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Biosorption of Chromium(III) by Biomass of Seaweed *Sargassum* sp. in a Fixed-Bed Column

ENEIDA SALA COSSICH
Department of Chemical Engineering, Universidade Estadual de Maringá, UEM. Av. Colombo, 5790, CEP: 87020-900, Maringá, PR, Brasil

EDSON ANTONIO DA SILVA
School of Chemical Engineering, West Paraná State University, UNIOESTE, Rua da Faculdade 2550, Jardim La Salle, CEP: 85903-000, Toledo, PR, Brasil

CÉLIA REGINA GRANHEN TAVARES AND LÚCIO CARDOZO FILHO
Department of Chemical Engineering, Universidade Estadual de Maringá, UEM. Av. Colombo, 5790, CEP: 87020-900, Maringá, PR, Brasil

TERESA MASSAKO KAKUTA RAVAGNANI
School of Chemical Engineering, Campinas State University, UNICAMP, Cidade Universitária Zeferino Vaz, Caixa Postal 6066-CEP, 13081-970, Campinas, SP, Brasil

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Abstract. This work aimed at modeling chromium biosorption using the biomass of seaweed *Sargassum* sp. in a fixed-bed column. The mathematical model used was obtained from the mass balance of the component in the liquid phase and in the biosorbent material. The effects of both axial dispersion in the column and the resistance to mass transfer in the solid were considered for the solution of the partial differential equations of the model, using the Galerkin method on finite elements. To represent the equilibrium data of the batch system the Langmuir isotherm were used. The chromium ion adsorption capacity of the seaweed *Sargassum* sp., at a temperature of 30°C and pH 3.5, was 2.61 mmol/g. The model performance was evaluated from experimental data obtained at 30°C for flow rates of 2, 6 and 8 mL/min. The parameters of the model, mass transfer and axial dispersion coefficients, were adjusted from these experimental data. The model proved adequate to describe chromium biosorption dynamics in fixed-bed columns.

Keywords: biosorption, chromium, modeling, fixed-bed column, *Sargassum*

1. Introduction

The environmental impact and building up toxicity of heavy metals have been a cause of great concern in recent years. This has given raise to a significant increase of studies with the objective of effectively developing alternative technologies for the removal of substances from industrial effluents that are potentially noxious to the environment (Cossich, 2000).

Traditional technologies for the removal of heavy metals, especially in low concentrations (below 10 mg/L) are often inefficient and/or expensive, usually generating great volume of sludge containing high level of heavy metals, which need to be disposed of somehow (Wilde and Benemann, 1993).

New technologies are necessary so that the concentration of heavy metals liberated to the environment is within the levels allowed by law, at an acceptable cost. The biosorption, a process by which solids of natural origin or their derivatives are used to retain heavy metals, has great potential to achieve this objective (Wilde and Benemann, 1993; Sandau et al., 1996).

Compared to other technologies, biosorption presents the advantage of a high purity of effluent treated and the low cost of the adsorbent, since they may be obtained from residual products from other industries (e.g. bioproducts of fermentation, pharmaceutical industry), or from naturally abundant biomass seaweed, (sea algae, macrophyites) (Schiewer and Volesky, 1996).

A factor that has encouraged the development of new biosorbent materials using seaweed biomass is its great availability, since the algae can be collected and/ or cultivated in many parts of the world (Yu et al., 1999).

Several studies carried out with seaweed, especially those of the species Sargassum, show that this biomass can bond selectively with several metal cations, such as gold, cadmium, copper, nickel, iron and zinc (Kuyucak and Volesky, 1989; Leusch et al., 1995).

Apart from the facts related to the biomass characteristics, the development of a competitive technology for recovering heavy metals depends also on the kind of operational system employed (Kratochvil and Volesky, 1998).

Volesky (1990) suggests several kinds of reactor configurations for the removal of metals using particles or active biomass powder. Continuous stirred tank reactors are useful when biosorbent in powder form is used. Fluidized bed systems, that operate continuously, demand high flow rate to keep the biosorbent particles in suspension (Muraleedharan et al., 1991).

Operational systems that employ fixed bed columns permit the operation in continuous flow by means of regeneration cycles. After the column saturation, the biosorbent may be regenerated using suitable eluent solutions. The regeneration yields small volumes of concentrated metal solutions, suitable for conventional processes of metal recovery (Kratochvil and Volesky, 1998). The column project is somehow complex because in most cases, besides the choice of the most adequate adsorbate, the effluents of industries contain other components that may hinder the removal efficiency of cations of interest.

