

PREDICTING METAL BIOSORPTION PERFORMANCE

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ABSTRACT

Heavy metals can be removed from solutions and recovered using physico-chemical mechanisms including biosorption, precipitation and microbial reductive processes. *Sargassum fluitans* brown seaweed biomass is well known for its outstanding metal biosorption performance. Biosorption of Cu^{2+} , Zn^{2+} and Cd^{2+} by *S. fluitans* biomass pre-loaded with Ca^{2+} is based on ion exchange mechanism accompanied by a release of Ca^{2+} into the solution phase. Carboxylic, sulfonate and phosphonate moieties of the biomass were confirmed quantitatively to be involved in the uptake process of heavy metals.

Biosorption equilibrium data for Cu^{2+} , Zn^{2+} and Cd^{2+} were analyzed through the concept of ion exchange sorption isotherms. The dynamics of Cu sorption in a fixed-bed flow-through sorption column was eventually predicted by numerically solving the equations of the ion exchange model proposed taking into account the mass transfer process.

The results allowed computer simulation and prediction of the biosorbent behavior for sorption systems containing one, two, and multiple metal ionic species. The simulation offers a new and responsive tool for application in the metal recovery/removal processes that can thus be meaningfully optimized.

Key words: *Sargassum fluitans*, **FEMLAB** software, Multi-component metal solutions, Modeling biosorption

INTRODUCTION

The influential role of non-living microorganisms in controlling the mobility and bioavailability of metal ions in aqueous environmental systems is well known and has been extensively studied [1-4]. The use of biomass to extract heavy metals from effluents is an area of current research and development activity [5-7]. Biosorption is a process employing a suitable dead biomass to sorb heavy metals from aqueous solutions [8]. The advantages of biosorption are the low cost and the high efficiency of heavy metal removal from diluted solutions [9].

The biomass examined in this work is brown alga of the *Sargassum* family having a metal binding capacity superior to other biosorbents [10]. Interdisciplinary approach is required in order to quantify metal uptake of *Sargassum fluitans* seaweed biomass known for its outstanding metal biosorption performance [11, 12] and to determine the mechanism responsible for metal immobilization [13].

Recently, ion exchange has been recognized as the principal mechanism of metal biosorption by algal biomass [14, 15]. Consequently, mathematical models have been proposed to predict biosorption in multimetal systems and to model the influence of ionic strength on the binding of toxic metals [16, 17]. Numerical inversion techniques have also been developed to calculate the affinity distributions during metal sorption from experimental data. Various constrained and regularized least-squares algorithms are available in literature for the solution of such problems [18, 19].

However, the few models in the literature attempting to model biosorption in flow-through fixed-bed columns are considering the biosorption process as similar to the adsorption on activated carbon [20]. Recently, also Janson-Charrier (1996) [21] used the Bohart-Adams sorption model [22] developed for sorption on granulated activated carbon (GAC) to analyze the performance of a biosorption column.

The objective of this work was to model the biosorption of Cu^{2+} , Zn^{2+} and Cd^{2+} by *S. fluitans* in a flow-through fixed-bed column. This reporting mainly focuses on the simulation-prediction of experimental results by Kratochvil (2000) [23], 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. In the present work, the model of Tan and Spinner [24] modified by Kratochvil [19] has been adopted and adapted for sorption systems containing one-, two- and multi-metal cations. It is based on 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.

THEORETICAL BACKGROUND

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 [25] or the uptake of Cu onto Na-alginate [18]. It has been agreed on that the major mechanism involved in heavy metal uptake by organic biomass, and implicitly by algae, is ion exchange [26-30]. Consequently, ion exchange models have been introduced to fit and interpret the data obtained from both equilibrium and dynamic biosorption experiments [17, 19].

Furthermore, because algal biosorbents, similar to ion exchange resins, can be prepared in different ionic forms, such as the Ca-form, biosorption of metal ions by Ca-preloaded algal biomass can be viewed as a simple ion exchanger. Hence 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.

