Biosorption of lanthanum using *Sargassum fluitans* in batch system

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Abstract

Separation and purification of lanthanum from other rare-earth (RE) elements are highly complex processes comprising several steps of extraction using organic solvents or ion-exchange resins at high costs. In order to study the biosorption process as an alternative for conventional lanthanum recovery, this work investigated some basic aspects of lanthanum–*Sargassum* biomass interactions in batch equilibrium contact. The dynamics of biosorption, influence of pH, and the desorption of this RE were investigated. Maximum biosorption coefficient (q_{max}) increased from 0.05 at pH 2 to 0.53 mmol g^{-1} at pH 5 for lanthanum sulfate. When lanthanum chloride was used, a higher q_{max} at pH 5 (0.73 mmol g^{-1}) was observed as compared to the sulfate salt ($q_{max} = 0.53$ mmol g^{-1}) at the same pH. Adsorption and desorption curves pointed out a complete recovery of metal adsorbed in the *Sargassum fluitans* biomass, showing a reversibility of this process and indicating the potential of biosorption for lanthanum removal and recovery.
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1. Introduction

Similar physical and chemical behavior of metals from the rare-earth (RE) group makes it difficult to separate individual elements. Several extraction steps are necessary for the purpose using organic solvents or ion-exchange resins. These physicochemical processes are rather expensive. Due to biosorption characteristics close to that observed in the ion-exchange columns process, it can be considered as a potential alternative, economically attractive for rare-earth recovery or separation.

From the RE elements, lanthanum has currently garnered special attention due to its technological importance because of increasing demands for advanced new materials. Current applications of lanthanum as a pure element or in association with other compounds are in super alloys, catalysts, special ceramics, and in organic synthesis.

In solution, this element has a stable valence of $+3$ and its ionic radius is very close to that of the calcium ion ($+2$), which might substitute this ion in inorganic compounds or in some biomolecules (Mayer et al., 1999; Brown et al., 1994).

Biosorption of heavy metals by microbial cells has been recognized as a potential alternative to existing technologies for removal of these contaminants from polluted waters. This phenomenon is generally des-

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cribed as retention of ions from solution by microbial cells and this metal uptake is normally very efficient and frequently selective (Ledin, 2000; Ozer et al., 1999). Characteristics of the biosorption process can also be exploited for concentration and selective recovery of more valuable metals.

The uptake of metal ions by microorganisms has been shown to occur in two ways: passive and/or active uptake. During the passive uptake (biosorption), the metal ions are quickly adsorbed onto the cell surface of the biomass during its contact with the metal solution (physical adsorption or ion exchange at the cell surface). The active uptake (bioaccumulation) is a slower process involving the transport of ions across the cell membrane toward the cytoplasm occurring only in living cells (Donmez et al., 1999). Nonliving cells have been preferred over live biomass in biosorption processes due to nonlimiting conditions imposed by cellular growth.

From the biomass that can be used in biosorption, brown seaweed has been normally selected due to its high performance for ionic adsorption and availability. *Sargassum* sp. can be found on several oceanic coasts in Brazil, Cuba, Australia, part of the United States and Southeast Asia.

The algal cell walls contain biopolymeric substances that could provide binding groups for metal sorption such as amino, carboxyl, phosphate, and sulphate anions acting as a cationic resin. The nitrogen and oxygen from amino and carboxyl groups in the peptides could be available for characteristic coordination bonding with metallic ions. Such bond formation could be accompanied by displacement of protons dependent in part on the extent of dissociation of these groups as determined by the pH in an ion-exchange mechanism (Kratochvil and Volesky, 1998).

Despite their strategic and economic importance, RE elements have not been much evaluated regarding their potential to be concentrated and eventually separated by the biosorption process. Only in the last few years have some investigations been published on this matter. Texier et al. (1999) investigated the ability of *Pseudomonas aeruginosa* to adsorb selectively La(III), Eu(III) and Yb(III). A preferential biosorption for europium and ytterbium than lanthanum was observed using this bacteria. Also, Palmieri et al. (2000) demonstrated that neodymium can be recovered by *Monoraphidium* sp., baker's yeast and

Penicillium sp. utilizing biosorption in nonliving microorganisms.

In the present study, some basic aspects of biosorption and desorption of lanthanum by nonliving biomass of *Sargassum fluitans* in batch system are reported.

2. Materials and methods

2.1. Macroalgae and biosorbent preparation

The brown seaweed *S. fluitans* was collected in Florida, USA. The biomass was washed and sun-dried for storage. For biosorption experiments the algae was chopped into particles (0.3–0.5 cm), washed twice in distilled water and twice in acidic solution (0.1 mol l^{-1} hydrochloric acid or 0.05 mol l^{-1} sulfuric acid) and after that in distilled water until pH stabilized at approximately 4.0 (each step took one h).