Chromium, like the majority of heavy metals, is toxic but it has been widely used in galvanoplasty and tanning industries, and as biocide in electric plants cooling water. Therefore, this work was developed with the objective of modeling the chromium biosorption process by means of the seaweed *Sargassum* sp. biomass in a fixed-bed column, aiming at proposing an alternative treatment for effluents that may contain this pollutant.

2. Model Description

The mathematical model for biosorption of a metal ion in a fixed bed column was obtained by means of the mass balance equations applied to an element of volume of the column in the liquid phase and in the solid phase (biosorbent).

In the model development the following hypothesis were considered:

- Isobaric and isothermic process;
- Constant physical properties;
- Superficial adsorption;
- Negligible radial dispersion.

The mass balance equation for the fluid phase is:

$$\frac{\partial C}{\partial \tau} + \rho_b \frac{1}{\varepsilon_b} \frac{\partial q}{\partial \tau} = -u \frac{\partial C}{\partial \xi} + \frac{1}{\mathrm{Pe}_b} \frac{\partial^2 C}{\partial \xi^2} \tag{1}$$

with the following initial and boundary conditions:

$$C(\xi, 0) = C_0 \tag{2}$$

$$\frac{\partial C}{\partial \xi} = \mathrm{Pe}_b(C(\tau, 0) - C_F) \quad \text{in } \xi = 0 \tag{3}$$

$$\frac{\partial C}{\partial \xi} = 0 \quad \text{in } \xi = 1 \tag{4}$$

To obtain the modeling of the chromium adsorption rate in the biosorbent it is assumed that the driving force for the mass transfer is linear with the concentration for the solid phase (biosorbent), and the adsorption rate is represented by the following equation:

$$\frac{\partial q}{\partial \tau} = -\mathrm{Sh}_m(q - q_{\mathrm{eq}}) \tag{5}$$

with the following initial condition:

$$q(\xi, 0) = q_0 \tag{6}$$

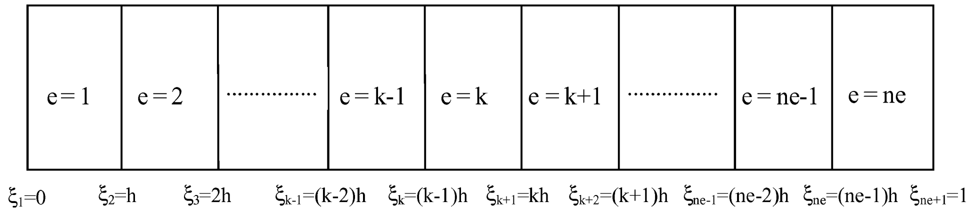

Figure 1. Discretization in the axial coordinate.

The equilibrium concentration of chromium adsorption in the algae (q_{eq}) was calculated by Langmuir isotherm model, described by the following equation:

$$q_{\text{eq}} = \frac{q_{\max}\, b\, C_{\text{eq}}}{1 + b\, C_{\text{eq}}} \tag{7}$$

The domain of the investigated problem, the dimensionless axial coordinate (ξ), was discretized in (ne) elements using the mesh spacing (h) as illustrated in Fig. 1, where

$$h = \frac{1}{ne} \tag{8}$$

The partial differential equation system of the model was solved by the Galerkin Method on finite elements (Chung, 1978; Finlayson, 1980). A mesh with 50 and 100 elements was used in the model discretization. The results obtained for both discretizations were very similar.

The chromium concentration in the bulk fluid phase and the biosorbent were approximated in each element using Lagrange polynomials of degree (n) for trial functions, represented by the following equations:

$$C \approx \tilde{C} = \sum_{k=1}^{ne} \sum_{i=0}^{n} \phi_i^{(k)}(x)\, C_i^{(k)}(\xi, \tau) \tag{9}$$

$$q \approx \tilde{q} = \sum_{k=1}^{ne} \sum_{i=0}^{n} \phi_i^{(k)}(x)\, q_i^{(k)}(\xi, \tau) \tag{10}$$

where

$$\phi_i^{(k)} = \begin{cases} \phi_i(x) & se \quad \xi \in [\xi_k, \xi_{k+1}] \\ 0 & se \quad \xi \notin [\xi_k, \xi_{k+1}] \end{cases} \tag{11}$$

and $\phi_i(x)$ is the base Lagrange polynomial.

Linear, quadratic and cubic polynomial Lagrange base functions are given by Lapidus and Pinder (1982). The use of trial functions that are defined only over part of the region and piece together the adjacent functions provides an approximation over the whole domain, being more advantageous when the solution has steep gradients (Finlayson, 1980). The coefficients of the Lagrange polynomials present in the Eqs. (9) and (10) represent the values of the dependent variables (C, q) at x_i point.

