Column biosorption of lanthanum and europium by Sargassum

Vivian Diniza, Martin E. Webera, Bohumil Voleskya,*, Ghinwa Najab

aDepartment of Chemical Engineering, McGill University, 3610 University Street, Montreal, Quebec, Canada H3A 2B2
bBiotechnology Research Institute, National Research Council Canada, Montreal, Quebec, Canada H4P 2R2

ABSTRACT

Batch and column biosorption of La\(^{3+}\) (lanthanum) and Eu\(^{3+}\) (europium) was studied using protonated Sargassum polycystum biomass. The ion exchange sorption mechanism was confirmed by the proportional release of protons and by the total normality of the solution, which remained constant during the process. Equilibrium isotherms were determined for the binary systems, La/H and Eu/H for a total normality of 3 meq g\(^{-1}\), which produced separation factors of 2.7 and 4.7, respectively, demonstrating a higher affinity of the biomass towards europium. Column runs with a single metal feed were used to estimate the intra-particle mass transfer coefficients for La and Eu (6.0 \(\times\) 10\(^{-4}\) and 3.7 \(\times\) 10\(^{-4}\) min\(^{-1}\), respectively). Modeling batch and column binary systems with proton as the common ion was able to predict reasonably well the behavior of a ternary system containing protons. The software FEMLAB was used for solving the set of coupled partial differential equations. Moreover, a series of consecutive sorption/desorption runs demonstrated that the metal could be recovered and the biomass reused in multiple cycles by using 0.1 N HCl with no apparent loss in the biosorbent metal uptake capacity.

© 2007 Elsevier Ltd. All rights reserved.

1. Introduction

The biosorption process represents an effective passive sequestration of organic or inorganic substances by certain types of non-living biomass. For practical application considerations, it is important to select biomass types that are either naturally abundant, such as seaweeds, or industrial biomass wastes especially from fermentation or seaweed processing plants (Volesky, 2003a). Biosorption has mainly been considered for heavy metal removal in order to detoxify metal-bearing effluents. The process features a high heavy-metal selectivity and cost-effectiveness for low metal concentrations as compared with ion exchange resins. There is also no hazardous sludge by-product generation in both processes and biosorbents can also be easily regenerated for multiple reuse (Volesky, 2001). Biosorption studies have utilized biomass types such as seaweed, bacteria, fungus and yeast (Naja et al., 2005; Veglio and Beolchini, 1997), and even human hair for copper removal (Tan et al., 1985). Cationic metals are effectively removed by brown algae (Davis et al., 2003), with Sargassum species probably the most widely studied because of their high metal uptake capacity and both mechanical and chemical resistances (Yang and Volesky, 1999; Kratochvil and Volesky, 1998). Crab shells have been discovered to bind anionic metal complexes (Niu and Volesky, 2003).

Considerable attention has been paid especially to batch equilibrium studies and to modeling of the isotherms. While ion exchange is considered to be the main mechanism involved in the biosorption process (Davis et al., 2003; Volesky, 2003a), most of the isotherms derived under constant pH are usually conveniently modeled using Langmuir and Freundlich...
equations. However, none of these two models reflects the ion exchange mechanism involved in which ions are released from the biosorbert while others become bound. During this process, the total normality of the solution, i.e., the total concentration of cations in terms of the number of equivalents, remains constant, the electroneutrality of the solution thus being maintained. Correspondingly, with no pH adjustment it would vary naturally according to the exchange of ions during the process. This approach is also used in order to follow the behavior of a fixed-bed flow-through sorption column where the pH cannot be conveniently controlled inside the column and will vary with the ion exchange and speciation of the ions present in solution, especially if protons are the exchanged species. The same total normality should be used to feed the column. Modeling the batch equilibrium isotherm could then be used as a basis for simulation and for predicting the fixed-bed sorption column behavior. Equilibrium equations should be simple enough in order to be used in the column combined model in a direct way with no need for often troublesome iterations. Other equilibrium isotherm models for simulating the biosorption process have been used for simulating single- and multi-component systems such as multi-component Langmuir, combination Langmuir–Freundlich, BET (Texier et al., 1997), the ideal adsorbed solution theory (Radke and Prausnitz, 1972) and the surface complexation model (Jeon and Holl, 2004) among others. However, many of these largely empirical models have serious limitations and more often do not represent the ion exchange mechanism occurring during the process. Other models reflecting sorbate speciation, pH and electrostatic attraction have also been suggested (Schiewer and Volesky, 1996, 1997) and their advantages and disadvantages are summarized in the literature (Volesky, 2003a). Moreover, ion exchange systems can also be modeled by using the separation factor concept between two elements, which represents the ratio of the distribution coefficients between them. While a constant-separation-factor approach is frequently applied to systems involving ions with the same valence, this concept may also be applied to heterovalent systems with good approximation (Tondeur and Klein, 1967).