The model used in the present study assumes the existence of one type of a binding site in the biomass reacting with ions from the solution following equation (1). This assumption was verified by the quantification of carboxylic moieties and sulfonate groups considered as the two major binding sites of the type of biomass examined. It was shown that for the pH range considered the contribution of the biomass sulfonate groups could be considered negligible as compared to the contribution of the carboxyl groups, allowing the application of this assumption.



Where M represents the sorbate metal ion (Cu²⁺, Zn²⁺ or Cd²⁺) and B is the binding site of the biomass (Ca loaded).

Based on the system reflected in equation (1), equation (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⁻¹), 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 equation (3).

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

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

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

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⁻¹), 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. x and y of the metal and calcium are related through equations (5) and (6).

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

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

Rearranging equation (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 equation (7):

$$y^*_M = \frac{K_{M,Ca}x_M}{K_{M,Ca}x_M + (1-x_M)(C_0)} = \frac{K_{M,Ca}x_M}{C_0 + x_M(K_{M,Ca} - 1)} \quad (7)$$

Equation (7) could easily be generalized and applied 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 equations (8), (9) and (10).

$$y^*_{M1} = \frac{K_{M1,Ca}x_M}{C_0 + x_{M1}(K_{M1,Ca} - 1) + x_{M2}(K_{M2,Ca} - 1) + x_{M3}(K_{M3,Ca} - 1)} \quad (8)$$

$$y^*_{M2} = \frac{K_{M2,Ca}x_M}{C_0 + x_{M1}(K_{M1,Ca} - 1) + x_{M2}(K_{M2,Ca} - 1) + x_{M3}(K_{M3,Ca} - 1)} \quad (9)$$

$$y^*_{M3} = \frac{K_{M3,Ca}x_M}{C_0 + x_{M1}(K_{M1,Ca} - 1) + x_{M2}(K_{M2,Ca} - 1) + x_{M3}(K_{M3,Ca} - 1)} \quad (10)$$

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 respectively determined by Kratochvil (2000) [23] for different metal ions by conducting batch sorption experiments.

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

Sorption Column Model

Studies of a biosorption column performance that are reported in the literature commonly use the conventional Bohart-Adams sorption model [21, 31]. However, the most complete column model taking into account the dominant intraparticle mass transfer was developed for ion exchange by Tan and Spinner (1994) [24]. In principle, this Mass Transfer Model can predict breakthrough curves for all of the species being removed by the biosorbent and 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 (2000) [23]. The model was transformed to enable its present application to studying binary systems as well as ternary and quaternary systems. This allowed testing the approach for the case of multicomponent biosorption systems. The adopted approach consisted on numerically solving a mixed system of partial differential, ordinary 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 equation (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:

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

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

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

Where:

t	time	[h]
ρ_b	packing density of dry biomass in the packed-bed	[g.L ⁻¹]
Q	concentration of binding sites in the biosorbent	[meq.g ⁻¹]
C_0	normality of the column feed	[meq.L ⁻¹]
ε	column void fraction	[-]
L_0	length of the column	[cm]
ν	interstitial fluid velocity	[cm.min ⁻¹]
D_z	dispersion coefficient in the liquid phase	[cm ² .min ⁻¹]
Sh_M	rate constant for ion exchange	[min ⁻¹]
C_M	concentration of species M in the liquid phase	[meq.L ⁻¹]
q_M	uptake of species M by the biosorbent	[meq.g ⁻¹]

The relationship for a metal species represented by equations (11) - (12) should be solved simultaneously. The specific initial and boundary conditions are specified in Kratochvil (2000) [23].

