

# Multi-metal biosorption in a fixed-bed flow-through column

Ghinwa Naja, Bohumil Volesky\*

Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, Que., Canada H3A 2B2

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## Abstract

Metal-biosorbent biomass of *Sargassum fluitans* brown seaweed biomass is capable of effectively removing toxic heavy metals from aqueous solutions. Involvement of physico-chemical mechanisms including biosorption, precipitation and microbial reductive processes has been established to play important roles in metal immobilization. Biosorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  by *S. fluitans* biomass pre-loaded with  $\text{Ca}^{2+}$  is based on ion exchange mechanism accompanied by a release of  $\text{Ca}^{2+}$  into the solution phase. Carboxylic, sulfonate and phosphonate moieties of the biomass were quantitatively established as being responsible for the sequestering of heavy metals.

Equilibrium biosorption ion exchange isotherms for  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  were determined. Metal biosorption dynamics in a fixed-bed flow-through sorption column was eventually predicted by numerically solving the equations of the ion exchange model proposed. This mathematical model, serving as a basis for sorption process computer simulations, takes into account also the mass transfer process. Computer simulation and prediction of the biosorbent behavior was carried out for sorption systems containing one, two, and multiple metal ionic species. The simulation offers a new and responsive tool for design and meaningful optimization of the metal recovery/removal processes.

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**Keywords:** *Sargassum fluitans*; FEMLAB software; Multi-component metal solutions; Modeling biosorption

## 1. Introduction

Materials of non-living microbial cells play an important role in controlling the mobility and bioavailability of metal ions in aqueous environmental systems [3]. The use of biomass for accumulation and concentration of toxic heavy metals from industrial metal-bearing effluents has been studied for some time [1,19,28]. Biosorption is a process employing dead biomass to sorb heavy metals from aqueous solutions [18]. Low costs and relatively high efficiency of heavy metal removal from diluted solutions are among the leading advantages of biosorption [25].

Ion exchange has been recognized as the principal mechanism of metal biosorption by algal biomass [9]. While only few mathematical models proposed take this fact into account, there have been attempts to predict biosorption in multimetal systems and to model the influence of ionic strength on the binding of toxic metals [23]. Numerical inversion techniques have also been developed to calculate the affinity distributions during metal sorption from experimental data. Various constrained and regu-

larized least-squares algorithms are available in the literature for the solution of such problems [11,15]. Biomass of brown alga (*Sargassum fluitans*), known for its outstanding metal biosorption performance [20], was examined in this work. Investigation of the mechanism responsible for metal immobilization [5] by *Sargassum* requires an interdisciplinary approach.

However, most of the models for flow-through fixed-bed columns reported on in the biosorption literature considered the biosorption process as similar to the adsorption on activated carbon [27]. Recently, also advanced Janson-Charrier's attempt [12] used the Bohart-Adams sorption model [2] developed for sorption on granulated activated carbon (GAC) to analyze the performance of a biosorption column.

The objective of the present work was to model the biosorption of  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  by *S. fluitans* in a flow-through fixed-bed column. It focuses on the simulation-prediction of experimental results by Kratochvil and Volesky [14], studying sorption of divalent cations of Cu, Cd, Zn and their respective mixtures Cu + Zn, Cu + Cd, Cd + Zn, Cu + Zn + Cd by Ca-preloaded *S. fluitans* biomass packed in a sorption column. The model of Tan and Spinner [26] modified by Kratochvil et al. [15] has been adopted and adapted in the present work for sorption systems containing one-, two- and multi-metal mixtures

\* Corresponding author. Tel.: +1 514 3984276; fax: +1 514 3986678.  
E-mail address: [boya.volesky@mcgill.ca](mailto:boya.volesky@mcgill.ca) (B. Volesky).

### Nomenclature

[A]	concentration of A in solution
B	binding site of the biomass
$C_M$	concentration of species M in the liquid phase (meq L <sup>-1</sup> )
$C_0$	normality of the column feed (meq L <sup>-1</sup> )
$D_Z$	dispersion coefficient in the liquid phase (cm <sup>2</sup> min <sup>-1</sup> )
$\varepsilon$	column void fraction
$F$	volumetric flow rate (cm <sup>3</sup> h <sup>-1</sup> )
$K_{fM}$	overall mass transfer coefficient of species M (min <sup>-1</sup> )
$K_{M,Ca}$	exchange equilibrium constant of a metal ion M present in a binary system with calcium
$L_0$	length of the column (cm)
$\rho_b$	packing density of dry biomass in the packed-bed (g L <sup>-1</sup> )
$q_M$	uptake of species M by the biosorbent (meq g <sup>-1</sup> )
$q_M^*$	dimensionless equilibrium uptake of species M at $C_M$
$Q$	concentration of binding sites in the biosorbent (meq g <sup>-1</sup> )
$t$	time (h)
$v$	interstitial fluid velocity (cm min <sup>-1</sup> )
$V_C$	volume of the packed-bed (cm <sup>3</sup> )
$x$	equivalent fraction in the liquid phase related to the total normality of the solution
$y$	equivalent fraction in the solid phase related to the total number of binding sites.

#### Dimensionless groups

$D_{gM} = \rho_b Q / C_0 \varepsilon$  solute distribution parameter

$Pe_c = L_0 v / D_Z$  column Peclet number

$Sh_M = K_{fM} L_0 / v$  modified Sherwood number

of cations. It consists of a coupled system of partial differential, ordinary differential and algebraic equations describing the dynamics of the multicomponent ion exchange in a flow-through fixed-bed.