2.2. Metal solution

Lanthanum stock solution was prepared by dissolving lanthanum oxide (Aldrich, 99.99%) in concentrated sulfuric or hydrochloric acid to a final metal concentration of 35 mmol l^{-1}.

2.3. Biosorption experiments

The time required for establishing the sorption equilibrium in contact systems was assessed from preliminary sorption experiments as described in the following. Batch biosorption experiments were carried out in 125 ml Erlenmeyer flasks by mixing 0.1 g of pretreated *S. fluitans* biomass in 40 ml of lanthanum acidic solution (H_2SO_4 or HCl) diluted as required. The flask content was gently mixed at 30 °C on an orbital shaker (180 rpm), and the pH of the suspension was adjusted using sodium hydroxide.

After the sorption system reached equilibrium, supernatant samples were withdrawn after decantation for lanthanum analysis by ICP-AES (Thermo Jarrel Ash, Trace Scan).

The lanthanum biosorption uptake (q) was calculated using the following mass balance relationship:

$$q = (C_f - C_i)V/M \tag{1}$$

where C_i and C_f—the initial and final concentrations of lanthanum in solution, respectively (mmol l^{-1}); V—volume of metal solution (l); M—dry mass of *S. fluitans* (g).

2.4. Desorption experiments

Desorption experiments were carried out using 0.1 g of biomass previously loaded with lanthanum sulfate at pH 5 as described above. The loaded biomass was drained to remove all lanthanum solution, washed with 20 ml of distilled water at pH 5.0 and then resuspended in 50 ml of hydrochloric acid 0.24 mol l^{-1} at 30 °C in an orbital shaker for 30 h to reach the equilibrium. Supernatant samples were taken for metal and pH determination. The desorption coefficient (q_d) was calculated as follows:

$$q_d = C_f V / M \qquad (2)$$

3. Results and discussion

3.1. Dynamics of biosorption

Biosorption of metals by nonliving biomass is normally a rapid process; its overall rate is known to be limited by the intraparticle mass transfer (Puranik et al., 1999; Volesky and Holan, 1995). Fig. 1 shows the time course of lanthanum biosorption by *S. fluitans*. In
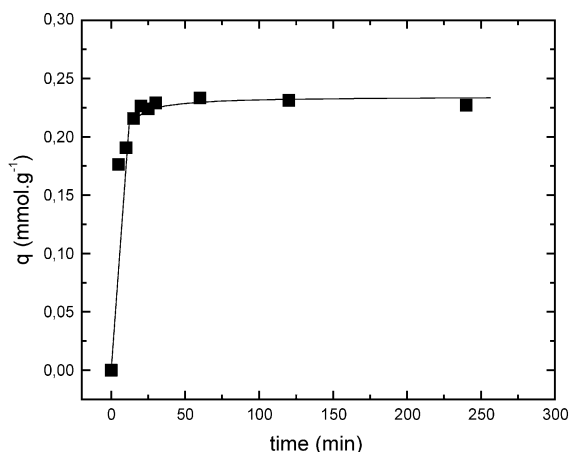

Fig. 1. Time course of lanthanum sulfate biosorption on *S. fluitans*.

the first 25 min, a fast accumulation of the metal in the biomass was observed, reaching about 95% of the total biosorption capacity. After that, the rate of biosorption slowed down reaching the equilibrium with the maximum uptake of 0.24 mmol g^{-1}, in around 40 min.

The pH value in these experiments was not controlled in order not to disturb the equilibrium. From the initial value of 4.0, the pH decreased to 3.7 (values measured in the first and last flasks) due to the exchange of lanthanum for protons from the biomass binding sites.

3.2. Dependence of lanthanum biosorption on pH

The literature has demonstrated that the carboxyl groups present in the biomass have a very important role in metal biosorption, being responsible for around 90% of the metal immobilization in the process (Kratochvil and Volesky, 1998). Brown et al. (1994) also reported that lanthanides appear to bind specifically to anionic groups in the membrane matrix, possibly to the negatively charged groups on the mucopolysaccharide/ protein complex. They may also bind to the polar head, phosphate head groups or the lipid bilayer. These groups in the biomass act like sites for ion exchange with metals (lanthanum, in this work), resulting in the biosorption of these ions.