Ion exchange reactions occur between an electrolyte in solution and an insoluble electrolyte with which the solution is contacted. Early applications of ion exchangers were limited to water-softening problems. In 1935, synthetic materials were introduced such as insoluble polymeric resins containing sulfonic, carboxylic or phenolic groups, while different cations would have a different affinity to the resin (Treybal, 1987). The rate of ion exchange depends on the following processes: (a) diffusion of ions from the bulk of the liquid to the external surface of the exchanger particle or sorbent in this case; (b) intra-particle diffusion of ions through the solid to the binding sites; (c) exchange of the ions; (d) diffusion of the released ions to the surface of the solid; and (e) diffusion of the released ions from the surface to the liquid bulk (Treybal, 1987). In the biosorption process using Sargassum sp. as a sorbent, intra-particle mass transfer resistance appears to be dominant (Kratochvil et al., 1997; Volesky, 2003a).

The application of flow-through fixed-bed sorption columns constitutes the most preferable process device for biosorption operations due to the most effective use of the concentration gradient that can drive the process even at low levels of metal concentrations encountered. This leads to the maximization of the (bio)sorbent uptake capacity even though the pH cannot be feasibly controlled inside the column. During the ion exchange mechanism, the ions are naturally exchanged and the total normality of the solution is supposed to remain constant; however, the pH will likely vary when protons are released into the solution. The equilibrium batch system should be able to represent such a system whereby the total normality of the solution is constant. Therefore, an ion exchange equilibrium isotherm should be derived based on the same normality with varying final equivalent fractions of the elements present in both liquid and solid phases. This model can then be used for predicting the behavior of a breakthrough curve with the column being fed a solution under the same total normality as used in the batch equilibrium experiments.

Recently, biosorption in fixed-bed columns and its modeling has been receiving more attention. As it is virtually useless to carry out column experimentation without an appropriate understanding and interpretation of the results, empirical and mechanistic models have been used to describe the breakthrough curves obtained especially for single-metal systems, but also for a few multi-metal systems (Hatzikioseyian et al., 2001). Most of the multi-component ion