## 2. Theoretical basis

### 2.1. Equilibrium model

Several biosorption studies reported on in the literature attempted to develop mathematical equilibrium sorption models and to verify their suitability for describing biosorption of Cu by marine algal biomass [4] or the uptake of Cu onto Na-alginate [11]. Ion exchange has been identified and confirmed as the major mechanism involved in heavy metal uptake by organic biomass, and implicitly by algae [10,24]. As a result, ion exchange models have been used for fitting and interpreting the data obtained in both equilibrium and dynamic biosorption experiments [15,22].

Because algal biosorbents, similar to ion exchange resins, can easily be prepared in different ionic forms, also Ca-preloaded algal biomass can be viewed as a simple ion exchanger. Correspondingly, the classical ion exchange concept based on expressing the ion-exchange equilibrium constant can be applied for the case of ideal behavior of the exchanging species in both liquid and solid phases. There could be several types of binding sites on the biomass, each with different characteristics.

Only one type of a binding site was assumed to be functional in the biomass in the present study reacting with ions from the solution. This assumption was verified by the quantification of carboxylic moieties and phosphonate and sulfonate groups considered as the three major binding sites of the type of biomass examined. It was shown that for the pH range examined the contribution of the biomass sulfonate and phosphonate groups could be considered negligible as compared to the contribution of the carboxyl groups [6], allowing the application of this assumption. Correspondingly, the model used in the present study is based on the following equation (1).



where M represents the sorbate metal ion (Cu<sup>2+</sup>, Zn<sup>2+</sup> or Cd<sup>2+</sup>) and B is the binding site of the biomass (Ca loaded).

Based on the sorption system ion exchange reaction reflected in Eqs. (1) and (2) expresses the affinity constant  $K_{M,Ca}$  for the equilibrium uptake of the bivalent metal ion M present in a binary system with calcium.

$$K_{M,Ca} = \frac{[B_2M][Ca^{2+}]}{[M^{2+}][B_2Ca]} \quad (2)$$

Considering that the total number of binding sites,  $Q$  (meq g<sup>-1</sup>), is the sum of the metal and calcium uptakes by the biomass, the affinity constant  $K_{M,Ca}$  could also be expressed by the following Eq. (3).

$$K_{M,Ca} = \frac{[B_2M][Ca^{2+}]}{[M^{2+}](Q - [B_2M])} \quad (3)$$

By rearranging Eqs. (3) and (4) is obtained for describing metal M sorption as a function of the metal  $[M^{2+}]$  and calcium  $[Ca^{2+}]$  concentrations in solution.

$$[B_2M] = \frac{Q K_{M,Ca} [M^{2+}]}{K_{M,Ca} [M^{2+}] + [Ca^{2+}]} \quad (4)$$

The desirable dimensionless equations are obtained by introducing three new parameters  $C_0$ ,  $x$  and  $y$ .  $C_0$  represents the normality of the column feed (meq L<sup>-1</sup>),  $x$  characterizes the equivalent fraction in the liquid phase related to the total normality of the solution and  $y$  is attributed to the equivalent fraction in the solid phase related to the total number of binding sites. Equivalent fractions  $x$  and  $y$  of the metal and calcium are related through Eqs. (5) and (6).

$$x_M + x_{Ca} = 1 \quad (5)$$

$$y_M + y_{Ca} = 1 \quad (6)$$

Upon rearranging Eq. (4) and introducing the three new parameters  $C_0$ ,  $x$  and  $y$ , the model equation for the equilibrium uptake of a bivalent metal ion M present in a binary system with calcium can be written in the form of the following Eq. (7):

$$y_M^* = \frac{K_{M,Ca}x_M}{K_{M,Ca}x_M + (1 - x_M)} = \frac{K_{M,Ca}x_M}{1 + x_M(K_{M,Ca} - 1)} \quad (7)$$

Eq. (7) could easily be generalized and applied even for quaternary systems containing bivalent species M1, M2 and M3. The expressions for uptakes of each of the species can be written as the following Eqs. (8)–(10).

$$y_{M1}^* = \frac{K_{M1,Ca}x_M}{1 + x_{M1}(K_{M1,Ca} - 1) + x_{M2}(K_{M2,Ca} - 1) + x_{M3}(K_{M3,Ca} - 1)} \quad (8)$$

$$y_{M2}^* = \frac{K_{M2,Ca}x_M}{1 + x_{M1}(K_{M1,Ca} - 1) + x_{M2}(K_{M2,Ca} - 1) + x_{M3}(K_{M3,Ca} - 1)} \quad (9)$$

$$y_{M3}^* = \frac{K_{M3,Ca}x_M}{1 + x_{M1}(K_{M1,Ca} - 1) + x_{M2}(K_{M2,Ca} - 1) + x_{M3}(K_{M3,Ca} - 1)} \quad (10)$$

when applying the model to the present study, the constants  $K_{M1,Ca}$ ,  $K_{M2,Ca}$  and  $K_{M3,Ca}$  will be equilibrium binding constants of metals sorbed on *S. fluitans* biomass loaded with  $Ca^{2+}$ . These constants were determined by Kratochvil and Volesky [14] for different metal ions by conducting batch sorption experiments.

The present model provides explicit formulas for metal uptakes as functions of respective final concentrations of the species present in the system. These equations are appropriate for being used in numerical simulations of dynamic sorption column systems.

## 2.2. Sorption column model

While the conventional Bohart–Adams sorption model [12,17], mainly developed for carbon sorption, has often been used in studies of a biosorption column performance, it is not an appropriate model that would reflect the uptake mechanism of ion exchange. Other types of models need to be sought. The most complete column model taking into account also the dominant intraparticle mass transfer was developed for ion exchange by Tan and Spinner [26]. In principle, this mass transfer model can predict breakthrough curves for all of the species being removed by the biosorbent and also the elution curves obtained during sorbent regeneration.

