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Behavior of the Mass Transfer Zone in a Biosorption Column

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Modeling of the mass transfer zone behavior under variable conditions in a flow-through fixed-bed sorption column enabled the prediction of breakthrough curves for Cu^{2+} and Ca-preloaded *Sargassum fluitans* biomass. The mass transfer resistance, particle diffusion, and the axial dispersion were incorporated in the model. The dynamics of the mass transfer zone was described under variable sorption column operating conditions including different column lengths and fluid flow rates. Accurate estimation of the behavior of the mass transfer zone as it progressed through the column, reflected eventually in the breakthrough curve, assisted in its relevant interpretations. Furthermore, the proposed mathematical model of the biosorption process was capable of demonstrating the expanding and broadening of the mass transfer zone linked to the equilibrium sorption isotherm. The fundamental understanding of the mass transfer zone dynamics is particularly important for process scale-up where maintaining the process efficiency is critical.

Introduction

Biosorption is a process whereby certain types of inactive, dead biomass may bind and concentrate heavy metals from aqueous solutions (*1*, *2*). Many types of biomass including bacteria (*3*), fungi (*4*, *5*), or seaweeds (*6*) possess the ability to sequester significant quantities of metals from an aqueous solution. Large-scale application of biosorption in cleaning metal-bearing industrial effluents is ultimately the impetus for biosorption research (*7*, *8*). The main advantage to using biosorption technology is the cost-effectiveness of using the biosorbent, since it may be derived from various cheap raw materials (*9*, *10*).

Earlier work revealed that Sargassum seaweed has a high efficiency for biosorption removal of toxic heavy metals (*11*). The biomass examined in this work was brown alga of the Sargassum genus having a metal binding capacity superior to other biosorbents. An interdisciplinary and quantitative approach is required to assess the feasibility of using *Sargassum fluitans* seaweed biomass (*12*) in a large-scale process of removing metals from solutions. *Sargassum fluitans* biosorbent, either raw or pretreated very simply, should be used in a continuous-flow sorption column which represents by far the most effective and convenient utilization of the contactor volume (*13*).

The general purpose of the present work was not only to predict the metal binding capacity but also to evaluate the performance of the biosorption column operation under different process conditions. The objective of this work was to model the biosorption of divalent cations Cu^{2+} by Ca-preloaded *S. fluitans* in a flow-through fixed-bed column. Copper has been chosen as a typical toxic heavy metal with simple solution chemistry where the Cu^{2+} cation predominates in pure water solutions at low pH (>99.9% Cu^{2+}). Caution should be taken with more complex media (such as natural running waters, wastewater effluents) at circum neutral pH, as copper speciation might be far from simple physically (strong binding to abiotic particles), chemically (complexation by carbonates, hydroxides, dissolved organic matter, reduced sulfur species, etc.), and biologically (assimilation by bacteria and phytoplankton). Cu^{2+} cations also happen to be well sequestered by *S. fluitans* as indicated in earlier studies (*2*). Copper is a frequent contaminant in wastewaters originating from mining operations (often with Pb, Zn, Ni, and others) or in electroplating effluents (spent baths). Particularly these two types of toxic industrial effluents are quite common and usually relatively well defined where the biosorption process could very effectively be used as a possible alternative technique for removal of copper as well as other heavy metal cations.

A computerized process simulation was carried out to provide the necessary information for process design and optimization. For this purpose, effective mathematical models were developed based on a type of metal-sequestering biosorption mechanism defined earlier.

Mathematical models for fixed sorption beds have originated mainly from research on activated carbon sorption and chromatography applications (*14*−*16*). The approach used in the present work was based on solving the mass balance equations for the solute being transported throughout the liquid and solid phases and biosorbed by the latter. The mass transfer resistance, particle diffusion (*17*), and axial dispersion (*18*) were incorporated in the model for determining the controlling rates in the fixed-bed column sorption operation.

In the present work, the model of Tan and Spinner (*19*), modified by Kratochvil (*20*) and 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, was employed. The computerized process simulations were also used for predicting the process performance under different operating conditions such as the column length and flow rate. Successful computer simulations can provide quick answers to questions that would be time-consuming and difficult to explore experimentally. They are beneficial for design, scale-up, and optimization studies because they help reducing the number of experiments to only those that are key (*21*).

The performance of fixed-bed sorption columns is usually described through the concept of the breakthrough curve. The mass transfer zone length and behavior, the time for breakthrough appearance, and the shape of the breakthrough curve are all very important process characteristics and are also used in the present work for determining the operation and dynamic response of a biosorption column.

Theoretical Background

Mass Transfer Zone. The overall performance of flow-through sorption columns is strongly related to the length and shape of the ion-exchange zone that develops during the solid−liquid contact. This zone develops between the section of the column that gradually becomes saturated with the sorbate and the virgin biosorbent section. At the very beginning of a sorption process the upper sorbent layer in the column is “hit” with a high sorbate concentration. Theoretically, this is where there is the highest mass transfer.

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However, as it takes some time (and column length) for the mass transfer zone (MTZ) to establish itself, the initial column behavior cannot reasonably be considered as it represents a transient and unsteady-state regime. When the mass transfer zone eventually fully develops inside the bed, it can be followed as it advances along the length of the column. At the end of the bed, the breakthrough curve reflects the shape of the MTZ. The MTZ may be considered as a region inside the column in which the sorbate concentration changes from 90% to 10% of its inlet value. This is the region where most of the mass transfer takes place.