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_M$</td>
<td>metal equivalent fraction in the liquid</td>
</tr>
<tr>
<td>$y_M$</td>
<td>metal equivalent fraction in the solid</td>
</tr>
<tr>
<td>$y^*_M$</td>
<td>metal equilibrium equivalent fraction in the solid</td>
</tr>
<tr>
<td>$H$</td>
<td>separation factor between metal and proton</td>
</tr>
<tr>
<td>$Q$</td>
<td>total number of ion-exchangeable binding sites (meq g$^{-1}$)</td>
</tr>
<tr>
<td>$q_i$</td>
<td>element concentration in the solid phase (meq g$^{-1}$)</td>
</tr>
<tr>
<td>$K_{mM}$</td>
<td>mass transfer coefficient in the solid (min$^{-1}$)</td>
</tr>
<tr>
<td>$z$</td>
<td>dimensionless bed size</td>
</tr>
<tr>
<td>$L$</td>
<td>bed axial variable (cm)</td>
</tr>
<tr>
<td>$C_i$</td>
<td>element concentration in solution (meq L$^{-1}$)</td>
</tr>
<tr>
<td>$C^0$</td>
<td>total normality (meq L$^{-1}$)</td>
</tr>
<tr>
<td>$x_i$</td>
<td>element equivalent fraction in the liquid</td>
</tr>
<tr>
<td>$y_i$</td>
<td>element equivalent fraction in the solid</td>
</tr>
<tr>
<td>$\epsilon_b$</td>
<td>bed void fraction</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>bed packing density (g L$^{-1}$)</td>
</tr>
<tr>
<td>$\tau$</td>
<td>dimensionless time variable</td>
</tr>
<tr>
<td>$t$</td>
<td>time (min$^{-1}$)</td>
</tr>
<tr>
<td>$u$</td>
<td>superficial velocity (cm min$^{-1}$)</td>
</tr>
<tr>
<td>$v$</td>
<td>interstitial velocity (cm min$^{-1}$)</td>
</tr>
<tr>
<td>$K$</td>
<td>affinity constant</td>
</tr>
</tbody>
</table>
exchange studies used to consider local equilibrium theory whereby local equilibrium is assumed at all points at any time (Klein et al., 1967; Helfferich, 1967). Because this approach neglected mass transfer it was just barely useful for assessing the feasibility of ion exchange processes. Better models assumed either intra-particle mass transfer resistance and/or liquid film resistance (Weber and Crittenden, 1975; Weber and Liu, 1980) or even combined liquid and solid mass transfer resistances as the rate-controlling step (Tan and Spinner, 1994). Many of the modeling studies have concluded that axial dispersion effects could be neglected (Weber and Liu, 1980; Da Silva et al., 2002). For dilute solutions, however, liquid phase rate controlling is usually assumed (Tan and Spinner, 1994). Even neural networks have also been used to model the breakthrough curves (Texier et al., 2002).

More or less successful attempts have been made to model (and predict) the breakthrough curves resulting from biosorption column processes (Volesky et al., 2003; Klein et al., 1967). Other types of reactors such as membrane reactors have also been studied (Beolchini et al., 2005). Although many simulation models have been proposed, there is still a lack of suitable and reliable process simulation tools that would be efficient, realistic and user-friendly, especially for multi-component systems (Volesky, 2003b).

This study focused on the modeling of the breakthrough curves obtained from the binary metal pairs with protons being the common element. Moreover, in addition, the impact of the ternary system behavior based on the parameters estimated from the binary pairs was attempted. In prediction, the impact of consecutive sorption/desorption cycles was also studied. Lanthanides were chosen because of the increasing demand perspectives (Hedrick, 2001) and to give continuity to the work already done (Diniz and Volesky, 2005a, b). FEMLAB package software was used as a solver for finding the solution to the partial differential equations based on the finite element difference method.

2. Materials and methods

2.1. Biomass preparation for batch and flow-through sorption experiments

The biosorbent used in the experiments was the brown seaweed, Sargassum polycystum, collected in the Philippines. The sun-dried seaweed was washed with tap water and distilled water to remove sand and excess of sodium and potassium ions. After drying overnight at 55°C to avoid degradation of the binding sites, the biomass was ground and all particles larger than 0.5 mm were selected by sifting. Broken leaves, the main components of the particles smaller than 0.5 mm, are generally considered as weaker sorbent constituting only a minor part of the biomass. The biomass was subsequently protonated with 0.1 N HCl (biomass concentration of 10 g L−1) for 4 h under gentle agitation. Later, the biomass was washed with distilled de-ionized water to remove excess H ions until the mixture reached approximately pH 5. Finally, the biomass was again dried overnight at 50–55°C.

Biomass preparation for continuous-flow sorption column experiments followed the same steps except that the biomass was broken into ~1 cm pieces, protonated and wetted, and then inserted into the column one at a time. Distilled water was used in column experiments for both biomass and solution preparation.

2.2. Batch equilibrium experiments—binary pairs (La/H, Eu/H)

Batch sorption tests were performed at the same initial total normality for derivation of the equilibrium isotherms for both elements La and Eu present, respectively, in binary pairs with hydrogen ions. Samples of 0.025 g of prepared biomass (as above) were contacted with 0.05 L of solution of known total normality concentrations of 3 meq L−1 with equivalent fractions of both metal and protons ranging from values close to 0 to values close to 1, whereby the sum of the equivalent fractions was always equal to 1. The sorption suspension samples (in duplicates) were contacted for 24 h on a rotatory shaker at 150 rpm, filtered through a 0.2 μm washed membrane and analyzed for residual metal content by using the ICP atomic emission spectrometer (ICP-AES, Thermo Jarrell Ash, Model Trace Scan). The pH was not adjusted in order to maintain a constant total normality at equilibrium. Solutions containing the metals were individually prepared using distilled de-ionized water and nitrate salts: La(NO3)3·6H2O, Eu(NO3)3·6H2O (all Alfa Aesar supplied).

