto et al. (2007)
Pb ²⁺	1.25	Martins et al. (2006)
Cd ²⁺	1.07	Cruz et al. (2004)
Cu ²⁺	1.30	Antunes et al. (2003)

Table 5. Adjusted isotherm parameters-Fixed-bed column studies.

	Temperature (K)	Q_0 (mmol/g)	K_L (L/mmol)	SSE
Langmuir isotherm	298	1.82	0.709	0.016
	Temperature (K)	K_F	n	SSE
Freundlich isotherm	298	0.840	3.591	0.057