The saturation of the bed within the transfer zone varies from zero (front) to the full saturation (rear). This zone of partial saturation moves through the column in the direction of the flow at a certain velocity which is predominantly determined by the sorbate loading, sorbent capacity, and the column feed rate. The column is operational until the MTZ reaches the end of the column. Until that time the effluent leaving the column is virtually sorbate free. When the transfer zone reaches the column end, the sorbate concentration in the effluent starts to gradually increase. At the breakthrough point, the end-portion of the column contains the transfer zone with only partially saturated sorbent in it. The fact that real mass transfer zones appear S-shaped in the plot is due to the sorption mechanism and mass transport conditions. These parameters are generally taken into consideration in deriving the column mass balance.

Adsorption and ion exchange equilibrium data are typically plotted in the form of an *adsorption isotherm* with the amount of immobilized (sorbed) sorbate on the *y*-axis and its remaining concentration in the fluid on the *x*-axis. The shape of the curve is significant and factors heavily into design. “Favorable” isotherms signify higher solid loadings at lower solution concentrations. These types of isotherms tend to start out steep and level off at higher equilibrium concentrations. Isotherms which start out flat are “unfavorable”, since such sorption systems only work well at high concentrations of solute.

According to the theory of chromatography, different parts of the transfer zone move with different speeds depending on the shape of the equilibrium isotherm for the given sorption system. If the concentration points upstream in a zone move faster than the concentration points downstream, the zone is called sharp since it has a tendency to shrink as it travels along the column. In contrast to sharp zones, broad zones develop if the concentration points downstream in the zone move faster than the points upstream. It has been proven that favorable sorption isotherms eventually lead to the formation of sharp zones in sorption columns. Conversely, unfavorable equilibrium isotherms give rise to broad and expanding zones in the column.

While the favorable steep equilibrium sorption isotherm tends to sharpen the breakthrough curve by making it steeper, mass transfer and fluid flow deviations from the ideal piston flow, caused by axial and radial mixing in the flow within the column, invariably tend to negatively affect the breakthrough curve by flattening it. The exact shape of the breakthrough curve then depends not only on the column operating parameters but also on its length. The concentration profiles for sorption in a packed-bed column at various positions and times in the bed, as well as the breakthrough curves at the column outlet indicating the breakthrough point and the mass transfer resistance, are discussed in some detail and graphically depicted in textbooks and most recently by Volesky (*2*).

Modeling of the MTZ behavior for the optimization of the sorption column performance eventually becomes a very challenging task. Computer process simulations can model the behavior of the mass transfer zone and the breakthrough curve under different conditions. Then the important experiments can be selected to verify the model-based computer simulations predicting the process behavior.

Equilibrium and Sorption Column Models. As opposed to activated carbon sorption, metal biosorption is much closer to the heterovalent ion exchange model (*22*) since a considerable amount of ions are being released from the biosorbents in exchange for the sorbed metal ion. A good modeling of a dynamic ion-exchange system needs to be based on the proper choice of an equilibrium isotherm to characterize competitive ion exchange. The equilibrium model used in the present study assumes the existence of one type of binding sites in the biomass reacting with ions from the solution. This assumption was verified by the quantification of carboxylic moieties and sulfonate groups, using a potentiometric titration technique (*1*), considered as the two major binding sites of the type of biomass examined (*2*). It was shown that for the pH 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. The general equation that can be used in the present case of a monocomponent sorption system is the following dimensionless eq 1:

$$y^*_{\mathrm{M}} = \frac{K_{\mathrm{M,Ca}}x_{\mathrm{M}}}{K_{\mathrm{M,Ca}}x_{\mathrm{M}} + (1 - x_{\mathrm{M}})} = \frac{K_{\mathrm{M,Ca}}x_{\mathrm{M}}}{1 + x_{\mathrm{M}}(K_{\mathrm{M,Ca}} - 1)} \qquad (1)$$

where x characterizes the equivalent fraction in the liquid phase related to the total normality of the solution, y is attributed to the equivalent fraction in the solid phase related to the total number of binding sites, $K_{\mathrm{M,Ca}}$ represents the affinity constant of the metal-for-calcium ion-exchange-based sorption reaction.

Based on mass conservation, the general mathematical eq 2 describes macroscopic fluid flow. It incorporates the diffusive and bulk solute movement as well as the sorption process

$$\frac{C_{\mathrm{M}}}{\partial z} - \frac{1}{\mathrm{Pe_c}}\frac{\partial^2 C_{\mathrm{M}}}{\partial z^2} + \frac{\partial C_{\mathrm{M}}}{\partial t} + D_{\mathrm{gM}}\frac{q_{\mathrm{M}}}{t} = 0 \qquad (2)$$

where t represents the time (h), C_{M} is the concentration of species M in the liquid phase (meq/L), and q_{M} is the uptake of species M by the biosorbent (meq/g). D_{gM} is the solute distribution parameter relating the capacity of the column $\rho_{\mathrm{b}}Q$ (meq/L) to the total normality of ions in the feed C_0 (meq/L). In general, the lower the D_{gM}, the greater is the chance that the rate of sorption is controlled by intraparticle diffusion (*17*). Pe is the Peclet number involving the interstitial velocity v or the area flow rate (in the present case) and the axial dispersion D_z of the flow through the column packed bed and thus reflecting the deviation from the ideal plug-flow ($\mathrm{Pe} = \infty$) in the column. Irregularities of the flow are characterized by low values of Pe. The nonuniformity of the packed bed is usually brought about by different sizes and/or shapes of particles and by the presence of bed void spaces (ϵ).