The original model used in the present study to predict biosorption in fixed-bed columns is based on the work of Kratochvil and Volesky [14]. In order to use the model in the present application to studying binary systems as well as ternary and quaternary systems, it had to be adapted. Its transformation allowed testing the modeling approach for the case of multicomponent biosorption systems. The adopted approach consisted on numerically solving a mixed system of partial differential, ordi-

nary differential and algebraic equations describing the dynamics of multicomponent ion exchange in a flow-through fixed-bed.

Assuming isothermal conditions and constant physical properties for the feed solution, the differential molar balance for a sorbate species M is:

$$\frac{C_M}{\partial z} - \frac{1}{Pe_c} \frac{\partial^2 C_M}{\partial z^2} + \frac{\partial C_M}{\partial t} + D_{gM} \frac{q_M}{t} = 0 \quad (11)$$

The sorption rate equation can be written as Eq. (12), assuming a linear driving force for the sorption process and a combined film and intraparticle mass transfer resistance.

$$\frac{\partial q_M}{\partial t} = Sh_M(q_M^* - q_M) \quad (12)$$

With

$$D_{gM} = \frac{\rho_b Q}{C_0 \varepsilon} \quad (13)$$

$$Sh_M = \frac{K_{fM} L_0}{\nu} \quad (14)$$

$$Pe_c = \frac{L_0 \nu}{D_z} \quad (15)$$

where  $t$  is the time (h),  $\rho_b$  the packing density of dry biomass in the packed-bed ( $g L^{-1}$ ),  $Q$  the concentration of binding sites in the biosorbent ( $meq g^{-1}$ ),  $C_0$  the normality of the column feed ( $meq L^{-1}$ ),  $\varepsilon$  the column void fraction,  $L_0$  the length of the column (cm),  $\nu$  the interstitial fluid velocity ( $cm min^{-1}$ ),  $D_z$  the dispersion coefficient in the liquid phase ( $cm^2 min^{-1}$ ),  $Sh_M$  the rate constant for ion exchange ( $min^{-1}$ ),  $C_M$  the concentration of species M in the liquid phase ( $meq L^{-1}$ ),  $q_M$  the uptake of species M by the biosorbent ( $meq g^{-1}$ ),  $q_M^*$  the dimensionless equilibrium uptake of species M at  $C_M$ ,  $D_{gM}$  the solute distribution parameter,  $K_{fM}$  the overall mass transfer coefficient of species M ( $min^{-1}$ ), and  $Pe_c$  is the column Peclet number.

The relationship for a metal species represented by Eqs. (11) and (12) should be solved simultaneously. The specific initial and boundary conditions were specified by Kratochvil and Volesky [14].

The set of two coupled partial differential equations for the case of a binary-component system was solved numerically by using *FEMLAB* multiphysics modeling computer software. For multi-component systems, the number of coupled equations to be solved increases with the number of components. Correspondingly, the complexity of the computational solution for the set of equations is also increased.

In this work, instead of using time on the horizontal axes of relevant diagrams, the dimensionless throughput  $T$  has been adopted for the purpose, defined by Eq. (16):

$$T = \frac{C_0 F t}{\rho_b Q V_c} \quad (16)$$

where  $F$  is the volumetric flow rate ( $cm^3 h^{-1}$ ) and  $V_c$  represents the packed-bed volume ( $cm^3$ ).

### 3. Materials and methods

The dimensionless numbers  $Sh_M$ ,  $D_{gM}$  and  $Pe$ , together with the equilibrium parameters for a given system, represent the parameters of the fixed-bed flow-through sorption column model. The equilibrium parameters can be determined from batch equilibrium studies and the values of  $C_0$ ,  $v$ ,  $L_0$ ,  $Q$  and  $\rho_b$  are usually known or can be calculated. The only remaining unknowns in the model are  $K_{FM}$  and  $D_z$  and they have to be determined simultaneously by fitting the fixed-bed model to an experimental breakthrough curve.

#### 3.1. Biosorbent

The *Sargassum* seaweed biomass used for column sorption experiments was first washed in the laboratory with distilled water until a constant pH and conductivity of the spent rinse water was obtained. Then, the biomass was protonated by washing it with 0.2 M  $H_2SO_4$  followed by a distilled water rinse in a 3.5 L beaker for 3 h until the pH of the rinse water reached a constant value of 4. The subsequent conversion to Ca-biomass was accomplished by another wash with a 0.016 M solution of  $Ca(OH)_2$ . The Ca-biomass was rinsed and dried in the oven overnight at 50 °C before packing inside the column or using it in the batch experiments.

Based on Kratochvil [13], the biosorbent used was characterized by the total number of binding sites  $Q = 2.2 \text{ meq g}^{-1}$  and by the following affinity constants:  $K_{Cu,Ca} = 2.01$ ;  $K_{Zn,Ca} = 0.4524$ ;  $K_{Cd,Ca} = 0.6774$ . The constants were evaluated from batch biosorption equilibrium data as described earlier [13]. According to the values of the constants, the metal species can be arranged in the order of decreasing affinity towards the *Sargassum* biosorbent as follows:  $Cu > Cd > Zn$ .

#### 3.2. Column experiments and modeling

Dry Ca-biomass was packed in a 50 cm long column of 2.5 cm yielding an approximate packing density of 200 g/L [14].

When a column feeding solution containing  $Cu^{2+}$  ( $1 \text{ meq L}^{-1}$ ) was pumped into the column (down-flow manner at a rate of  $4 \text{ cm min}^{-1}$ ), a binary sorption system resulted in conjunction with Ca-loaded biomass. The  $CuSO_4$  solution pH was adjusted to pH 5 using NaOH and was continuously monitored. The pH value was chosen after studying the metal and solid behavior at different pH values.