The approximation for the dependent variables by trial functions (Eqs. (9) and (10)) results in a residual which is generally not equal to zero; it is represented by the following equation:

$$R_\Omega = \frac{\partial \tilde{C}}{\partial \tau} + \rho_b \frac{1}{\varepsilon_b} \frac{\partial \tilde{q}}{\partial \tau} + \frac{\partial \tilde{C}}{\partial \xi} - \frac{1}{\text{Pe}_b} \frac{\partial^2 \tilde{C}}{\partial \xi^2} \tag{12}$$

The residual of approximation is forced to be zero, in the average sense, by setting weighed integrals of the residual, represented by the following equation:

$$\int_\Omega w_m\, R_\Omega\, d\Omega = 0; \quad \text{with } m = 0, 1, 2, \ldots, n. \tag{13}$$

where w_m is the weighing function and R_Ω is the residual of approximation.

In the Galerkin Method, the weighing functions are equal to trial functions, thus:

$$w_m(x) = \phi_m(x), \quad \text{with } m = 0, 1, 2, \ldots, n \tag{14}$$

Substituting the Eqs. (12) and (14) into Eq. (13), it is obtained:

$$\int_0^1 \phi_m \frac{\partial \tilde{C}}{\partial \tau} d\xi + \rho_b \frac{1}{\varepsilon} \int_0^1 \phi_m \frac{\partial \tilde{q}}{\partial \tau}\, d\xi + u \int_0^1 \phi_m \frac{\partial \tilde{C}}{\partial \xi}\, d\xi - \frac{1}{\text{Pe}_b} \int_0^1 \phi_m \frac{\partial^2 \tilde{C}}{\partial \xi^2}\, d\xi = 0 \tag{15}$$

Integrating by parts the term of second derivative in Eq. (15), we obtain:

$$\int_0^1 \phi_m \frac{\partial^2 \tilde{C}}{\partial \xi^2}\, d\xi = \phi_m \frac{\partial \tilde{C}}{\partial \xi}\bigg|_0^1 - \int_0^1 \frac{\partial \phi_m}{\partial \xi} \frac{\partial \tilde{C}}{\partial \xi} d\xi \tag{16}$$

Substituting the Eq. (16) into Eq. (15), we found:

$$\begin{aligned}&\int_0^1 \phi_m \frac{\partial \tilde{C}}{\partial \tau} d\xi + \rho_b \frac{1}{\varepsilon} \int_0^1 \phi_m \frac{\partial \tilde{q}}{\partial \tau} d\xi \\ &\quad + u \int_0^1 \phi_m \frac{\partial \tilde{C}}{\partial \xi} d\xi - \frac{1}{\mathrm{Pe}_b} \phi_m \frac{\partial \tilde{C}}{\partial \xi}\bigg|_0^1 \\ &\quad + \frac{1}{\mathrm{Pe}_b} \int_0^1 \frac{\partial \phi_m}{\partial \xi} \frac{\partial \tilde{C}}{\partial \xi} d\xi = 0 \qquad (17)\end{aligned}$$

The contribution of the term $\frac{1}{\mathrm{Pe}_b} \phi_m \frac{\partial \tilde{C}}{\partial \xi}|_0^1$ in Eq. (17) is restricted only to the elements of contour ($k = 1$) or ($k = ne$), due to the definition of the interpolation functions of each element represented by Eq. (11). Thus, these elements are treated separately. The advantage of using this equation is that the boundary conditions automatically appear in the problem formulation.

In order to apply the Galerkin method, it is necessary to solve the following equations:

- for elements ($k = 2, 3, 4, \ldots, ne$):

$$\sum_{i=0}^{n} \alpha_{mi} \frac{dC_i^{(k)}}{d\tau} + \sum_{i=0}^{n} \beta_{mi} \frac{dq_i^{(k)}}{d\tau} + \sum_{i=0}^{n} \gamma_{mi} C_i^{(k)} = 0 \qquad m = 0, 1, 2, \ldots, n \quad (18)$$