The sorption rate equation can be written as eq 3, assuming a linear driving force for the sorption process and a combined film and intraparticle mass transfer resistance.

$$\frac{\partial q_{\mathrm{M}}}{\partial t} = \mathrm{Sh}_{\mathrm{M}}(q^*_{\mathrm{M}} - q_{\mathrm{M}}) \qquad (3)$$

Sh_{M} is the Sherwood number connecting the mass transfer coefficient (diffusion) K_{fM} and the residence time in the column. It is the parameter eventually used in the column scale-up. q^*_M is the equilibrium uptake of species M by the biosorbents (meq/g) at C_M.

For the simulation of the breakthrough curve, the relationships for a metal species represented by eqs 1−3 should be solved simultaneously. Details of model equation derivations, the fundamental assumptions, and the boundary conditions are given in Naja and Volesky (*23*). The solution of these equations in space and time describes the performance and process dynamics of a packed sorption column. The sorption mechanism and mass transport conditions cause the S-shaped plot of breakthrough curves usually observed in sorption columns.

Materials and Methods

Biosorbent Materials and Column Experiments. The biosorbent material used for column sorption experiments was *Sargassum* seaweed biomass collected on the Gulf coast of Florida. The "raw" biomass was first washed in the laboratory with distilled water until a constant pH and conductivity of the spent rinsewater 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 into the column. The pretreatment removes loosely bound metals and cations by saturating biomass active binding sites with calcium (or another selected cation). While calcium is later eventually easily replaced by copper, as opposed to protons, it does not affect the solution pH as it is released during the ion exchange reaction with the metal. The Ca-presaturated biomass is labeled as a Ca-*S. fluitans*.

The *Sargassum* used was characterized by a total number of binding sites $Q = 2.2$ meq/g and by an affinity constant $K_{Cu,Ca} = 2.01$ evaluated from batch biosorption equilibrium data as described earlier (*24*).

The column experiment was conducted using the dry Ca-biomass packed in a 45 cm long column of 2.5 cm diameter, yielding an approximate packing density of 150 g/L. The biomass was used in the column sorption experiments without any special granulation since the seaweed form is naturally such as to provide for effective surface and intraparticle sorption (mass transfer) and to allow good liquid flow through the column biosorption bed. A $Cu(NO_3)_2$ solution (1 meq/L of Cu^{2+} in distilled water) was fed to the column from the top, flowing quite uniformly through its fixed sorption bed at a velocity of 4 cm/min. The feed solution pH was adjusted to 5. A higher pH could lead to complexation and precipitation of copper while a lower pH could reduce copper sorption efficiency through protonation of binding sites.

Knowing the cross-section of the column ($\pi d^2/4$), the true flow rate in mL/min can easily be obtained (19.6 mL/min) through an "area conversion factor" that, for *FEMLAB* calculations (*25*), also takes into account the column void spaces (ϵ). The void fraction (ϵ) can be easily determined by filling the packed bed with water and letting it come out with the help of gently blowing air. The void fraction is the volume of the water (out) divided by the total empty bed volume.

Samples of the column effluent were collected by a fraction collector (Gilson, model FC205), and the concentrations of Ca^{2+} and Cu^{2+} in the samples were determined by atomic absorption spectrometry (Perkin-Elmer 3100).

Modeling Column Experiments. The equilibrium parameters of the proposed model can be determined or calculated from batch equilibrium studies based on the values of C_0 (1 meq/L), v (4 cm/min), ϵ (0.82), L_0 (45 cm), Q (2.2 meq/L), and ρ_b (150 g/L). The only remaining unknowns in the model are K_{fM} and D_z that have to be determined simultaneously by fitting the fixed-bed model to an experimental breakthrough curve. Comparisons with obtained experimental data are also important to ensure the accuracy and overall performance of the model. Once these two unknown values are established, the model can be applied under different conditions, e.g., different column lengths (20, 30, 45, 60, 90, and 100 cm) and area flow rates (2, 4, 6, 8, and 16 cm/min), to simulate the behavior of the mass transfer zone and the breakthrough curve. *FEMLAB* software (*25*) was used to solve the model equations presented in the present paper.