There were three ternary sorption systems (a–c) simulated in the present work. They resulted when Ca-loaded biomass was used together with a column feed solution (down-flowing at the rate of  $3 \text{ cm min}^{-1}$ ) containing:

- (a)  $Cu^{2+}$  ( $1 \text{ meq L}^{-1}$ ) and  $Zn^{2+}$  ( $0.2 \text{ meq L}^{-1}$ );
- (b)  $Cu^{2+}$  ( $1 \text{ meq L}^{-1}$ ) and  $Cd^{2+}$  ( $0.1 \text{ meq L}^{-1}$ );
- (c)  $Cd^{2+}$  ( $1 \text{ meq L}^{-1}$ ) and  $Zn^{2+}$  ( $0.2 \text{ meq L}^{-1}$ ).

Eventually, the quaternary system studied consisted of the Ca-loaded biomass and a solution, fed into the column from the top at the rate of  $3 \text{ cm min}^{-1}$ , containing  $Cu^{2+}$  ( $2 \text{ meq L}^{-1}$ ),

$Zn^{2+}$  ( $2 \text{ meq L}^{-1}$ ) and  $Cd^{2+}$  ( $2 \text{ meq L}^{-1}$ ). All the solutions used in this work had sulphate ( $SO_4^{2-}$ ) as a counter-ion.

### 4. Results and discussion

#### 4.1. FEMLAB software

With the advance of powerful and small computers, the development of mathematical models capable of describing the sorption column performance is not only essential for analyzing and meaningfully interpreting experimental data, but it can also assist in predicting the response of the sorption system to changing conditions. A contemporary specialized computer software [21] was employed in this work in order to solve the equations of the proposed mathematical model for the metal biosorption process studied.

*FEMLAB* is a powerful tool with an interactive environment for modeling and solving scientific and engineering problems based on partial differential equations [7]. It is the first engineering tool that performs equation-based multiphysics modeling in an interactive environment [30]. Free-form entry of partial differential equations or the use of specialized physics application modes are possible. In its basic configuration, *FEMLAB* offers modeling and analysis power for many different areas of application [16,21] that are characterized by sets of partial differential equations, even for a system of eight coupled equations.

With regard to biosorption modeling, *FEMLAB* was able to solve equation sets for mono- and multi-component systems, using the equations mentioned above, in order to simulate breakthrough curves resulting from operation of flow-through fixed-bed experimental biosorption columns. The results obtained could easily be applied for design and optimization of a large-scale sorption process.

The biosorption process examined here was reflected in a set of partial differential equations developed in a general form suitable for non-linear models. The necessary boundary conditions for the solution of model equations were defined according to Dirichlet and Neumann types suggested and used by the *FEMLAB* software package. Once the equations were inputted through the software interface, and the different constants specified (length of the column, feed concentration, sorbent packing density, the affinity constants, etc.), the computer process simulation could be run whereby the equations are solved very quickly. When solving the set of partial differential equations, the software runs the finite element analysis together with adaptive meshing and error control using a variety of numerical solvers [29].

The column length was divided into appropriately selected elements via different discretizations that were used for the solution procedure to ensure that the model solution and convergence were mesh-independent. It is important that the finite element procedure accurately capture local variations in the solution such as stress concentrations. Comparisons with available experimental data are important to ensure the accuracy and overall performance of the model.

The *FEMLAB* output files were easily transformed to MS-Excel files where the results could easily be graphed and



compared to the experimental data as reported by Kratochvil and Volesky [14]. For the current modeling purposes, all the parameters of the fixed-bed model and specifically the mass-transfer coefficients for all of the ionic species in the system must be known. The values of these coefficients can be estimated, specifically derived [31] or determined by fitting the model to experimental data.

The equilibrium parameters of the proposed model could be determined from batch equilibrium studies and the values of  $C_0$ ,  $v$ ,  $\varepsilon$  (0.82),  $L_0$ ,  $Q$  (2.2 meq/L) and  $\rho_b$  were known from the experimental conditions. The only remaining unknowns in the model were  $K_{fM}$  and  $D_z$  that had to be determined simultaneously by fitting the fixed-bed model to an experimental breakthrough curve, using an optimization-search procedure minimizing the sum of the squares of the relative deviations between the model and the experimental data. The minimization method was performed with respect to the concentration  $C_M$  of species M in the liquid phase.

#### 4.2. Modeling experimental data

As for any continuous-flow sorption process, biosorption of  $\text{Cu}^{2+}$  in a fixed-bed column containing Ca-loaded *S. fluitans* is influenced by both the sorption equilibrium and the mass transfer resistance phenomena. The column experimental data obtained by Kratochvil and Volesky [14] were interpreted through the concept of ion exchange equilibrium isotherms and by taking into account the effect of intra-particle mass transfer, the latter considered as the rate-limiting step.