The sorption equilibrium is dependent on the pH because it affects the dissociation of these groups (pK of carboxylic groups is about 4.8). The extent of the carboxyl group dissociation is higher as the value of pH increases, producing more free sites for lanthanum biosorption (Ledin, 2000). This behavior was observed in the experiments to determine biosorption isotherms of lanthanum sulphate on *S. fluitans*. The maximum biosorption uptake (q_{max}) increased from 0.049 mmol g^{-1} at pH 2.0 to 0.53 mmol g^{-1} at pH 5.0, more than a 10-fold increase (Fig. 2). Lanthanum biosorption at pH higher than 5.0 was not considered because precipitation occurred in the solution, especially at concentrations above 1.0 mmol l^{-1}, indicating the hydrolysis of the metal ion with the formation of corresponding insoluble hydroxide.

3.3. Desorption of lanthanum

As indicated in the literature and in the present work, biosorption is a reversible ion-exchange equili-
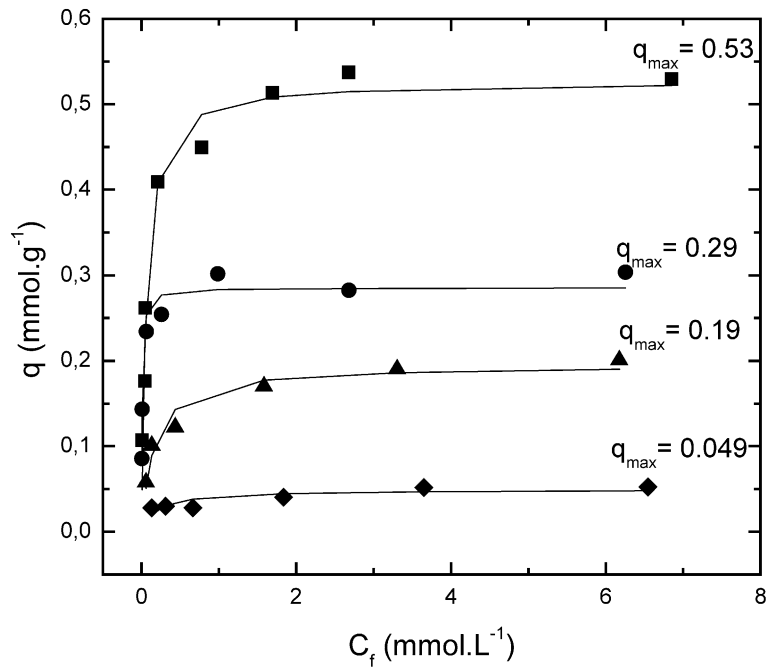
Fig. 2. Adsorption isotherms at different pH values for lanthanum sulfate on *S. fluitans*. Symbols: (♦) pH 2; (▲) pH 3; (●) pH 4; (■) pH 5.

brium. In this way, desorption of metal ions can be obtained by shifting the ion-exchange equilibrium in order to release the metal bound to the biomass. Many

chemicals can be used to achieve this displacement such as EDTA, salts, acid or bases (Kapoor et al., 1999). Usually, a diluted strong mineral acid, such as
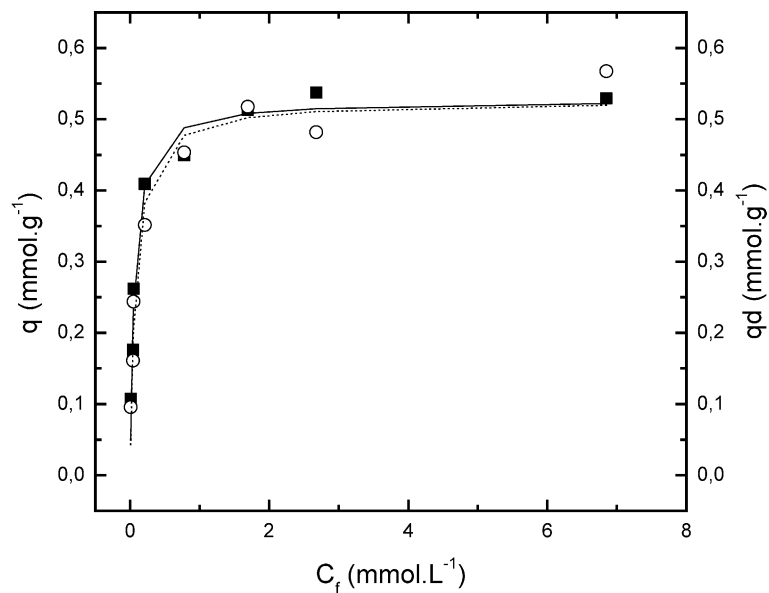

Fig. 3. Adsorption (■) and desorption (○) isotherms for lanthanum sulfate on *S. fluitans*.

HCl, is sufficient to affect the biosorption equilibrium to release the metal ions. This effect can be observed in Fig. 3 for lanthanum desorption. Desorption equilibrium can also be plotted as isotherm curves which relates the amount of metal desorbed and the concentration of metal in the desorption equilibrium. The close behavior for adsorption and desorption isotherms (Fig. 3) pointed out this reversibility and the complete recovery of lanthanum initially adsorbed onto *S. fluitans*.