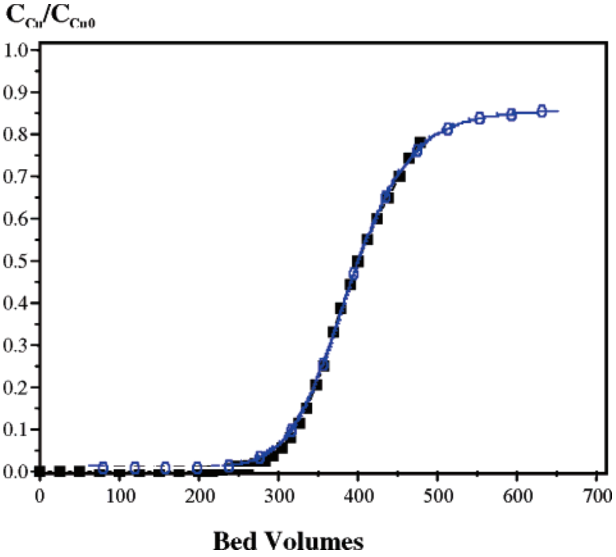

FIGURE 1. Comparison of experimental (■) and model (blue) breakthrough curves for Ca-*S. fluitans* and feed containing 1 meq/L Cu^{2+}.

The partial differential equations related to biosorption were described in a general form suitable for nonlinear 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 were specified (length of the column, feed concentration, sorbent packing density, 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 (*26*, *27*). Different discretizations dividing the column into elements were used for the solution procedure to ensure that the model solution and convergence were mesh-independent. Details about the software use are given elsewhere (*23*).

Results and Discussion

Copper Sorption Column Experiments. 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, with the latter considered as the rate-limiting step. As the columns were packed tight and quite uniformly, all the columns used were virtually identical. The column flow pattern influence was minimal as there was no "channelling" of fluid flow. In addition, the backmixing could be neglected as confirmed by the Peclet number characterizing the flow properties for the column. The relatively good agreement between the theoretical and the experimental breakthrough curves in Figure 1, obtained for Cu sorption onto the 45 cm long packing of Ca-biomass, reveals that the set of equations (*1*−*3*) can be used as a suitable mathematical representation for the first biosorption cycle carried out in a fixed-bed column. Similar agreements between the (extended) model predictions and experimental data were obtained for other column verification systems with a different multi-metal column feed (Cu−Cd−Zn) (*23*). The study of Naja and Volesky (*23*) mainly focused on the simulation-prediction of experimental results studying sorption of divalent cations of Cu, Cd, Zn and their respective mixtures Cu + Zn, Cu + Cd, Cd + Zn, and Cu + Zn + Cd by Ca-preloaded *S. fluitans* biomass packed in the same type of sorption column as the one used in the present work. In the case of a ternary mixture, successful solution of 8 coupled differential equations based on the same model, extended to a multi-metal system, demonstrated not only that a numerical solution can converge but it also resulted in a good agreement between the theoretical and the experimental breakthrough curves.

Model parameters K_{fM} and D_z were determined simultaneously by fitting the fixed-bed model to the experimental breakthrough curve. Following the operating conditions outlined in the present work, the best fit was achieved when the overall mass transfer coefficient $K_{fM} = 7.3 \times 10^{-6}$ m/s and the apparent axial dispersion coefficient $D_z = 8.83 \times 10^{-9}$ m^2/s. These values were determined by matching experimental results with model calculations, using a standard optimization-search procedure that minimizes the sum of squares of 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.

The model parameters agree well with the values found in the literature. Indeed, the value of the overall mass transfer coefficient for a given species generally depends on the flow rate, the axial dispersion coefficient, and values of the diffusivities of the species in the liquid and in the solid phase. The diffusion coefficients of Cu^{2+} and Ca^{2+} in diluted aqueous solutions are 0.714×10^{-9} and 0.792×10^{-9} m^2/s, respectively, as tabulated by Mills and Lobo (*28*). The diffusivity of Cu in alginate gels measured by Jang et al. (*29*) was determined to lie in the range of $(1-1.4) \times 10^{-9}$ m^2/s. Chen et al. (*30*) reported the diffusivity parameter (1.2×10^{-10} m^2/s), the external mass transfer coefficient (2×10^{-5} m/s), and the longitudinal dispersion coefficient (1.68×10^{-6} m^2/s) in their study of copper sorption onto activated carbon fixed-bed columns. The ranges of the film mass transfer (K_{fM}) and the effective surface diffusivity (D_s) coefficients were found to be $(2.0-5.0) \times 10^{-6}$ m/s and $(0.5-5.0) \times 10^{-8}$ cm^2/s, respectively, obtained by Weber and Liu (*31*) who used the "micro-column" technique. Based on these values, the transport parameters used here for Cu^{2+} may be considered reasonable and physically possible.

The model breakthrough in Figure 1 yields important information from the process feasibility standpoint by providing an excellent simulation of the breakthrough curve. The C/C_0 maximum value, the service time of the 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 and for assessing the process feasibility. It could provide the basis for process optimization.

Dynamics of the Mass Transfer Zone. To ensure the accuracy and the overall performance of the model, it has been applied for different sorption process conditions such as column length and flow rate. The behavior of the mass transfer zone length and the breakthrough curve was simulated under these changing conditions.

Another method used to describe and follow the mass transfer zone behavior was based on using short columns (*31*) where the MTZ is analyzed although it is not even fully developed when it exits. However, the short column methodology is more demanding and time-consuming than the computer simulation using the model developed in the present work.