2.3. Sorption column experiments

The column internal diameter was 2.5 cm and the length was 25 cm. After weighing the dry broken biomass, the column was packed after wetting the sorbent. The packed bed void fraction was determined by measuring the liquid volume upon draining the flooded column and blowing air through it to remove all residual interstitial water. The void volume value was compared with the volume of the column without biomass in order to account for the volume of connecting tubings. All measurements were done in triplicate.

The feed solution containing the total metal concentration of 3 meq L−1 was pumped downward through the column at the volumetric flow-rate of 15 mL min−1, which corresponds to the superficial velocity of 3 cm min−1 and the interstitial velocity of 5.2 cm min−1. No pressure increase across the column was observed during the experiments.

2.4. Model equations

2.4.1. Equilibrium batch

The biosorption mechanism involving Sargassum has been established as an ion exchange reaction type between cations already bound to the biomass and the others present in the aqueous phase (Diniz and Volesky, 2005a; Naja and Volesky, 2006a; Yang, 2000). In the case where hydrogen ions are initially attached to the sorbent binding sites (the monovalent carboxylate functional groups), and the lanthanides are present in solution, the reaction can be represented as
follows:

\[ \text{La}^{3+} + 3\text{HB} \leftrightarrow \text{LaB}_3 + 3\text{H}^+. \] (1)

The total number of moles of protons released by the biosorbent is three times the number of moles of the lanthanide ion removed from the aqueous solution (Diniz and Volesky, 2005a). Therefore, the total normality, which represents the sum of the equivalent concentrations of all competing cations that can be exchanged during the reaction, remains the same when equilibrium is achieved. Considering a system containing one metal and protons, the total normality is expressed by

\[ C^\text{a} = C_\text{M} + C_\text{H}. \] (2)

The metal concentration in meq L\(^{-1}\) can be obtained by dividing the concentration in mg L\(^{-1}\) by its atomic weight and multiplying by the ion valence. In addition, if ions are exchanged during the process, the exchangeable binding sites are always occupied by the competing ions; thus, the total number of exchangeable binding sites is the sum of the concentrations in the solid phase of the elements involved and can be represented as follows:

\[ q_\text{M} + q_\text{H} = Q. \] (3)

The equivalent fraction of one component in the liquid phase is the ratio between its own concentration and the total normality of the solution, whereas the equivalent fraction in the solid is its active concentration in the solid divided by the number of exchangeable binding sites.

\[ x_i = \frac{C_i}{C^\text{a}}, \] (4)

\[ y_i = \frac{q_i}{Q}, \] (5)

where \(C^\text{a}\) represents the total normality of the solution and \(Q\) the total number of exchangeable binding sites. This way, the sum of the equivalent fractions is equal to 1.

For this reason, the sum of the equivalent fractions in both solid and liquid phases would be equal to 1. For a heterovalent binary pair as it is the case in this work, it is recommended to express concentrations in both liquid and solid phases as meq L\(^{-1}\) and meq g\(^{-1}\), respectively:

\[ x_\text{M} + x_\text{H} = 1, \] (6)

\[ y_\text{M} + y_\text{H} = 1. \] (7)

For a binary system, the separation factor represents in this case the relative selectivity of the metal to the hydrogen ion and it is defined by

\[ z_{i\text{M}} = \frac{y_{i\text{M}}}{x_{i\text{M}}} \] (8)

This expression is the same as used by other authors (Treybal, 1987; Klein et al., 1967; Tan and Spinner, 1994) to describe the multi-component ion exchange equilibrium relationship. In general, the separation factor at a certain temperature varies with total normality in solution, \(C^\text{a}\), and also with the metal concentration, \(C\). However, in some cases, \(z\) has shown to be essentially constant at a fixed \(C^\text{a}\) with varying \(C\) (Treybal, 1987). The equivalent hydrogen fraction can be expressed by subtracting the metal fraction from 1.