The experimental breakthrough curve (Fig. 1), obtained for  $\text{Cu}^{2+}$  sorption onto the 50 cm long packing of Ca-biomass, appears to agree very well with the one generated by the proposed model. These results confirm that the model set of equations can be used as a suitable mathematical representation of

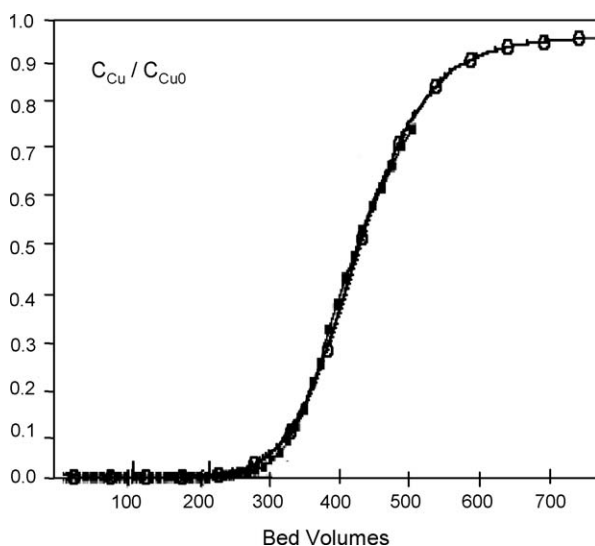


Fig. 1. Comparison of experimental (■) and model (□) breakthrough curves for Ca-*Sargassum* in a sorption column fed with  $1 \text{ meq L}^{-1} \text{ Cu}^{2+}$ . The column length, the biomass packing density and the flow rate were 50 cm,  $4 \text{ cm min}^{-1}$  and  $200 \text{ g/L}$ , respectively.

a biosorption process carried out in a flow-through fixed-bed column.

The  $C/C_0$  maximum value, the service time of a column and the slope of the breakthrough curves can all be well estimated from the simulation. The model breakthrough in Fig. 1 yields important information from the process feasibility standpoint by providing a perfect simulation of the breakthrough curve. It could provide the basis for process optimization. This type of information is essential for scaling up of the biosorption process to an industrial level and for estimating the process feasibility.

When there is more than one metal in the solution, the sorption models reported in the literature for such cases very often become more problematical with non-converging equation solutions. The assessment and prediction of the sorption performance for these systems then becomes more complicated or just simply impossible. The contribution of this work is in the applicability of the present process model that is not limited to binary systems and could conveniently be applied to three and multi-component solution systems.

Figs. 2–4 depict the breakthrough curves obtained with more complicated ternary metal mixtures consisting of ( $\text{Cu}^{2+}$ – $\text{Zn}^{2+}$ ), ( $\text{Cu}^{2+}$ – $\text{Cd}^{2+}$ ), and ( $\text{Cd}^{2+}$ – $\text{Zn}^{2+}$ ). The experimental breakthrough concentration profiles are compared in these figures with breakthrough curves predicted and calculated by the model.

The column feed mixtures were fed individually into sorption columns packed with Ca-preloaded biosorbent. The concentration of  $\text{Cu}^{2+}$  in the ( $\text{Cu}^{2+}$ – $\text{Zn}^{2+}$ ), and the ( $\text{Cu}^{2+}$ – $\text{Cd}^{2+}$ ) mixtures was  $30 \text{ mg L}^{-1}$  ( $\sim 0.5 \text{ mmol L}^{-1}$ ) and the concentrations of Zn and Cd in these mixtures were approximately  $4 \text{ mg L}^{-1}$ . The ( $\text{Cd}^{2+}$ – $\text{Zn}^{2+}$ ) mixture contained  $50 \text{ mg L}^{-1}$  ( $\sim 0.5 \text{ mmol L}^{-1}$ ) of  $\text{Cd}^{2+}$  and  $4 \text{ mg L}^{-1}$  of  $\text{Zn}^{2+}$ . The flow rate, the biomass packing

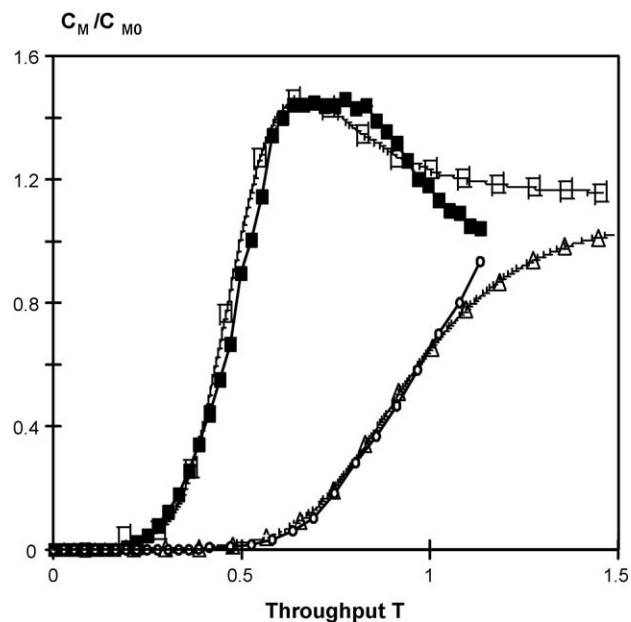


Fig. 2. Comparison of experimental (○, ■) and model (△, □) breakthrough curves for Ca-*Sargassum* and feed containing  $1 \text{ meq L}^{-1} \text{ Cu}^{2+}$  and  $0.2 \text{ meq L}^{-1} \text{ Zn}^{2+}$ , respectively. The column length, the biomass packing density and the flow rate were 50 cm,  $3 \text{ cm min}^{-1}$  and  $200 \text{ g/L}$ , respectively.