Figure 2 shows the development of the mass transfer zone length during Cu^{2+} biosorption in a fixed-bed column containing Ca-loaded *S. fluitans* under different conditions. Different column lengths were used (20, 30, 45, 60, 90, and 180 cm) as well as different (area) flow rates (2, 4, 6, 8, and 16 cm/min). Every plot of Figure 2 shows the progressive saturation of the column during copper sorption. For the column length of 20 cm, the MTZ length is still expanding and it does not stabilize under the chosen flow rates. As the column length increases, the mass transfer zone length becomes stabilized at small flow rates. For a column length of 45 cm, Figure 2 clearly indicates that the MTZ length is stabilized for the area flow rate of 2 or 4 cm/min. For the column length of 90 cm, only the flow rate of 16 cm/min is too fast to produce a stabilized MTZ. For the column length of 180 cm, the MTZ is stabilized under all the chosen flow rates. These results are of importance because the column is operational until the MTZ reaches the end of the column. Until that time, the effluent leaving the column is virtually sorbate free. When the transfer zone reaches the column end, the sorbate concentration in the effluent starts to gradually increase and, for all practical purposes, the working life of the column is over. The MTZ length parameter is the most important one from the process design point of view because it directly affects the feasibility and economics of the sorption process as it determines the degree (%) of column bed utilization. The information on the MTZ length and its behavior throughout the column is also required for the prediction and relevant explanation of breakthrough curves for different sorption column operating conditions.

The model proposed in the present work was able to describe the dynamics of the mass transfer zone through the column. Knowing the behavior of the MTZ can serve as a base for conducting meaningful experiments whereby the length and the flow rate could be chosen according to the results presented in Figure 2.

The values of process operating parameters (flow rate and column length) for the optimum overall sorption column performance (stabilized mass transfer zone) could be chosen on the basis of results obtained from modeling column performance predictions. Based on the results with the laboratory column reported here, the key experiments to be performed should be with a column of 45 or 60 cm long and the area flow rate varying between 2 or 4 cm/min. The MTZ length under these conditions is stabilized with the bed volumes between 150 and 200. Higher length of the column is also possible but will be unreasonable from a process engineering point of view. The column scale-up would reflect this laboratory input.

Mass Transfer Zone Properties. *Length of the Column.* Figure 3a represents the MTZ length versus time under various column lengths. Knowing the usual definition of the bed volumes stated in eq 4, Figure 3a could be compared to the different plots of Figure 2.

$$\text{Number of Bed Volumes} = \frac{\text{Volume of solution treated}}{\text{Volume of biomass bed}} \tag{4}$$

where the volume of the fixed bed depends on the column length.

Figure 3a indicates clearly that the MTZ length (if stabilized) does not depend on the column length (*2*) and that the MTZ length gets gradually stabilized as it proceeds along the column. With a long enough column, the zone has a better chance to fully develop. The MTZ was not fully developed in the shorter columns used in this study (Figure 2a and b). From another point of view, it is obvious that the overall copper uptake in the column increased with the