- for elements ($k = 1, 2, 3, 4, \ldots, ne$)

$$\frac{\partial q_i^{(k)}}{\partial \tau} = -\mathrm{Sh}_m \left(q_i^{(k)} - q_{\mathrm{eq}}^{(k)} \right) \quad \text{and} \quad i = 0, 1, 2, \ldots, n \quad (19)$$

where:

$$\gamma_{mi} = \int_{-1}^{1} \frac{d\phi_i}{dx} \phi_m dx + \frac{2}{h\mathrm{Pe}_b} \int_{-1}^{1} \frac{d\phi_i}{dx} \frac{d\phi_m}{dx} dx \quad (20)$$

$$\alpha_{mi} = \frac{h}{2} \int_{-1}^{1} \phi_m(x)\, \phi_i(x)\, dx \quad (21)$$

$$\beta_{mi} = \rho_b \frac{1}{\varepsilon_b} \alpha_{mi} \quad (22)$$

- for element ($k = 1$), it is necessary to consider the boundary condition in the inlet of the column in Eq. (17):

$$\begin{aligned}&\sum_{i=0}^{n} \alpha_{mi} \frac{dC_i^{(1)}}{d\tau} + \sum_{i=0}^{n} \beta_{mi} \frac{dq_i^{(1)}}{d\tau} + \sum_{i=0}^{n} \gamma_{mi} C_i^{(1)} \\ &\quad + \phi_m(0)\left(C_0^{(1)} - C_F\right) = 0 \quad m = 0, 1, 2, \ldots, n \qquad (23)\end{aligned}$$

- for element ($k = ne$), it is necessary to consider the boundary condition in the outlet of the column in Eq. (17):

$$\begin{aligned}&\sum_{i=0}^{n} \alpha_{mi} \frac{dC_i^{(ne)}}{d\tau} + \sum_{i=0}^{n} \beta_{mi} \frac{dq_i^{(ne)}}{d\tau} \\ &\quad + \sum_{i=0}^{n} \gamma_{mi} C_i^{(ne)} = 0 \quad \text{and } m = 0, 1, 2, \ldots, n \qquad (24)\end{aligned}$$

In this work, quadratic polynomial Lagrange has been used, therefore, the integrals represented by Eqs. (21) and (22) can be analytically solved. Finlayson (1980) presents the value of these integrals for Lagrange polynomials of degrees one and two.

To generate a global matrix to be solved, some elements of the local matrix must be superposed, because there are nodal points that belong to two consecutive elements. The most detailed procedure to obtain the global matrix may be obtained in Finlayson (1980) and Chung (1978).

The resulting equation system was solved using the DASSL subroutine (Petzold, 1982), whose source code is in the FORTRAN computer language.

The DASSL code solves a system of algebraic/differential equations, and for this it requires an initial set that consists of the dependent variable values and their respective derivatives in relation to time. Thus, it is necessary to modify the feed concentration, transforming it in a continuous function (Madras et al., 1994), represented by the following expression:

$$C_F = C_F(1 - e^{-s\tau}) + C_0\, e^{-s\tau} \quad (25)$$

with $s = 10^{10}$.

The parameters of the model, that is, solid mass transfer (K) and axial dispersion (D_L) coefficients, had their estimated values obtained by minimizing an objective function using the Nelder and Mead method (Nelder and Mead, 1965). The minimized objective function was:

$$F = \sum_{i=1}^{np} \left(C_{\mathrm{out}}^{\mathrm{EXP}} - C_{\mathrm{out}}^{\mathrm{MOD}}(K, D_L) \right)^2 \quad (26)$$

where: $C_{\mathrm{out}}^{\mathrm{EXP}}$—Experimental concentration of the chromium in the outlet of the column; $C_{\mathrm{out}}^{\mathrm{MOD}}$—Concentration of the chromium determined by the solution of the model in the outlet of the column; np—Number of experimental data points.

3. Materials and Methods

3.1. Biomass

The biomass used was the brown seaweed *Sargassum* sp. It was washed in water, rinsed with distilled water and dried in an oven at 60°C for 24 hours. Dry weight of biomass was obtained after drying at 105°C for 24 hours. Dry biomass was chopped and sieved to different fraction sizes. Dry particles with an average diameter of 0.625 mm were used for sorption experiments in batch. Whole biomass (with leaves and thallus) was used for the experiments in fixed bed column.

3.2. Chromium Solution

Chromium solutions were prepared from $CrK(SO_4)_2 \cdot 12H_2O$.

3.3. Sorption Equilibrium Experiments

Batch equilibrium sorption experiments were carried out in 125 mL Erlenmeyer flasks, containing 50 mL of the metal solution (initial concentration range from 2 to 12 mmol/litre), into which 0.14–0.15 g of dry biomass particles were added. The suspensions were agitated on a rotary shaker at 160 rpm at 30°C and pH 3.5. After 48 hours, the sorption equilibrium was reached, the solution was then separated by vacuum filtration and analyzed by atomic absorption spectroscopy. Two runs were carried out, a test with pH correction (fixed at 3.5) and another without correction.