In the case of a binary-component system, the set of 2 coupled partial differential equations was solved numerically by using **FEMLAB** multiphysics modeling computer program. 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 of 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 equation (16):

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

Where:

F	volumetric flow rate	[cm ³ .h ⁻¹]
V_c	volume of the packed-bed	[cm 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 model. The equilibrium parameters can be determined from batch equilibrium studies and the values of C_0 , v , L_0 , Q and ρ_B are usually known or can be calculated. The only remaining unknowns in the model are K_{fM} and D_z and have to be determined simultaneously by fitting the fixed-bed model to an experimental breakthrough curve.

Biosorbent

In Kratochvil's experiments [23], the collected *Sargassum* seaweed biomass was first protonated with 0.2M H_2SO_4 , followed by a rinse with distilled water. Next, the conversion of the protonated biomass to Ca-biomass was carried out with a 1.2 g/L solution of $Ca(OH)_2$. The Ca-biomass was dried in the oven overnight at 50°C.

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:

$$\begin{aligned}K_{Cu, Ca} &= 2.01; \\K_{Zn, Ca} &= 0.4524; \\K_{Cd, Ca} &= 0.6774.\end{aligned}$$

The constants were evaluated from batch biosorption equilibrium data as described in [32]. 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 $Cu > Cd > Zn$.

Column Experiments and modeling

In Kratochvil's experiments [23], the dry Ca-biomass was packed in a 50 cm long column of 2.5 cm yielding an approximate packing density of 200 g/L.

The binary sorption system resulted when Ca-loaded biomass was used and a solution containing Cu^{2+} (1 meq.L⁻¹) was fed into the column from the top at a rate of 4 cm.min⁻¹.

Three ternary systems (a-c) will be 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 cm.min⁻¹, containing:

- Cu^{2+} (30 mg.L⁻¹) and Zn^{2+} (4 mg.L⁻¹);
- Cu^{2+} (30 mg.L⁻¹) and Cd^{2+} (4 mg.L⁻¹);
- Cd^{2+} (50 mg.L⁻¹) and Zn^{2+} (4 mg.L⁻¹).

The quaternary system consisted of the Ca-loaded biomass and a solution, fed into the column from the top at the rate of 3 cm.min⁻¹, containing Cu^{2+} (2 meq.L⁻¹), Zn^{2+} (2 meq.L⁻¹) and Cd^{2+} (2 meq.L⁻¹).

RESULTS AND DISCUSSION

FEMLAB Software

The development of mathematical models capable of describing the sorption column performance is not only essential for analyzing and interpreting experimental data, but it can also assist in predicting the response of the sorption system to changing conditions. However, in order to solve the model equations, it is possible nowadays to employ a specialized and powerful computer program [33].

FEMLAB is a powerful tool with an interactive environment for modeling and solving scientific and engineering problems based on partial differential equations [34]. It is the first engineering tool that performs equation-based multiphysics modeling in an interactive environment [35]. Free-form entry of partial differential equations or use specialized physics application modes are possible. In its basic configuration, *FEMLAB* offers modeling and analysis power for many application area problems based on partial differential equations even for a system of 8 coupled equations [33, 36].

Concerning 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 a large-scale process.

The partial differential equations related to biosorption were described in a general form suitable for non-linear models. The boundary conditions for the solution of model equations were defined according to Dirichlet and Neumann types used in *FEMLAB*. 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 simulation can be run whereby the equations are solved very quickly. When solving the partial differential equations, the software runs the finite element analysis together with adaptive meshing and error control using a variety of numerical solvers [37].

Different discretizations dividing the column into elements were used for the solution procedure to ensure that the model solution and convergence were mesh-independent. It is important that the finite element 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 compared to the experimental data as reported by Kratochvil (2000) [23].

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 [38] or determined by fitting the model to experimental data.

Modeling experimental data

The process of Cu^{2+} biosorption 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 (2000) [23] were interpreted through the concept of ion exchange equilibrium isotherms and by taking into account the effect of intra-particle mass transfer, considered as the rate-limiting step.