Rearranging the above equation by eliminating the hydrogen equivalent fraction, the following expression is obtained:

\[ y_\text{M} = \frac{x_{i\text{M}}}{1 + (x_{\text{M}} + 1 - 1)q_{i\text{M}}}. \] (9)

For a ternary mixture containing two metals such as La and Eu and protons, whereby the latter are the common ions in both binary mixtures, the ion exchange reactions are represented by

\[ \text{La}^{3+} + 3\text{HB} \leftrightarrow \text{LaB}_3 + 3\text{H}^+, \] (10)

\[ \text{Eu}^{3+} + 3\text{HB} \leftrightarrow \text{EuB}_3 + 3\text{H}^+. \] (11)

The separation factors can be expressed exactly the same way as for the binary pair:

\[ \frac{y_{i\text{M}}}{x_{i\text{M}}} = \frac{y_{i\text{M}} x_{\text{M}}}{x_{i\text{M}} y_{\text{M}}}, \] (12)

\[ \frac{y_{i\text{M}}}{x_{i\text{M}}} = \frac{y_{i\text{M}} x_{\text{M}}}{x_{i\text{M}} y_{\text{M}}}. \] (13)

When the proton is the common ion in both parallel reactions, both Eqs. (12) and (13) are interrelated and the hydrogen ion equivalent fraction can once again be eliminated, resulting in the following expressions:

\[ x_{i\text{M}} + x_{i\text{M}} + x_\text{H} = 1, \] (14)

\[ y_{i\text{M}} + y_{i\text{M}} + y_\text{H} = 1. \] (15)

One expression containing both metal fractions can be obtained by eliminating the proton equivalent fractions and combining Eqs. (12) and (13). The proton equivalent fraction which is the same in both equations can be eliminated to obtain one expression relating both metals present in solution (Tan and Spinner, 1994):

\[ y_{i\text{M}} = \frac{x_{i\text{M}} x_{\text{M}}}{1 + (x_{\text{M}} + 1 - 1)q_{i\text{M}}}, \] (16)

\[ y_{i\text{M}} = \frac{x_{i\text{M}} x_{\text{M}}}{1 + (x_{\text{M}} + 1 - 1)q_{i\text{M}}}. \] (17)

By combining Eqs. (11) and (12), the selectivity of one metal over the other is obtained by the ratio of both metal separation factors as described next:

\[ \frac{x_{i\text{H}}}{y_{i\text{H}}} = \frac{x_{i\text{H}} x_{\text{M}}}{y_{i\text{H}} y_{\text{M}}} = \frac{x_{i\text{H}} x_{\text{M}}}{x_{i\text{M}} y_{\text{M}}}. \] (18)

\[ z_{i\text{M}} = \frac{x_{i\text{M}} y_{\text{M}}}{x_{i\text{M}} x_{\text{M}}}. \] (19)

### 2.4.2. Dynamic column

Assuming isothermal conditions, constant physical properties for the feed solution and plug flow (neglecting axial dispersion), the mass balance in the liquid and solid phases assuming a linear driving force for the solid phase rate-controlling step gives the following respective equations developed by Yang (2000):

\[ \frac{\partial x_{\text{M}}}{\partial t} = -\frac{\partial x_{\text{M}}}{\partial x} \cdot \frac{\partial \phi_{\text{M}}}{\partial C_{\text{M}}} \cdot \frac{\partial t}{\partial x}, \] (20)
\[ \frac{\partial q_M}{\partial t} = k_{M,H}(y_M^* - y_M). \]

With boundary conditions:

\[ q_M = 1 \text{ at } \zeta = 0, \]

\[ \frac{\partial x}{\partial \zeta} = 0 \text{ at } \zeta = 1. \]

Initial conditions at \( t = 0 \) and at any \( \zeta \)

\[ x_M = 0, \]

\[ y_M = 0. \]

The following dimensionless variables are also introduced:

\[ x = \frac{C_M}{C^*}, \]

\[ y = \frac{q}{Q^*}, \]

\[ \tau = \frac{t}{L/(u/\nu^*)^{-1}}, \]

\[ \zeta = \frac{2}{L^*}. \]

where \( k_{M,H} \) is the mass transfer coefficient in the solid and \( y_M^* \) is the batch equilibrium relation from the binary or ternary system. In the case of a ternary system, the four mass balances in the solid and liquid phases for both metals should be solved simultaneously using the ternary equilibrium isotherm described by Eqs. (16) and (17). It should be pointed out that the ion exchange process is a stoichiometric process, and therefore the proton concentrations are determined indirectly based on the concentrations of the elements present in the system.