Before and during the sorption experiments, pH was adjusted to 3.5, by adding 0.1 N NaOH or 0.1 N H_2SO_4, as required. This pH value was selected, since Cossich (2000) observed a precipitate formation at pH 4.0 in continuous-flow sorption experiments with *Sargassum* biomass.

Initial and final concentrations of metal ions in the solutions of each flask were measured by atomic absorption spectroscopy (Varian SpectrAA-10 plus).

The equilibrium concentration of metal ion in the solid phase (q_{eq}) was calculated from the initial concentration (C_0) and the equilibrium concentration (C_{eq}), in each flask, using the following equation:

$$q_{eq} = \frac{V(C_0 - C_{eq})}{m_D} \tag{27}$$

where V is the volume of the solution and m_D the biosorbent mass (dry weight).

All equilibrium sorption experiments were carried out in duplicate.

3.4. Continuous-Flow Sorption Column System

Continuous-flow sorption experiments were conducted in a steel column with controlled temperature. The column used had a height of 50 cm and a diameter of 2.8 cm. The bed length used in the experiments was 30.6 cm.

A peristaltic pump fed the chromium(III) solution (pH 3.5) to the bottom of the column with a flow rate of 2, 6 and 8 mL/min. The temperature of stream feeding solution and of the column was controlled at 30°C through a thermostatic bath.

Liquid samples in the exit of the column were collected at pre-defined time intervals. The total concentration of chromium(III) in liquid samples was determined by Atomic Absorption Spectroscopy (Varian SpectrAA-10 plus).

When the system reaches equilibrium, the metal concentration in the fluid phase is constant throughout the column and equal to the feed concentration ($C = C_{eq} = C_F$). The biosorption capacity of the chromium(III) was calculated from the experimental breakthrough curves, using the following equation:

$$q_{eq} = \frac{C_F\, Q}{1000\, m_D} \int_0^t (1 - C|_{z=L}/C_F)\, dt \tag{28}$$

The integral represented by Eq. (28) was analytically solved by means of the polynomial approach of the term $(1 - C/C_F)$.

3.5. Column Void Fraction

The column void fraction, ε_b, was determined by the measure of the void volume (volume of distilled water required to fill the bed), as the methodology proposed by Cossich (2000).

At the end of each experiment, the solution present inside the column was removed. The exhaustion of the solution was accomplished from the bottom of the column using a minimum period of 24 hours. Afterwards, a peristaltic pump (Cole Parmer) fed the column from a reservoir that contained a defined volume of distilled water. The necessary volume of water to fill the bed was initially determined 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:

$$\varepsilon_b = \frac{V_V}{V_b} \tag{29}$$

where V_V is the bed void volume and V_b is the bed volume.

4. Results

4.1. *Chromium Adsorption Isotherms by Seaweed* Sargassum *sp.*

Two runs of chromium ion adsorption by biomass of seaweed *Sargassum* sp. were carried out, as well as a test with pH correction (fixed at 3.5) and another without correction.

Initial and final values of the solution pHs, measured in the determination of the chromium isotherm without pH correction, are presented in Table 1. It may be observed a reduction in pH values, showing that during the adsorption of the chromium ion (III) a hydrolysis reaction occurs, and it is represented by:

$$Cr^{+3} + H_2O \leftrightarrow Cr(OH)^{+2} + H$$

This reaction generates bivalent cations $Cr(OH)^{+2}$ and protons. Since the ion $Cr(OH)^{+2}$ is being removed from the solution by the biomass, the reaction shifts to the right, increasing the solution acidity. The reduction of pH during removal of chromium ion by *Sargassum flutains* biomass was also observed by Kratochvil et al. (1998).

Table 1. Initial concentration and pH (initial and final) of chromium solutions.

Initial concentration (mmol/L)	Initial pH	Final pH duplicate 1	Final pH duplicate 2
2.78	3.47	3.35	3.42
3.32	3.52	3.14	3.12
4.08	3.39	3.01	3.05
4.75	3.42	2.97	3.04
5.46	3.4	3.00	2.97
6.53	3.4	2.97	2.97
8.54	3.36	2.88	2.88

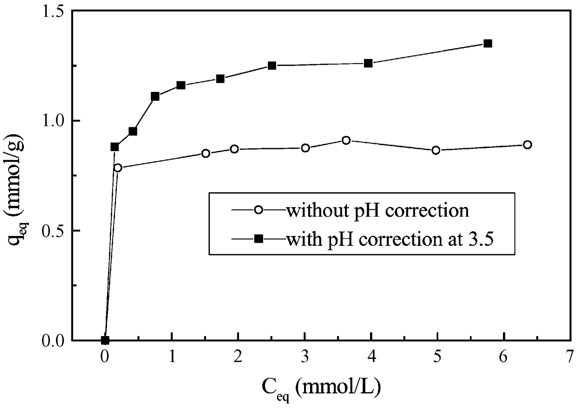

Figure 2. Chromium(III) sorption isotherms for *Sargassum* sp. in the batch system (temperature = 30°C).