3.4. Influence of anions present in solution

The binding of lanthanum ions by nonliving algal biomass is influenced by other ionic species, such as anions, present in solution. A higher q_{max} was observed for lanthanum chloride than when lanthanum sulfate was used at the same pH (Fig. 4). Ahuja et al. (1999) have already observed the same behavior reporting a higher inhibitory effect of sulfate ions on zinc biosorption by *Oscillatoria anguistissima* when compared with cases when zinc chloride or nitrate were used.

In the case of lanthanides, the formation of complexes with chloride or sulfate affects the coordination sphere of metal, leading to an influence on the net charge of the cation. Chloride ions are reported to have an outer sphere character with a less disturbance in the hydration sphere. On the other hand, sulfate and carboxylate anions present inner sphere character more pronounced in the complex formation with lanthanum (Choppin and Rizkalla, 1994). The higher biosorption values for lanthanum chloride than the sulfate-based solutions obtained in this work could suggest that the less disturbance on the inner coordination sphere caused by chloride anion facilitates the interaction with carboxylate groups present in the biomass. However, more studies must be conducted to elucidate and confirm this explanation.

The uptake of lanthanum from sulfate-containing solutions seems to be more sensitive to pH because q_{max} at pH 5.0 was almost two times the value observed for pH 4.0, while for lanthanum chloride the biosorption increased around 20% (Fig. 4).
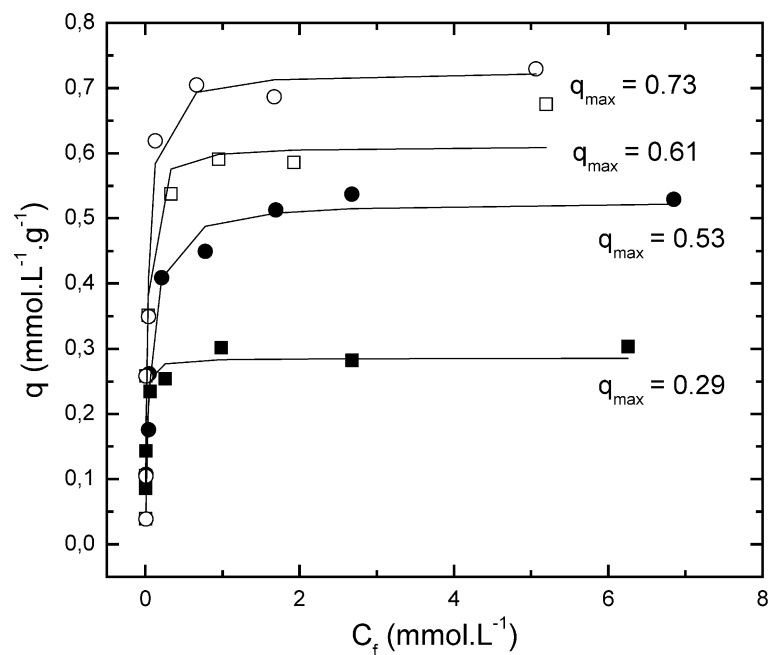

Fig. 4. Adsorption isotherms at pH 4 (squares) and pH 5 (circles) for lanthanum sulfate (closed symbols) and lanthanum chloride (opened symbols) on *S. fluitans*.

4. Conclusions

The aim of this work was to study some basic aspects of lanthanum biosorption using nonliving *S. fluitans*. This biomass immobilized lanthanum, resulting in isotherms closely related to the Langmuir model that is commonly used to fit biosorption process (Aksu and Açikel, 1999, 2000; Donmez et al., 1999). Lanthanum biosorption was influenced by the pH values, as expected for the ion-exchange mechanism involving mostly carboxyl groups. Higher values of pH resulted in higher quantity of metal adsorbed onto the biomass.

Desorption of lanthanum loaded onto the biomass was complete using a hydrochloric acid solution. The coincident behavior of adsorption and desorption isotherms confirms the reversibility of this equilibrium and the complete removal of the bound metal.

The two chemical systems investigated (chloride and sulfate salts) presented higher biosorption uptakes at higher pH values and the use of lanthanum chloride resulted in higher biosorption uptakes than observed with lanthanum sulfate. However, biosorption of the lanthanum using sulfate system was more extensively investigated in this work because it is usually present in solutions obtained from rare-earth extraction processes. The chloride system was used to compare the biosorption performance in some of the best conditions in order to observe that chemical anionic effect.

As the results suggest, biosorption onto nonliving *S. fluitans* showed a good potential to be an interesting alternative method for lanthanum recovery from solutions.

Acknowledgements

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