The partial differential equations were solved numerically using the FEMLAB software. The general form was selected to solve the non-linear coupled equations. Quadratic basis functions with dimensionless time increments of 0.1 were set. Mesh refinement was performed and 320 elements were chosen above which no change was observed in the output curves.

3. Results and discussion

3.1. Batch equilibrium

The dimensionless sorption isotherms obtained for the binary metal/proton equilibrium systems with a total normality of 3 meq L\(^{-1}\) are depicted in Fig. 1, presenting the results from the duplicates. Europium demonstrated a slightly higher affinity with respect to the hydrogen ion as compared with the lanthanum one, the respective affinity constants being 4.7 and 2.7. The affinity constant relating europium to lanthanum, determined by the ratio of the metal/proton binaries observed, was 1.7, which is lower than the individual ones relating to the proton. Both isotherms could be reasonably well represented by a constant separation factor throughout the entire range studied in this case for a fixed total normality of the solution. The same affinity sequence was observed for

![Graph showing ion exchange equilibrium isotherms for La and Eu at a constant total normality of 3 meq L\(^{-1}\).](image)

La and Eu in isotherms determined at a constant pH 4 (Diniz and Volesky, 2005a).

3.2. Column with a binary sorbate mixture (metal/proton)

Protonated biomass was used to pack the column and the metal solution was prepared with no adjustment of pH which was close to the distilled water pH. Therefore, it could be inferred that the concentration of protons in the feed stream was much lower than the metal concentration and could be neglected, considering only the metal in it and no protons. A linear relationship was observed between the bed void fraction and packing density:

\[ \epsilon_b = -0.0036v_b + 1.0032 \]  

(with an \( R^2 \) of 0.998, the corresponding plot is shown in Fig. SI-1 of the Supporting Information Section). The packing density used in the sorption column experiment was 123 g L\(^{-1}\) and the corresponding void fraction was 0.56.

The binaries studied in this case were the metal/proton system. The breakthrough curves plotted in dimensionless coordinates (Figs. 2a and b) demonstrated similar behavior in terms of the breakthrough point and saturation when the equivalent fraction approaches 1. The hydrogen equivalent fraction is also shown in the graphs, showing a much better agreement between the measured pH values and the ones obtained from the model with the Eu/H binary pair. The model assumed intra-particle resistance as the rate-controlling parameter and neglected axial dispersion. The mass transfer coefficients obtained were 0.0006 and 0.00037 min\(^{-1}\) for lanthanum and europium, respectively. The value was much lower than the metal concentration and could be neglected, considering only the metal in it and no protons. The incomplete saturation observed in the final stages of the breakthrough curves was also reported by others (Webber and Liu, 1980). It was most likely due to an underestimation of the total number of binding sites determined by the batch equilibrium isotherms and reflected in the total metal uptake capacity in the column dynamics. Another study (Da Silva
et al., 2002) suggested that equilibrium isotherms should be modeled through column runs rather than from batch tests that would not reflect the metal removal obtained by the column. In addition, the initial stage of a breakthrough curve would always be dominated by the film mass transfer and the final stage by the intra-particle mass transfer resistance (Weber and Liu, 1980; Naja and Volesky, 2006b). Another applicable hypothesis states that when mass transfer is approximated by only one overall resistance, even when calibrated with actual data, it may not accurately describe the behavior at high throughputs (Crittenden et al., 1978). Axial dispersion was demonstrated as negligible, as also confirmed by other studies (Da Silva et al., 2002). The calculations for the amount of metal removed during the sorption run based on the area under the curve for both metals are summarized in Table SI-1 of the Supporting Information Section (averages: 2.2 meq La g\(^{-1}\); 2.0 meq Eu g\(^{-1}\)). The sorption values obtained were close to the estimated number of binding sites obtained from the equilibrium isotherms.