Experimental data of adsorption equilibrium of chromium ion by seaweed biomass at 30°C are presented in Fig. 2. It was verified that the quantity of chromium retained by the seaweed biomass was greater when the isotherm was obtained with pH control at pH 3.5.

The pH effect in adsorption is related to the ionic condition of the functional groups of the biosorbent sites, and to the ionic form of metal ions. Reduced values of pH enhance the competition between the metal and H^+ ions by the biosorbent sites. Therefore, an increase in pH reduces the H^+ ion concentration favoring metal ion biosorption. Other factor that improves the removal of the chromium by the biomass is dissociation of carboxyl group. This dissociation promotes the increase of the number of available sites. The carboxyl group has been identified as the main chemical group responsible for the removal of ions by seaweed biomass (Kratochvil and Volesky, 1998).

For modeling the metal adsorption dynamics in a fixed bed column is necessary to know the conditions of the metal sorption equilibrium. Such information can be obtained from the equilibrium data isotherm. The equilibrium data isotherm can be obtained, basically, from experiment in batch or in dynamic columns.

The equilibrium data of chromium(III) biosorption system by seaweed *Sargassum* sp. (at pH 3.5, 30°C) and the Langmuir isotherm model curve obtained by adjusting the experimental data are shown in Fig. 3.

The Langmuir isotherm model constants had their values adjusted by the Maximum Likelihood method (Valkó and Vajda, 1987; Vamos and Haas, 1994). Minimizing the objective function using this method takes

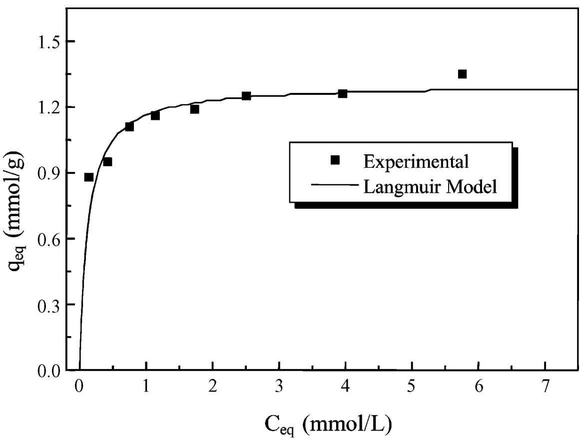

Figure 3. Chromium(III) sorption isotherm for *Sargassum* sp. in the batch system (pH = 3.5; temperature = 30°C).

into account errors involved in the measurement of dependent and independent variables, thus the parameters obtained are more precise. The computer program used was developed by Silva (2001).

The values obtained for $q_{\max}$ e b were 1.31 mmol/g and 8.20 L/mmol, respectively. Similar results were observed by Kratochvil et al. (1998).

Kratochvil et al. (1998) investigated the removal of chromium(III) by the seaweed *Sargassum* biomass in a protonated form. The chromium ion removal capacity was 0.769 mmol/g at pH 4.0. The use of biomass in a protonated form eliminates any other exchangeable ions present on the raw biomass, thereby enabling the study of a simple sorption system. However, this kind of biomass has a smaller number of available sites for ionic change due to acid treatment (Cossich, 2000).

4.2. *Chromium Removal by the Seaweed* Sargassum *sp. in a Fixed-Bed Column*

The results of the experimental and model simulated breakthrough curves, obtained for flow rates of 2, 6 and 8 mL/min are shown in Figs. 4–6.

Table 2 presents the column operational conditions, bed properties and the parameters (mass transfer and axial dispersion coefficients) estimated with the model presented in this article.

The model proposed in this work described adequately the chromium adsorption dynamics by seaweed *Sargassum* sp., independent of the flow rate, as illustrated in Figs. 4–6.

Parameter sensibility analysis showed that the axial dispersion effect may be neglected, a result that is in agreement with that obtained by Silva (2001) and Kratochvil et al. (1997).