The relatively good agreement between the theoretical and the experimental breakthrough curves in Figure 1, obtained for Cu^{2+} sorption onto the 40 cm long packing of Ca-biomass, reveals that the present set of equations can be used as a suitable mathematical representation of a biosorption process carried out in a flow-through fixed-bed column.

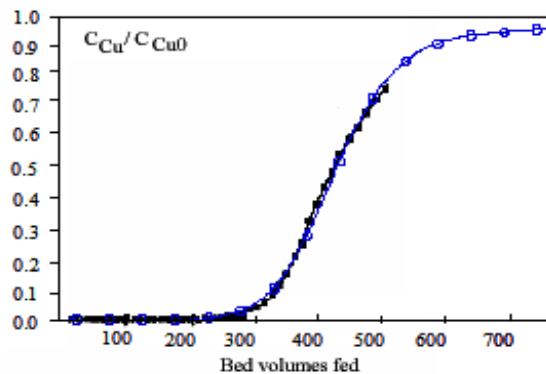


Figure 1. Comparison of experimental (■) and model (□) breakthrough curves for Ca-Sargassum and feed containing 1 meq.L⁻¹ Cu²⁺.

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

Very often models in the literature become more problematical with non-converging solutions when there is more than one metal in the solution. The assessment and prediction of the sorption performance then becomes more complicated or just plain impossible.

The contribution of this work is in the applicability of the present process model that is not limited to binary systems and could be applied to three- and multi-component solution systems.

In Figures 2, 3 and 4, the concentration profiles calculated and predicted by the model are compared to the experimental breakthrough curves obtained for the following mixtures (Cu^{2+} - Zn^{2+}), (Cu^{2+} - Cd^{2+}), and (Cd^{2+} - Zn^{2+}), respectively, fed into columns packed with Ca-preloaded biosorbent. The concentration of Cu^{2+} in the (Cu^{2+} - Zn^{2+}), and the (Cu^{2+} - Cd^{2+}) mixtures was 30 mg.L^{-1} ($\sim 0.5 \text{ mmol.L}^{-1}$), while the concentrations of Zn and Cd in these mixtures were approximately 4 mg.L^{-1} . The (Cd^{2+} - Zn^{2+}) mixture contained 50 mg.L^{-1} ($\sim 0.5 \text{ mmol.L}^{-1}$) of Cd^{2+} and 4 mg.L^{-1} of Zn^{2+} . The flow rate, the biomass packing density and the height of the packing were kept constant for all experiments.

The experimental breakthrough curves were compared to the results calculated after solving two systems of two partial differential equations. Figures 2 and 3 (modeling and experimental) show that for feeds containing Cu^{2+} , the column effluent concentrations of heavy metals Zn^{2+} and Cd^{2+} tend to overshoot the normal maximum dimensionless value of 1. However, Figure 4 reveals that Zn^{2+} did not overshoot when it was fed into the column in the mixture with Cd^{2+} .

As can be seen in Figure 2 and 3, the model not only confirmed the existence of the overshoot of Zn^{2+} for the (Cu^{2+} - Zn^{2+}) mixture and of Cd^{2+} for the (Cu^{2+} - Cd^{2+}) mixed system, both sorbing onto Ca-biomass, but it also yielded a very good estimate of the C/C_0 maximum value. 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 Figures 2, 3 and 4 yields important information from the process feasibility stand-point by providing the time intervals between the breakthroughs of the individual components, and the magnitude of the overshoots that inside the column translate as concentration extremes.