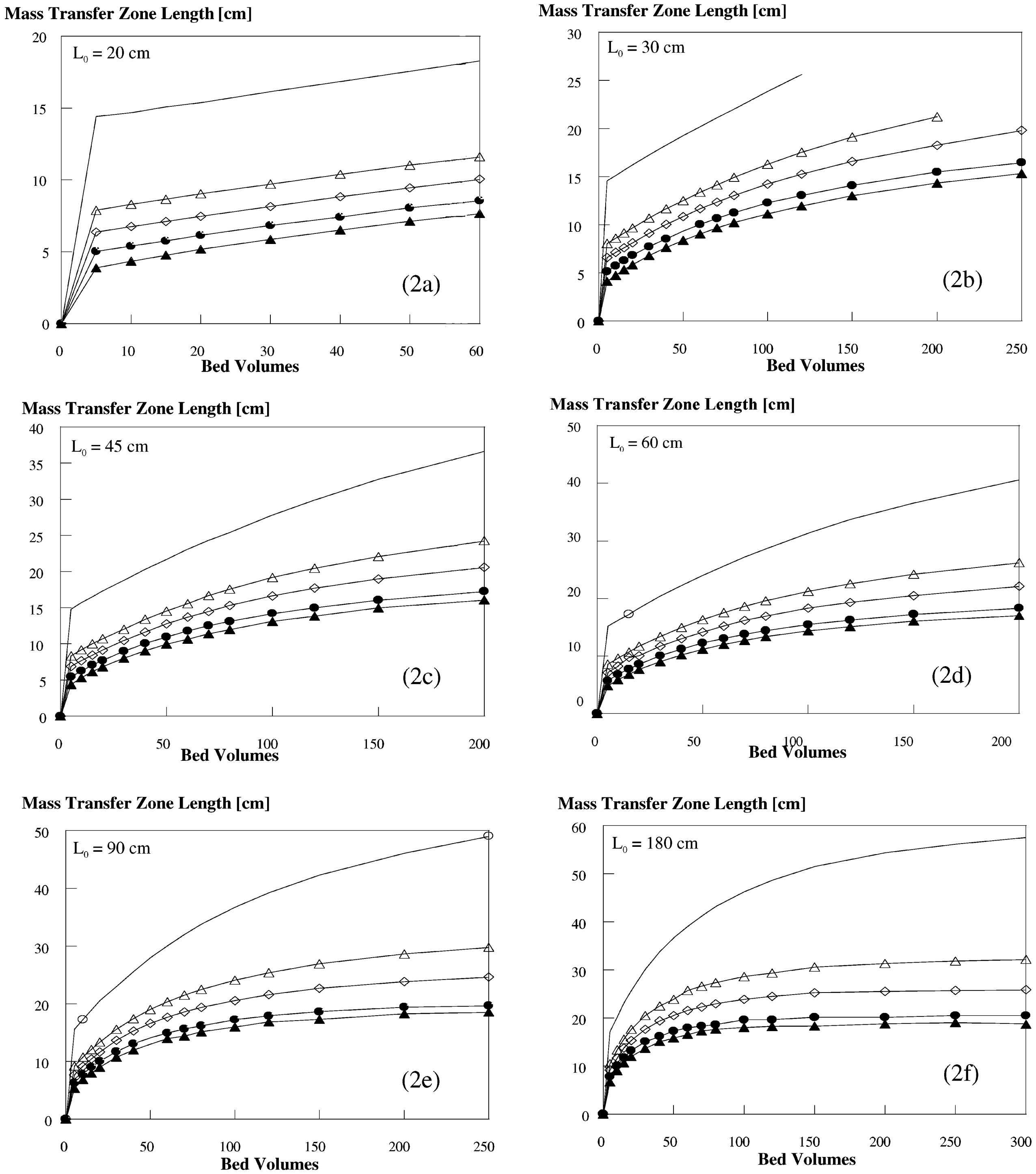

FIGURE 2. Development of the mass transfer zone length (cm) during Cu^{2+} biosorption in a fixed-bed column containing Ca-loaded *S. fluitans*. Different feed area flow rates (▲2, ●4, ◊6, △8, and ○16 cm/min) and column lengths (20, 30, 45, 60, 90, and 180 cm) were used.

increase in the column length from 20 to 180 cm (*32*). With a shorter column length, the column gets saturated early as compared to longer columns due to the lower overall number of available binding sites for the sorption.

Feed Flow Rate. Figure 3b represents the MTZ length under different column area feed flow rates for a column length of 60 cm. The column feed flow rate affects not only the extraparticle mass transfer coefficient but, in particular, the overall sorption kinetics. If the flow rate is high, not all the metal ions from the solution have enough time to penetrate to and react with functional groups, which consequently results in fewer bed volumes before the breakthrough occurs (*33*). If the residence time of the solute in the column is not long enough for the adsorption equilibrium to be reached, the metal solution leaves the column before the equilibrium occurs, resulting in a MTZ not fully developed. At the same time, dispersion becomes important in the metal transfer at higher flow rates. On the other hand, the bed volumes for the column use increase when the flow rate is low; there is enough time for the metal to be immobilized. Much sharper breakthrough curves and thus higher overall column uptakes are expected with decreasing flow rates. The degree of flow dispersion in the sorption column, described by the dimensionless Peclet number, tends to increase with the column

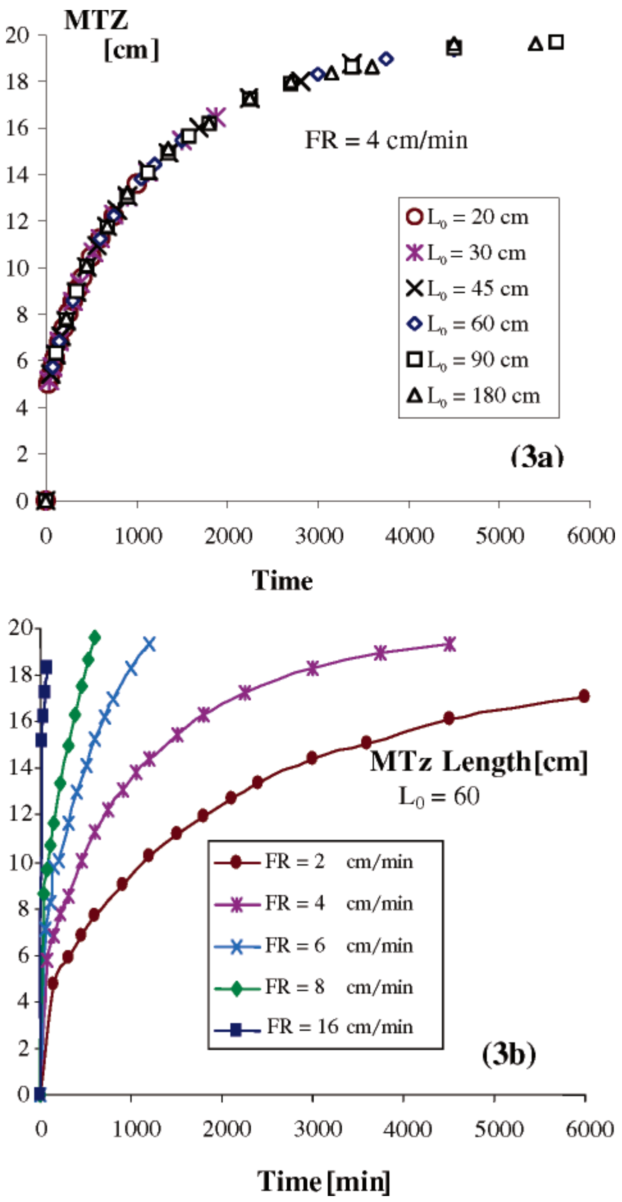

FIGURE 3. Development of the mass transfer zone length (cm) over time (min) during Cu^{2+} biosorption in a fixed-bed column containing Ca-loaded *S. fluitans*. Column lengths (3a, flow rate = 4 cm/min) and area flow rates (3b, L_0 = 60 cm) were varied.

length. Therefore, there is the optimum value of the feed flow: too high a flow rate would cause earlier breakthrough, while too low may not be desirable from the overall process effectiveness point of view.