### 3.3. Column with a ternary sorbate mixture

The ternary system was obtained by feeding the column with an equivalent mixture of both lanthanum and europium at natural pH around 6, i.e., without any pH adjustment. As the concentration of hydrogen ions was much lower than that of metals, the feed stream could be considered as containing only metals, neglecting the presence of protons in the solution. The breakthrough curves obtained are depicted in Figs. 3a and b corresponding to column lengths of 25 and 50 cm, respectively. It can be observed that the biomass has a higher affinity for europium, thus confirming the affinity sequence observed in the batch equilibrium experiments. It can be seen that lanthanum shows a somewhat steeper breakthrough curve while that for europium has a flatter pattern, indicating a lower mass transfer coefficient. That is why both elements break through at about the same time, although Eu has a higher affinity compared with La. The La exit concentration overshoot observed in the graph shows

![Graph](image1)

**Fig. 2** – Lanthanum (a) or europium (b) and proton column dynamics packed with protonated biomass. Total normality, \(C_0\): 3 meq L\(^{-1}\); feed flow-rate: 15 mL min\(^{-1}\); packing density: 123 g L\(^{-1}\); column length: 25 cm.

![Graph](image2)

**Fig. 3** – Lanthanum, europium and proton column dynamics packed with protonated biomass. Total normality, \(C_0\): 3 meq L\(^{-1}\); feed flow-rate: 15 mL min\(^{-1}\); packing density: 123 g L\(^{-1}\); column length: 25 cm (a) or 50 cm (b).
that this element occupied binding sites faster and with lower affinity than Eu, which only gradually was replacing La later as it proceeded to saturate the column, causing its exit concentration to rise above that in the feed.

The curves were obtained both experimentally and theoretically for the same column length and operating conditions. The models, calibrated through using the binary pair M/H data from both batch equilibrium and column dynamics experiments, could reasonably well predict the behavior of the ternary system upon solving all four coupled equations. This demonstrates that the approach using the calibration with the binary metal–proton pairs is capable of providing the prediction of the ternary mixture behavior when the proton is one of the ions present in the system. In this work, ion-exchanging protonated biomass was used to pack the column. The concentration of hydrogen ions was also confirmed by measuring the pH of the column exit samples. The good agreement also emphasizes the ion exchange nature of the mechanism involved in the Sargassum biosorption process already shown in the previous work (Diniz and Volesky, 2005a).

Although some earlier work implied that models should be calibrated based on the multi-component system only (Tan and Spinner, 1994), the approach used in this work simplifies the way multi-component systems can be modeled. A database with batch equilibrium constants for the binary pairs that include hydrogen ions as the common ion could be used to predict the behavior of multi-component systems when the hydrogen ion is present. The main advantage of this procedure is that only the binary pair metal/proton needs to be studied, eliminating thus repetitious studies of the whole multi-component system every time a new element is introduced.

The validation of the model for a longer column length was also performed. A column length of 50 cm was used in the experiment—twice as long as the one used for the model calibration (25 cm). Figs. 3a and b demonstrate that the model agreed well with the experimental results as well as with the model/experiment pH values. These observations also confirm the ion exchange mechanism of the biosorption process. The breakthrough point was well predicted for Eu, although the rest of the curve showed lower equivalent fraction compared with the model which underestimated somewhat the metal removal by the column.

Another fixed-bed study using Pseudomonas aeruginosa and the ternary mixture of La, Eu and Yb (Texier et al., 2002) resulted in the following sorption affinity: Eu$^{3+}$ > Yb$^{3+}$ > La$^{3+}$. Similarly, the exit concentration overshoot of La was also observed. Another software package (“IMPACT”) was used to simulate the ternary system containing K, Zn and Cd. However, it was not able to predict the breakthrough points of either Zn or Cd (Figueira et al., 2000). The equilibrium model adopted, developed by Schiewer and Volesky (1995), used the multi-component Langmuir approach to an ion exchange process and sorbates with fractional metal content. In addition, the program stopped calculating after a certain period of time due to malfunction of the solver. The weakness of this approach was its assumption that for a heterovalent exchange the equilibrium would be a function of the number of free binding sites. However, as there was an ion exchange process all exchangeable binding sites were occupied and no free binding sites really available.