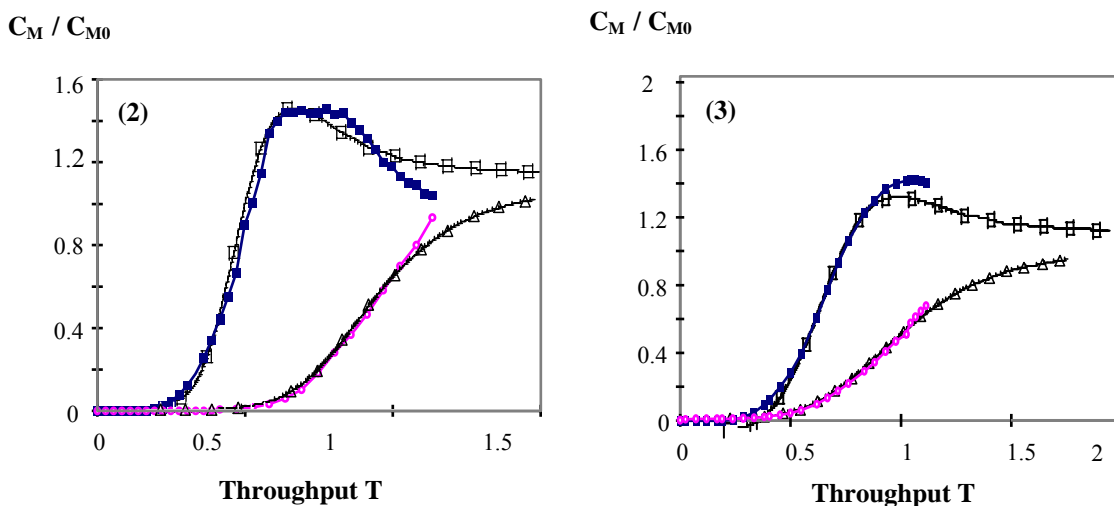


Figure 2. Comparison of experimental (\circ , \blacksquare) and model (\triangle , \square) breakthrough curves for Ca-Sargassum and feed containing $30 \text{ mg.L}^{-1} \text{ Cu}^{2+}$ and $4 \text{ mg.L}^{-1} \text{ Zn}^{2+}$, respectively.

Figure 3. Comparison of experimental (\circ , \blacksquare) and model (\triangle , \square) breakthrough curves for Ca-Sargassum and feed containing $30 \text{ mg.L}^{-1} \text{ Cu}^{2+}$ and $4 \text{ mg.L}^{-1} \text{ Cd}^{2+}$, respectively.

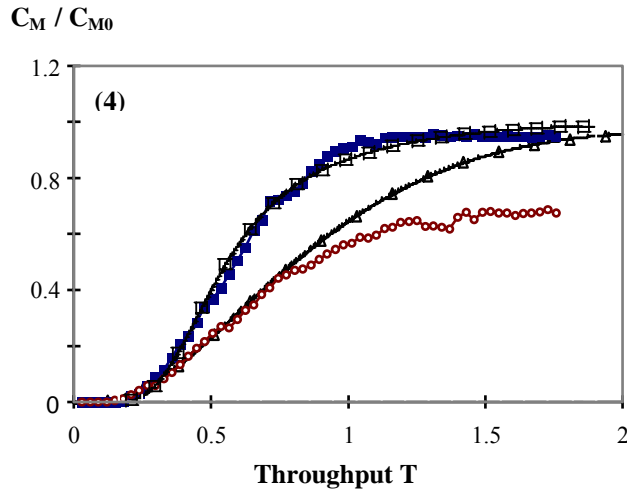
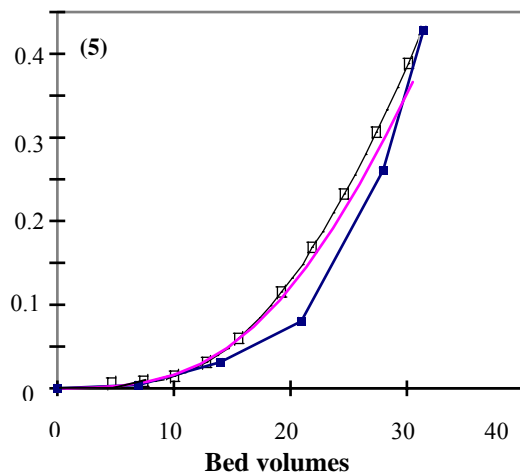


Figure 4. Comparison of experimental (\circ , \blacksquare) and model (\triangle , \square) breakthrough curves for Ca-Sargassum and feed containing $50 \text{ mg.L}^{-1} \text{ Cd}^{2+}$ and $4 \text{ mg.L}^{-1} \text{ Zn}^{2+}$, respectively.