Equilibrium Affinity Constant K. The mechanism of the sorption process is reflected in the equilibrium isotherm. According to a theory based on chromatographic work (*2*, *34*), the favorable equilibrium isotherm (concave) leads to the formation of "sharpening" (decreasing) MTZs in sorption columns (*35*). The sharpening zone is shortening until it stabilizes as it proceeds slowly in time and space through the column. Conversely, unfavorable equilibrium isotherms give rise to broad and broadening zones in the column. The broadening zone is expanding in length as is proceeds through the column.

Another view supported in the literature (*36*–*38*) agreed well with the MTZ behavior for unfavorable equilibrium isotherms. However, for favorable Langmuir and Freundlich isotherms the MTZs, after their natural initial expansion, quickly stabilize in length with respect to both position and time as they travel through the column. It is easier to estimate the full-size adsorber bed behavior based on the results from a small scale column when dealing with a stable MTZ of a favorable isotherm.

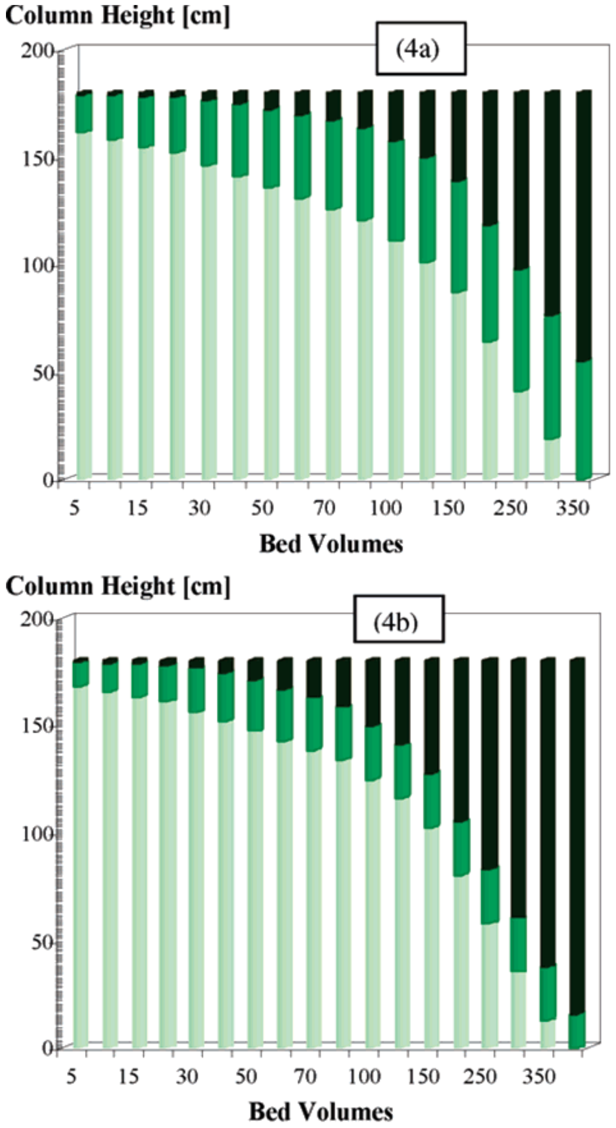

FIGURE 4. Development of the mass transfer zone length (cm) during Cu^{2+} biosorption in a fixed-bed column containing Ca-loaded *S. fluitans*. The darkest zone is the most saturated biomass. The medium-dark zone represents the mass transfer zone length. The lightest zone reflects the virgin biosorbent. (a) L_0 = 180 cm, area flow rate = 16 cm/min, *K* (equilibrium constant) = 2.01. (b) L_0 = 180 cm, area flow rate = 16 cm/min, *K* = 10 (assuming a different affinity).

Although the proposed model was able to show the expanding and broadening zone, it was not possible to demonstrate the shrinking zone, only a stabilized one. An example with two different values of equilibrium affinity constant *K* pH-dependent ($K_{Cu,Ca}$ = 2.01 at pH = 5 and assuming $K_{Cu,Ca}$ = 10 at a higher pH value) is presented in Figure 4 that was obtained when representing the development of the MTZ (or the MTZ length as it travels through the column) during Cu^{2+} biosorption until the end of the working life of the column. The typical dependence of metal uptake on the solution pH values (*39*) induced a change in the affinity constant *K* of the ion exchange sorption reaction. It clearly indicates that with a higher value of *K*, the column could be used longer and the mass transfer zone length was shorter than that for small constant *K*. With a higher value of *K*, the