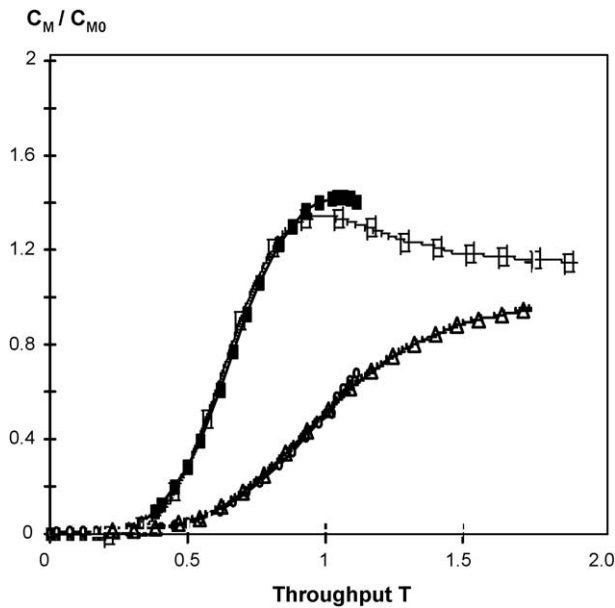


Fig. 3. Comparison of experimental ( $\circ$ ,  $\blacksquare$ ) and model ( $\triangle$ ,  $\square$ ) breakthrough curves for Ca-Sargassum and feed containing  $1 \text{ meq L}^{-1} \text{ Cu}^{2+}$  and  $0.1 \text{ meq L}^{-1} \text{ Cd}^{2+}$ , respectively. The column length, the biomass packing density and the flow rate were  $50 \text{ cm}$ ,  $3 \text{ cm min}^{-1}$  and  $200 \text{ g/L}$ , respectively.

density and the height of the packing were kept constant for all experiments.

The experimental breakthrough curves compare very well with the results calculated after solving two systems of two partial differential equations. Figs. 2 and 3 (modeling and experimental) show that for feeds containing  $\text{Cu}^{2+}$ , the column effluent concentrations of heavy metals  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  tend to overshoot the normal maximum dimensionless value of 1. This exit

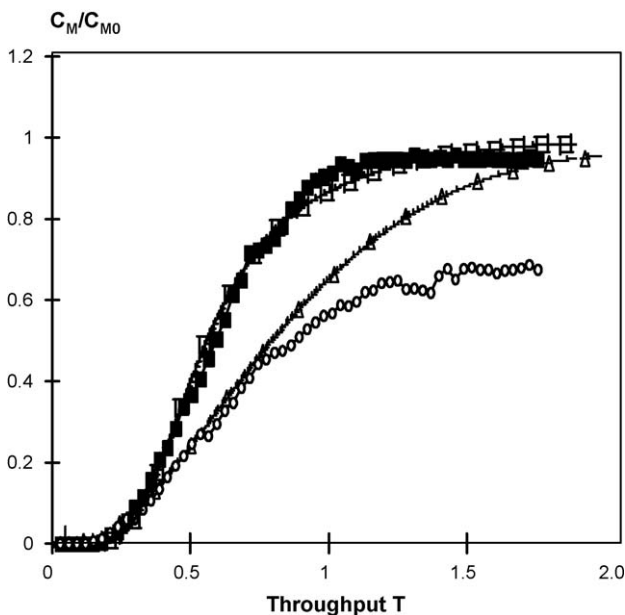


Fig. 4. Comparison of experimental ( $\circ$ ,  $\blacksquare$ ) and model ( $\triangle$ ,  $\square$ ) breakthrough curves for Ca-Sargassum and feed containing  $1 \text{ meq L}^{-1} \text{ Cd}^{2+}$  and  $0.2 \text{ meq L}^{-1} \text{ Zn}^{2+}$ , respectively. The column length, the biomass packing density and the flow rate were  $50 \text{ cm}$ ,  $3 \text{ cm min}^{-1}$  and  $200 \text{ g/L}$ , respectively.

concentration overshoot, observed also in earlier studies [8], is caused by the copper ion affinity for the biosorbent that is much higher than that of Cd or Zn causing the gradual replacement of these ions inside the column by Cu. Many models reported in the literature just could not reflect the concentration overshoot.

However, Fig. 4 reveals that  $\text{Zn}^{2+}$  did not overshoot upon exiting the column when it was fed into the column in the mixture with  $\text{Cd}^{2+}$ . That was because the affinities of those two metal ions are somewhat closer together and the amount of Zn in the feed was relatively small to produce a significant concentration wave.

The model not only confirmed the existence of the exit concentration overshoots of  $\text{Zn}^{2+}$  for the ( $\text{Cu}^{2+} + \text{Zn}^{2+}$ ) mixture and of  $\text{Cd}^{2+}$  in the ( $\text{Cu}^{2+} + \text{Cd}^{2+}$ ) mixed system, both sorbing onto Ca-biomass, but it also yielded a very good estimate of the  $C/C_0$  maximum value as can be seen in Figs. 2 and 3. It may be concluded that this model, in conjunction with *FEMLAB*, could serve as a very useful tool for examining multi-metal biosorption in dynamic flow-through systems.

The model breakthrough curves in Figs. 2–4 yield important information from the process feasibility stand-point by providing the time intervals between the breakthroughs of the individual components. The exit concentration overshoots translate as concentration wave extremes inside the column.

As the *FEMLAB* solution for the partial differential equations of the biosorption model is capable of illustrating the computer simulation results of dynamic sorption this was attempted for an equimolar feed stream. A multi-component solution containing an equimolar mixture of  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ( $2 \text{ meq L}^{-1}$  each), i.e.  $x_{\text{Cu}^{2+}} = x_{\text{Cd}^{2+}} = x_{\text{Zn}^{2+}} = 0.33$  was pumped through a Ca-Sargassum packed column. The sorption behavior results

