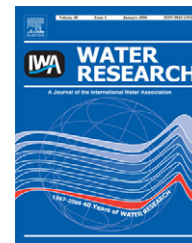


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# Column biosorption of lanthanum and europium by *Sargassum*

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## ABSTRACT

Batch and column biosorption of La<sup>3+</sup> (lanthanum) and Eu<sup>3+</sup> (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<sup>-1</sup>, 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 × 10<sup>-4</sup> and 3.7 × 10<sup>-4</sup> min<sup>-1</sup>, 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 0.1N HCl with no apparent loss in the biosorbent metal uptake capacity.

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## 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

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Nomenclature			
$X_M$	metal equivalent fraction in the liquid	$Z$	bed axial variable (cm)
$y_M$	metal equivalent fraction in the solid	$L$	total bed length (cm)
$y_M^*$	metal equilibrium equivalent fraction in the solid	$C_i$	element concentration in solution (meq L <sup>-1</sup> )
$\alpha_H^M$	separation factor between metal and proton	$C^0$	total normality (meq L <sup>-1</sup> )
$Q$	total number of ion-exchangeable binding sites (meq g <sup>-1</sup> )	$x_i$	element equivalent fraction in the liquid
$q_i$	element concentration in the solid phase (meq g <sup>-1</sup> )	$y_i$	element equivalent fraction in the solid
$k_{sM}$	mass transfer coefficient in the solid (min <sup>-1</sup> )	$\varepsilon_b$	bed void fraction
$\zeta$	dimensionless bed size	$\rho_b$	bed packing density (g L <sup>-1</sup> )
		$\tau$	dimensionless time variable
		$t$	time (min <sup>-1</sup> )
		$u$	superficial velocity (cm min <sup>-1</sup> )
		$v$	interstitial velocity (cm min <sup>-1</sup> )
		$K$	affinity constant

equations. However, none of these two models reflects the ion exchange mechanism involved in which ions are released from the biosorbent 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 feasibly be 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 (Hatzikiosyan et al., 2001). Most of the multi-component ion

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