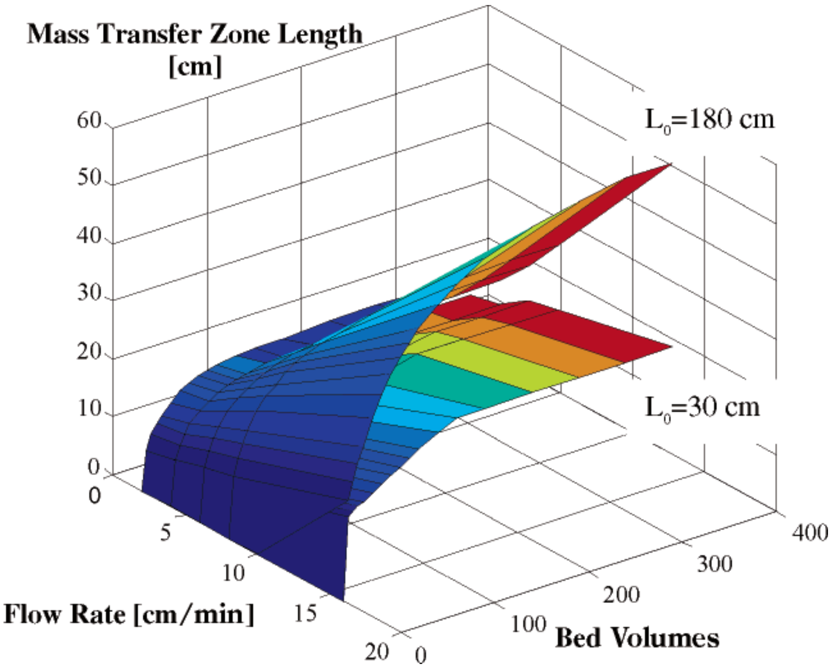

FIGURE 5. Mass transfer zone length (cm) behavior during Cu^{2+} biosorption in a fixed-bed column (L_0 = 180 or 30 cm) containing Ca-loaded *S. fluitans*.

affinity between functional groups and metal ions is higher, resulting in a broader fully saturated zone. A very important practical consideration arises from the affinity of different sorbates for the sorbent material (*40*). The two scenarios presented in Figure 4 will be reflected in the shapes of the breakthrough curves resulting from such column operations. The MTZ developed in the case of higher affinity (Figure 4b) is shorter and retains its shape as it moves along the column. However, in the case of a lower affinity (Figure 4a), MTZ extends across a large section of the column and is prone to further broadening as it travels along the column during its operation.

Using the model presented here, the behavior of the MTZ was predicted under several different key parameters such as the affinity constant between functional groups and the metal, the length of the column, and the area flow rate. The demonstrated simulation offers a new and responsive tool for application in metal removal/recovery by assisting the process optimization.

Generalization. Figure 5 represents the generalization of the MTZ behavior under different conditions during Cu^{2+} biosorption in a fixed-bed column containing Ca-loaded *S. fluitans* biomass.

Most often, there is more than one variable parameter in the process and in this case the assessment of the sorption performance of a fixed-bed column becomes more complicated. The mass transfer zone length observed in this work varied with the variation of the two key process parameters, and the results could be depicted in a 3-D surface plot. However, 3-D imaging requires more calculating power, now available in computers using appropriate software such as MATLAB (*41*).

Because the experimental or model points for the surface are likely to exhibit a certain degree of scattering, the obtained surface often needs to be smoothed to compensate for deviations of individual data points. The obtained overall surface could then be sliced by parallel planes which represent a certain desired flow rate or a selected column length. Their values can be conveniently chosen as whole numbers with equal intervals quite independent from the scattered experimental data points. Computer simulations can then replace tedious and expensive experiments to the extent that only the key experiments can be selected to be carried out to verify the model-based computer simulations predicting the process behavior.

Sorption process modeling is particularly useful for predicting the process performance under different conditions. Many models reported in the literature very often become more problematical with nonconverging solutions when there is more than one metal in the solution. The assessment and prediction of the sorption performance then becomes more complicated or simply impossible.

As the majority of industrial effluents may contain more than one toxic heavy metal, biosorption in columns would involve competitive ion exchange whereby several toxic heavy metals would compete for a limited number of binding sites. The two major types of relatively well-defined effluents originate from mining (acid mine drainage) and electroplating operations (e.g., electroplating effluents originating from spent zinc baths containing Cu^{2+} and Al^{3+}). The operation of the biosorption column has to be stopped as soon as the concentration of one of the toxic species in the column effluent exceeds the regulatory limit. The service time of biosorption columns can be reduced if the industrial effluent contains a nontoxic species interfering with the sorption of the toxic metals. This fact calls for preliminary testing and a careful selection of the biosorption process applications.

The contribution and the originality of this work are in the applicability of the present process model which is not limited to binary metal systems. It has been demonstrated that it could be extended and applied to three- and multicomponent solution systems (*23*). Thus, the model could be applied to the study of industrial biosorption processes depending on the properties of the chosen biosorbents and the composition of the wastewater.

The major advantage of the *FEMLAB* software used for solving the present model equations is that it can simulate and predict the performance of a column under various operating conditions, including different flow rates, feed compositions, column sizes, bed porosities, and ionic forms of the biosorbent. This model and the process simulations procedure can assist engineers to meaningfully develop the biosorption process by: (a) selecting the conditions under which to run pilot tests, and (b) 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.

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