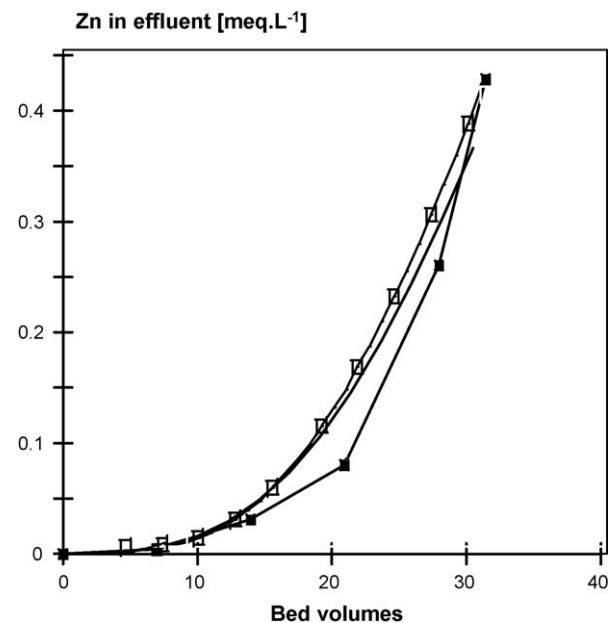


Fig. 5. Comparison of experimental ( $\blacksquare$ ) and model ( $\square$ ) Zn breakthrough curves for Ca-Sargassum and feed containing  $2\text{--}2 \text{ meq L}^{-1} \text{ Cu}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . The straight line corresponds to the Kratochvil model [14]. The column length, the biomass packing density and the flow rate were  $50 \text{ cm}$ ,  $3 \text{ cm min}^{-1}$  and  $200 \text{ g/L}$ , respectively.

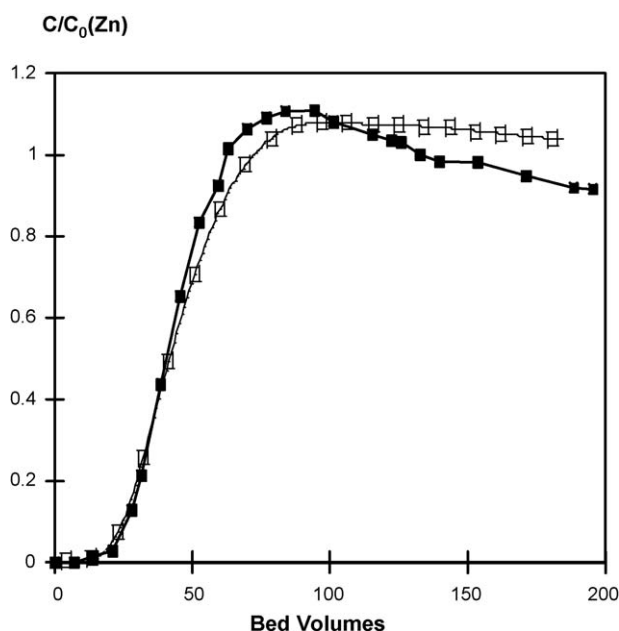


Fig. 6. Comparison of experimental (■) and model (□) Zn breakthrough curves for Ca-*Sargassum* and feed containing 2–2–2 meqL<sup>-1</sup> Cu<sup>2+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup>. The column length, the biomass packing density and the flow rate were 50 cm, 3 cm min<sup>-1</sup> and 200 g/L, respectively.

of model-based calculations are compared to experimental breakthrough curves in Figs. 5 and 6. Both types of curves are in very good agreement.

Furthermore, Fig. 5 shows the results of the calculations obtained by *FEMLAB* solving the system of equations presented in the present work and those obtained by Kratochvil and Volesky [14]. In order to avoid dealing with eight coupled differential equations, Kratochvil and Volesky [14] considered the system only as a binary one (Ca<sup>2+</sup> + Zn<sup>2+</sup>) and simulated it as such. The simulation halted early at one point, running into non-converging solution problems. Only the early stage of the resulting simulated breakthrough curve of Zn<sup>2+</sup> is compared in Fig. 5 to the corresponding stage of the breakthrough obtained experimentally from the four-component system (Cu<sup>2+</sup>–Cd<sup>2+</sup>–Zn<sup>2+</sup>–Ca<sup>2+</sup>).

Successful solution of eight coupled differential equations using *FEMLAB* demonstrated not only that the numerical solution can converge in this case (Fig. 6) but it also resulted in a better approximation of the experimental data by the computer-simulated sorption column breakthrough curve (Fig. 5).

## 5. Conclusion

The major advantage of the *FEMLAB* software used for solving the present model is that it can simulate and predict the performance of a (bio)sorption column operating under various conditions, including different flow rates, feed compositions, column sizes, bed porosities and ionic forms of the biosorbent. This model can thus assist in a meaningful study and design of the biosorption process by:

- (1) selecting the conditions under which to run pilot tests, and

- (2) simulating the performance of the final design based on the results of these tests.

This overall performance simulation of flow-through sorption columns is also necessary for estimation of the length and shape of the active dynamic ion-exchange zone that develops during sorption and regeneration, affecting the overall column utilization and process economics.

There may be only one disadvantage of the *FEMLAB* software in the fact that, theoretically, all the parameters of the fixed-bed sorption column model and specifically the mass-transfer coefficients for all of the ionic species in the system must be known. Consequently, the values of these coefficients need to be estimated, specifically derived or determined by fitting the model to experimental data.