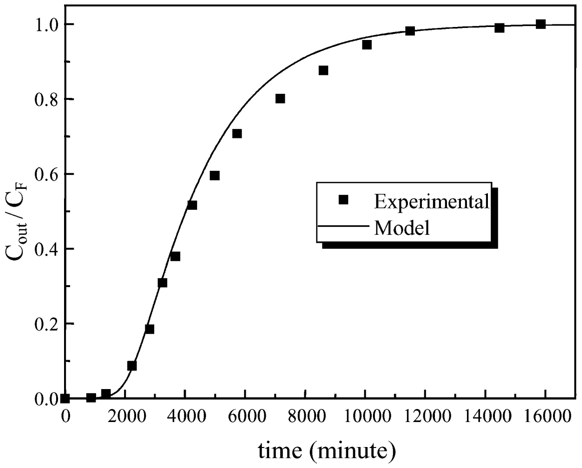

Figure 4. Experimental breakthrough curve and model calculated breakthrough curve for $C_F = 1.04$ mmol/litre ($\rho_b = 42.46$ g/litre; $\varepsilon_b = 0.90$; $Q = 2.0$ mL/min).

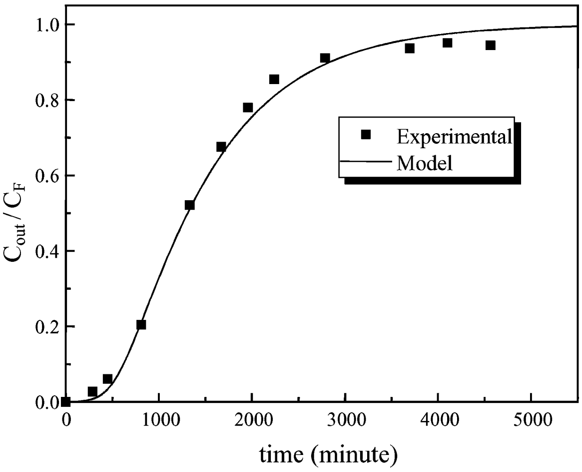

Figure 5. Experimental breakthrough curve and model calculated breakthrough curve for $C_F = 1.01$ mmol/litre ($\rho_b = 42.46$ g/litre; $\varepsilon_b = 0.90$; $Q = 6.0$ mL/min).

Kratochvil et al. (1997) simulated copper adsorption dynamics in a fixed-bed column using biomass of alga *Sargassum fluintans* in a protonated form. The model considers the mechanism of mass transfer in the solid as the controlling step, and the effects of axial dispersion in the bed. The equilibrium condition was represented by means of an ionic exchange isotherm. In the model suggested by Kratochvil et al. (1997) three parameter values were estimated: the mass transfer coefficient in the stationary phase, axial dispersion coefficient,

Table 2. Column operational conditions, bed properties and the parameters estimated with the model.

Flow rate (mL/min)	C_F (mmol/L)	ρ_b (g/L)	ε_b	$K \times 10^3$ (min^{-1})	$D_L \times 10^4$ (cm^2/min)
2	1.04	42.46	0.90	0.49	1.68
6	1.01	42.46	0.90	1.18	1.61
8	1.01	42.46	0.90	1.31	1.70

Table 3. Dynamics column and batch (calculated by Langmuir isotherm) chromium(III) uptake capacity.

Flow rate (mL/min)	q_{eq} (mmol/g) (column)	q_{eq} (mmol/g) (bacth)	Deviation (%)
2	1.28	1.17	8.7
6	1.16	1.16	0.7
8	1.31	1.16	11.4

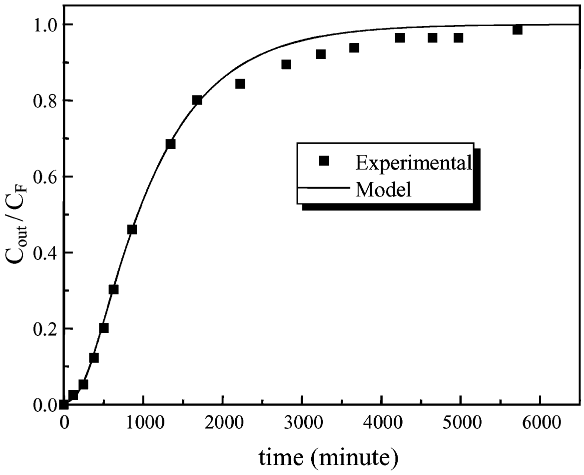

Figure 6. Experimental breakthrough curve and model calculated breakthrough curve for $C_F = 1.01$ mmol/litre ($\rho_b = 42.46$ g/litre; $\varepsilon_b = 0.90$; $Q = 8.0$ mL/min).

and the bed porosity. Although the model proposed by Kratochvil et al. (1997) had three estimated parameters it did not obtain a satisfactory description for all the presented cases.