In order to generalize the *FEMLAB* solution of the partial differential equations of the biosorption model, dynamic sorption from a multi-component solution by Ca-Sargassum packed into a column was simulated. A model profile was calculated for feed containing an equimolar mixture of Cu^{2+} , Cd^{2+} and Zn^{2+} (2 meq.L^{-1} each), i.e. $x_{\text{Cu}^{2+}} = x_{\text{Cd}^{2+}} = x_{\text{Zn}^{2+}} = 0.33$. The results of the calculations are shown in Figures 5 and 6 and are in good agreement with the experimental results obtained by Kratochvil (2000) [23].

Furthermore, Figure 5 shows the obtained results of the calculations obtained by *FEMLAB* solving the system of equations presented in the present work and those obtained by Kratochvil (2000) [23]. In order to not deal with 8 coupled differential equations, in his paper, Kratochvil (2000) considered the system only as a binary one (Ca^{2+} - Zn^{2+}) and simulated it as such. The early stage of the resulting simulated breakthrough curve of Zn^{2+} is compared in Figure 5 to the corresponding stage of the breakthrough obtained experimentally from the four-component system (Cu^{2+} - Cd^{2+} - Zn^{2+} - Ca^{2+}). Successful solution of 8 coupled differential equations using *FEMLAB* demonstrated not only that a numerical solution can converge (Figure 6) but it also resulted in a better proximity of the simulation curve to the experimental data (Figure 5).

Zn in effluent [meq.L^{-1}]



C / C_0 (Zn)

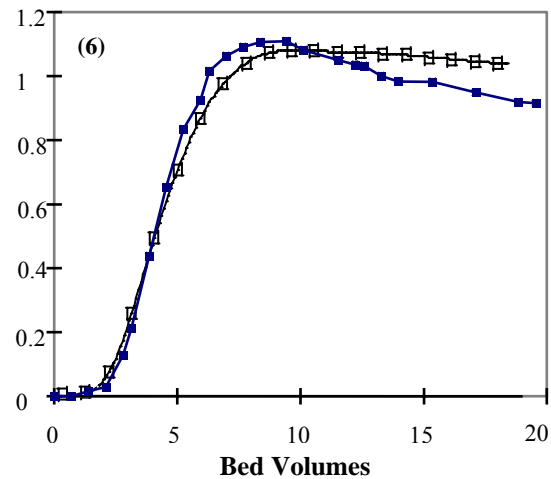


Figure 5. Comparison of experimental (\blacksquare) and model (\square) Zn breakthrough curves for Ca-Sargassum and feed containing $2\text{-}2\text{-}2 \text{ meq.L}^{-1} \text{ Cu}^{2+}$, Zn^{2+} and Cd^{2+} . The straight line corresponds to the Kratochvil model.

Figure 6. Comparison of experimental (\blacksquare) and model (\square) Zn breakthrough curves for Ca-Sargassum and feed containing $2\text{-}2\text{-}2 \text{ meq.L}^{-1} \text{ Cu}^{2+}$, Zn^{2+} and Cd^{2+} .

The major advantage of the *FEMLAB* software used for solving the present model is that it can simulate and predict the performance of a column under various conditions, including different flow rates, feed compositions, column sizes, bed porosities and ionic forms of the biosorbent. Therefore, this model can assist engineers to meaningfully study 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 to estimate the length and shape of the active dynamic ion-exchange zone that develops during sorption and regeneration.

The disadvantage of the *FEMLAB* software is that, theoretically, 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. Consequently, the values of these coefficients need to be estimated, specifically derived [38] or determined by fitting the model to experimental data.

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