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Effect of counterions on lanthanum biosorption by *Sargassum polycystum*

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Abstract

The effect of the presence of different anions on the biosorption of La^{3+} (Lanthanum) using *Sargassum polycystum* Ca-loaded biomass was studied in this work. Different types of metal salts were used, such as nitrate, sulphate and chloride. The presence of the anion sulphate decreased the metal uptake for tested pH values of 3–5 when compared to the nitrate and chloride systems. The presence of chloride ions did not seem to interfere with the lanthanum removal. The speciation of lanthanum in solution could explain the differences obtained for the different systems and the Mineql+ program was used for the calculations. A monovalent complex with sulphate and lanthanum was formed that had lower apparent affinity towards the biomass compared to the free trivalent metal ion. The La uptake varied from 0.6 to 1.0 mmol g^{-1}. The Langmuir model was used to describe quantitatively the sorption isotherms. The addition of sulphuric acid for pH adjustment decreased the metal uptake from lanthanum sulphate solutions when compared to the nitric acid addition. The effect was more pronounced with sulphuric acid due to the formation of complexes.

Keywords: Biosorption; Anions; Lanthanum; *Sargassum*; Speciation

1. Introduction

Biosorption is a process where metal ions in solution are removed by dead biomass such as seaweed, yeast, bacteria, and fungi. It can represent an attractive and cost-effective alternative for certain types of industrial waste water treatment (Volesky, 1990). In general, biomass considered could be an industrial waste or naturally grown and collected and, therefore, cheaper than manmade ion exchange resins (Zouboulis et al., 1997). On the other hand, bioaccumulation is a metabolically controlled process for the removal of metals by living organisms, which invariably involves more complex cultivation and toxicity issues. The use of biosorption technology to remove toxic heavy metal ions using naturally abundant commodities such as seaweeds, especially brown algae, has been greatly envisaged, showing high metal uptakes and selectivities (Davis et al., 2003). *Sargassum* is a brown seaweed that contains alginate with abundant carboxylic groups capable of capturing cations present in solution. The alginate matrix is present as a gel phase being easily penetrable for small metallic cations making it thus a suitable biosorbent with a high sorption potential (Yang and Volesky, 1999a). *Sargassum* is abundant in places such as Philippines, Thailand, Indonesia, Europe and the Caribbean. After drying, it could be stored indefinitely and would still keep its metal-binding capacity.

Biosorption studies involving the removal of heavy metal ions have most often made use of nitrate salts to

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prepare experimental solutions. These are less likely to form complexes with metals (Diniz et al., 2001; Diniz and Volesky, 2005) that can thus be present as free metal ions, simplifying the system studies. However, real industrial solutions may contain anions other than nitrate, for example, chloride and sulphate. Some studies reported in the literature have examined the effect of anions on the removal of metal ions from aqueous solutions (Ahuja et al., 1999a, b; Kuyucak and Volesky, 1989; Palmieri et al., 2003; Pulsawat et al., 2003). However, very little attention has been paid to the effect of metal speciation on their biosorption uptake in order to explain sometimes unexpected anomalies.

Lanthanides have a potential future in a number of industries. The demand for lanthanides is expected to correspondingly increase in time. Although they do not represent an environmental threat nowadays, more strict regulations will likely be imposed. New technologies are required to improve separation and recovery of these elements. Biosorption studies involving lanthanides using different types of sorbent materials have been the subject of interest (Palmieri, 2001; Palmieri et al., 2000, 2003).

An earlier work (Diniz and Volesky, 2005) studied the removal of lanthanum, europium and ytterbium from nitrate solutions using *Sargassum polycystum* brown seaweed biomass. The present study focuses on the effect of using different types of metal salts as nitrate, sulphate and chloride on the lanthanum removal from aqueous solutions using *S. polycystum* biomass.

2. Materials and methods

2.1. Biomass preparation

The biosorbent used in experiments was the brown seaweed, *S. polycystum*, collected at the Philippines. The sun-dried material was washed with tap water and distilled water to remove sand and excess of sodium and potassium ions. After drying overnight at a maximum temperature of 55 °C to avoid degradation of the binding sites, the biomass was ground and particles larger than 0.5 mm were selected. The biomass was subsequently loaded with calcium in a solution of 0.05 M $Ca(NO_3)_2$ (biomass concentration of 10 g L^{-1}) for 24 h under gentle agitation. Later, the biomass was washed with distilled de-ionized water to remove excess Ca ions until the mixture reached approximately pH 5. Finally, to increase its shelf-life, the biomass was again dried overnight at 50–55 °C.

2.2. Batch equilibrium experiments

Solutions containing the metals were individually prepared using distilled de-ionized water and different La salts: $La(NO_3)_3 \cdot 6H_2O$, $La_2(SO_4)_3 \cdot 6H_2O$, $LaCl_3 \cdot 6H_2O$ (all Alfa Aesar supplied). For the batch equilibrium experiments the initial metal concentrations ranged from 100 to 500 mg L^{-1}. In total, 0.1 g of dry biomass was contacted with 0.05 L of known-concentration solutions for 24 h and the suspension was agitated on a rotary shaker at 150 rpm. The pH adjustment was made when necessary with solutions containing a known concentration of nitric acid (0.025–0.2 mol L^{-1} HNO_3). The pH was adjusted in order to obtain the final equilibrium pH 3, pH 4 or pH 5 for which the equilibrium isotherms were eventually plotted. The pH of some of the chloride solutions was adjusted with hydrochloric acid (0.025–0.2 mol L^{-1} HCl) while the pH in some of the sulphate solutions was adjusted using sulphuric acid (0.05 mol L^{-1}).

2.3. Metal analysis

Metal content present in solution for La and Ca was determined by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrell Ash, Model Trace Scan).

2.4. Metal uptake

The lanthanide metals uptake by the biomass was calculated from the difference between the initial and final concentrations in the liquid phase using the biomass dry weight.

3. Results and discussion

The earlier work (Diniz and Volesky, 2005) presented equilibrium sorption isotherms for lanthanum using nitrate salt and *S. polycystum* biomass at pH levels of 3–5. In this work, the effect of preparing the metal solution with the different types of salts NO_3^-, Cl^- and SO_4^{2-} was investigated.

3.1. Effect of NO_3^-, Cl^- and SO_4^{2-} on lanthanum biosorption

The effect of counterions in a system is an important issue as industrial wastes can contain anions other than nitrate, such as chloride and sulphate. Usually, nitrate salts are chosen for biosorption studies due to solubility reasons. More importantly, they do not form complexes with metals easily and could be considered as an inert in solution where all the metal present would be in the free form, in this case there would be only one lanthanum species, the free trivalent cation.

Sorption isotherms relate the uptake of a certain metal and the final equilibrium metal concentration. Fig. 1 shows the equilibrium isotherms for solutions