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## References

- [1] B.W. Atkinson, F. Bux, H.C. Kusan, Considerations for application of biosorption technology to remediate metal-contaminated industrial effluents, *Water SA* 24 (1998) 129–135.
- [2] G.S. Bohart, E.Q. Adams, Some aspects of the behavior of charcoal with respect to chlorine, *J. Am. Chem. Soc.* 42 (1920) 523–544.
- [3] C.L. Brierley, J.A. Brierley, Immobilization of biomass for industrial application of biosorption, in: A.E. Torma, M.L. Apel, C.L. Brierley (Eds.), *Biohydrometallurgical Technologies*, Proceedings of the International Biohydrometallurgy Symposium, vol. 2, The Minerals, Metals & Materials Society, Warrendale, Pennsylvania, 1993, pp. 35–44.
- [4] K.H. Chong, B. Volesky, Description of two-metal biosorption equilibria by Langmuir-type models, *Biotechnol. Bioeng.* 47 (1995) 451–460.
- [5] T.A. Davis, C.E. Martimbeau, A. Mucci, B. Volesky, Bioremediation of mercury in aquatic environments by the marine algae *Sargassum fluitans*, in: V.S.T. Ciminelli, J.O. Garcia (Eds.), *Biohydrometallurgy: Fundamentals, Technology and Sustainable Development*. Part B. Biosorption and Bioremediation, Elsevier Science B.V., Amsterdam, 2001, pp. 155–163.
- [6] S. Deng, Y.P. Ting, Fungal biomass with grafted poly(acrylic acid) for enhancement of Cu(II) and Cd(II) biosorption, *Langmuir* 21 (2005) 5940–5948.
- [7] J.M. Drake, Technological tools, *Ecol. Soc. Am. Bull.* 3 (2003) 193–195.
- [8] M.M. Figueira, B. Volesky, K. Azarian, V.S.T. Ciminelli, Biosorption column performance with a metal mixture, *Environ. Sci. Technol.* 34 (2000) 4320–4326.
- [9] B. Greene, J.L. Gardea-Torresday, J.M. Hosea, R.A. McPherson, D.W. Darnal, Algal ion exchangers for waste metal reclamation, in: *Chemical and Biological Detoxification of Hazardous Wastes*, Lewis, Chelsea, Michigan, 1990.
- [10] V.K. Gupta, A.K. Shrivastava, N. Jain, Biosorption of chromium(VI) from aqueous solutions by green algae *Spirogyra* species, *Water Res.* 35 (2001) 4079–4085.
- [11] L.K. Jang, D. Nguyen, G.G. Geesey, Selectivity of alginate gel for Cu vs. Co., *Water Res.* 29 (1995) 307–313.
- [12] M. Jansson-Charrier, E. Guibal, J. Roussy, R. Surjous, P. LeCloirec, Dynamic removal of uranium by chitosan: influence of operating parameters, *Water Sci. Technol.* 34 (1996) 169–177.
- [13] D. Kratochvil, A study of the metal biosorption process utilizing *Sargassum* seaweed biomass, Ph.D. thesis, Chemical Engineering, McGill University, 1997.

- [14] D. Kratochvil, B. Volesky, Multicomponent biosorption in fixed beds, *Water Res.* 34 (2000) 3186–3196.
- [15] D. Kratochvil, B. Volesky, G. Demopoulos, Optimizing Cu removal/recovery in a biosorption column, *Water Res.* 31 (1997) 2327–2339.
- [16] D.P. Mahoney, Innovative Interfaces, *Computer Graphics World* 23 (2000).
- [17] T.R. Muraleedharan, L. Philip, L. Iyengar, C. Venkobachar, Application studies of biosorption for monazite processing industry effluents, *Bioresour. Technol.* 49 (1994) 179–186.
- [18] G. Naja, C. Mustin, J. Berthelin, B. Volesky, Lead biosorption study with *Rhizopus arrhizus* using a metal-based titration technique, *J. Colloid Interface Sci.* 292 (2005) 537–543.
- [19] G. Naja, C. Mustin, B. Volesky, J. Berthelin, A high resolution titrator: a new approach to studying binding sites of microbial biosorbents, *Water Res.* 39 (2005) 579–586.
- [20] M.C. Palmieri, B. Volesky, O. Garcia Jr., Biosorption of lanthanum using *Sargassum fluitans* in batch system, *Hydrometallurgy* 67 (2003) 31–36.
- [21] F.W. Ramirez, *Computational Methods for Process Simulation*, Butterworths, Boston, 1989.
- [22] S. Schiewer, B. Volesky, Ionic strength and electrostatic effects in biosorption of divalent metal ions and protons, *Environ. Sci. Technol.* 31 (1997) 2478–2485.
- [23] S. Schiewer, B. Volesky, Modeling of multi-metal ion exchange in biosorption, *Environ. Sci. Technol.* 30 (1996) 2921–2927.
- [24] D. Schmitt, A. Müller, Z. Csögör, F.H. Frimmel, C. Posten, The adsorption kinetics of metal ions onto different microalgae and siliceous earth, *Water Res.* 35 (2001) 779–785.
- [25] S.M. Siegel, M. Galun, B.Z. Siegel, Filamentous fungi as metal biosorbent. A review, *Water Air Soil Pollut.* 53 (1990) 335–344.
- [26] H.K.S. Tan, I.H. Spinner, Multicomponent ion exchange column dynamics, *Can. J. Chem. Eng.* 72 (1994) 330–341.
- [27] E.M. Trujillo, T.H. Jeffers, C. Ferguson, H.Q. Stevenson, Mathematically modeling the removal of heavy metals from wastewater using immobilized biomass, *Environ. Sci. Technol.* 25 (1991) 1559–1565.
- [28] B. Volesky, *Sorption and Biosorption*, BV Sorbex, Montreal, Canada, 2003.
- [29] Y.X. Wu, H.W. Yu, C.B. Ching, Computational fluid dynamics simulation of the adsorption separation of three components in high performance liquid chromatography, *Chromatographia* 55 (2002) 439–445.
- [30] Y.X. Wu, H.W. Yu, C.B. Ching, A computational fluid dynamics study of binary adsorption separation in chromatography, *Chem. Eng. Technol.* 27 (2004) 955–961.
- [31] J. Yang, B. Volesky, Intraparticle diffusivity of Cd ions in a new biosorbent material, *J. Chem. Technol. Biotechnol.* 66 (1996) 355–364.