Very similar simulations were obtained assuming intra-particle mass transfer resistance as dominant and axial dispersion, with Freundlich model used for the equilibrium isotherm (Gabaldon et al., 2000). The modeling results agreed well with the experiment except for the tailing zone. Simulations using local equilibrium gave poorer predictions.

### 3.4. Consecutive sorption/desorption cycles

The regeneration capacity of the Sargassum biosorbent using 0.1N HCl was examined in three consecutive sorption/desorption operation cycles. There was no difference among the curves (magnitude and timing of the resulting breakthrough curves) for both sorption (Fig. SI-2) and desorption (Fig. 4) cycles, indicating that there was no loss of the uptake capacity when using protonated biomass for packing the column. The resulting breakthrough curves for the sorption cycles followed the experimental pattern shown in Fig. 2a (see also Fig. SI-2 in the Supporting Information Section). The desorption breakthrough curves showing the concentrated metal-rich output are seen in Fig. 4. For the three consecutive sorption/desorption cycles, the metal uptake averaged 2 meq g$^{-1}$, and the desorption concentration averaged 1.9 meq g$^{-1}$ with a metal recovery of 95.2% (Table SI-2 in the Supporting Information Section).

Earlier work of Texier et al. (2002) demonstrated that desorption of La from bacterial biomass of P. aeruginosa was possible using 0.1M EDTA and it varied from 92% to 100%. This eluant was chosen due to possible damage to the biosorbent. Sargassum species offer greater advantage because of their chemical resistance. While a metal uptake loss of 28–30% was noticed by Kratochvíl et al. (1997) after the first operating cycle that used an HCl wash for the regeneration of virgin raw Sargassum biomass (no pre-treatment protonation), no further decrease in the uptake capacity was reported for the second and third cycles. The current work utilized

---

**Fig. 4 – Lanthanum consecutive dynamic desorption cycles.**

Eluting agent: 0.1N HCl; feed flow-rate: 15 mL min$^{-1}$; packing density: 123 g L$^{-1}$; column length: 25 cm.

Concentration factor is the percentage of metal released.
biomass already pre-treated, and batch desorption studies confirmed a biomass weight loss of about 27% during this procedure, confirming thus the observation reported by Kratochvil et al. (1997). This loss was probably due to the partial destruction of the biosorbent binding sites by consecutive desorption with HCl. However, for a proper assessment of the reusability of the biomass, more consecutive cycles would be required.

4. Conclusions

1. Computer prediction of the biosorption performance for the ternary mixture of La, Eu and H was possible by using estimated model parameters based on the binary pairs La/H and Eu/H at the same total constant normality.

2. The binary equilibrium isotherms could be modeled by a relatively constant separation factor. The binary equations could be easily developed for predicting the ternary equilibrium for the multi-metals and proton system. Metals were removed from the feed stream while protons were released during the sorption column run. The breakthrough curves could be well approximated by modeling that assumed no axial dispersion effect and intra-particle resistance as rate controlling.

3. Mass transfer coefficients were estimated for the metals in the binary pair experiments and were used to simulate the biosorption behavior of a ternary mixture. The separation factors obtained from the binary pairs could be used to simulate the ternary system, with protons being the common ion. The model was calibrated for a 25-cm long sorption column and could also predict the behavior of the ternary mixture in a column 50 cm long.

4. The Sargassum polycystum biomass used could be employed in at least three consecutive uptake/desorption cycles with no loss of the metal uptake capacity. The metal was recovered in a concentrated form and the biomass could be regenerated by 0.1N HCl.

5. The FEMLAB software provided a fast, powerful and user-friendly model-solving platform successfully used for solving the set of coupled partial differential equations characterizing the multi-component ion exchange systems.

Acknowledgments

The international CAPES (Brazil) Scholarship to V. Diniz enabled this work.

The valuable discussions with Professors J. Vera and M.E. Weber were greatly appreciated.

Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.watres.2007.07.027

R E F E R E N C E S