Matos et al. (1998) simulated the dynamics of chromium biosorption in a fixed-bed columns using "arribadas" seaweed as biosorbent. The suggested model considers the mass transfer in the liquid film as the predominant mechanism and disregards the diffusive term contribution. A linear relation between the concentrations was used to represent the equilibrium between the phases, in the form of Henry's Law. The mass transfer coefficient and the equilibrium constant were estimated. However, experiments were not carried out with different flow rates to verify the effect of axial dispersion.

Silva (2001) investigated the removal of chromium and copper ions by the seaweed *Sargassum* sp. in fixed-bed columns. Three models were evaluated to represent the experimentally obtained breakthrough curves: (i) the first considers the resistance to mass transfer in the film liquid as a controlling step, (ii) the second considers the resistance to mass transfer in the solid as the controlling step, and (iii) the third is based on an empirical kinetics of adsorption. The model based on the resistance to mass transfer in the solid as the controlling step described the biosorption best, independent of ion concentration.

Table 3 shows the experimental values obtained for the chromium equilibrium concentration in the biosorbent column (Eq. (28)), and those calculated by the Langmuir isotherm (Eq. (7)) using estimated parameters from experimental values obtained in batch, as well as the corresponding percentage error.

The proper representation of equilibrium data, by means of isotherms or mathematical expressions that describe the adsorption kinetics, is a necessary condition for a model to successfully represent a fixed bed column operation (Ernest et al., 1997). Thus, it is possible to conclude that the Langmuir isotherm, obtained in batch experiments, represented the column equilibrium, because the percentage errors between the experimental and calculated values obtained for the column were lower than 12%.

5. Conclusion

The chromium ion adsorption capacity of the seaweed *Sargassum* sp., at a temperature of 30°C and pH 3.5, was 1.31 mmol/g.

The used model appropriately represents the chromium ion adsorption dynamics in a fixed-bed column using the seaweed *Sargassum* sp. as biosorbent, and it may be applied to other mono or multicomponent biosorption systems.

The Langmuir isotherm model described adequately the equilibrium condition of the chromium-seaweed *Sargassum* sp. system. Indeed, it is remarkable that a simple Langmuir isotherm model can be used to describe adequately the biosorption equilibrium condition involving ion exchange mechanisms.

The Galerkin method on finite elements, used in the solution of the partial differential equation system, was shown to be a robust and efficient method, since dispersion problems and/or numerical oscillations, common to this type of solutions, were not observed. Results of the modeling of column were not affected by change of discretization mesh.

Nomenclature

a	Transversal section area of the column (cm^2)
b	Langmuir isotherm constant (litre/mmol)
C	Concentration of the chromium(III) in the bulk fluid phase (mmol/litre)
C_0	Initial concentration of the chromium(III) in the bulk fluid phase (mmol/litre)
C_{eq}	Equilibrium concentration of the chromium(III) in the bulk fluid phase (mmol/litre)
C_F	Feed concentration of the chromium(III) in the column (mmol/litre)
D_L	Axial dispersion coefficient (cm^2/min)
K	Overall mass transfer coefficient in the biosorbent $(\text{min})^{-1}$
L	Length of the bed (cm)
m_D	Dry weight of biomass (g)
n	Lagrange polynomial of degree
ne	Number of discretization elements
Q	Volumetric flow rate (mL/min)
q	Concentration of chromium(III) in the algae (mmol/g)
q_0	Initial concentration of the chromium(III) in the algae (mmol/g)
q_{eq}	Equilibrium concentration of chromium(III) in the algae (mmol/g)
$q_{\max}$	Langmuir isotherm parameter (mmol/g)
R_Ω	Residual of approximation
t	Time (min)
u	Velocity ($u = Q\big/a\,\varepsilon_b$) (cm/min)
V	Volume of solution (litre)
V_b	Bed volume (litre)
V_V	Void volume (litre)
w_m	Weighting functions
z	Axial coordinate (cm)
ε_b	Column void fraction
ρ_b	Fixed bed density (g/litre)
ϕ	Trial functions (Lagrange Polynomial)

Dimensionless group

Pe_b	Peclet number for the bed (Lu/D_L)
Sh_m	Sherwood number modified ($K\,u/L$)
τ	Dimensionless time coordinate (tu/L)
ξ	Dimensionless axial coordinate (z/L)

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