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Desorption of lanthanum, europium and ytterbium from *Sargassum*

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Abstract

The desorption of La, Eu and Yb was studied in this work. The purpose of this work was to verify the reversibility of the sorption reaction, and thus the possibility of the desorption process for simultaneous metal recovery and regeneration of the biomass. The desorption of calcium ions at different levels of pH using mineral acid was also verified and the Ca release increased with decreasing pH, achieving 2.5 mequiv. g^{-1} at pH 2 and 2.8 mequiv. g^{-1} using 0.1 mol L^{-1} HNO_3. Several eluting agents at different concentrations were tested to desorb the lanthanides including nitric and hydrochloric acids, calcium nitrate and chloride salts, EDTA, oxalic and diglycolic acids. 95–100% desorption for all metals was obtained with 0.3 mol L^{-1} HCl. La desorption with the other eluting agents was 70% with 2 mol L^{-1} $CaCl_2$, 83.7%, with 0.5 mol L^{-1} EDTA and 88.4% with 0.023 mol L^{-1} diglycolic acid. A plateau was reached when a liquid to solid ratio (L/S) of 2 L g^{-1} was used with 0.1 mol L^{-1} HNO_3. Desorption levels ranged between 85 and 95%. At the same (L/S) ratio, 0.2 mol L^{-1} HCl was able to elute all the metals from the individual metal loaded biomass, although it could not remove the metals completely from the mixed-metal loaded biomass. The desorption levels decreased with increasing metal sorption affinity as follows, 94.0, 86.3 and 75.2% for Yb, La and Eu, respectively when the eluting agent was 0.1N HCl. There was no difference between not washing the biomass at all and washing it either once or twice after the sorption process.

Keywords: Desorption; Lanthanum; Europium; Ytterbium; *Sargassum*

1. Introduction

Biosorption is a process where metal ions in solution are removed by dead biomass such as seaweed, yeast, bacteria, and fungi. This represents an attractive and cost-effective alternative for waste water treatment [1]. On the other hand, bioaccumulation is a metabolically controlled process for the removal of metals by living organisms, which requires cultivation and toxicity issues. The usage of biosorption technology to remove toxic heavy metal ions using natural abundant products as seaweed, specifically brown algae, has been greatly acknowledged, showing high metal uptake and selectivity [2].

Many studies have reported the outstanding uptake capacity of those biomasses, mainly *Sargassum* for the removal of cations from solution, functioning by this way as a cation exchanger. Cadmium [3,4], chromium [5], copper and lead [6], uranium [3,4], among others, have been removed from solutions using this biomass. The reason for this is that *Sargassum* contains in its structure carboxylic groups capable of capturing cations present in solution. In its composition, the alginic acid is the main constituent, and especially for the guluronic acid which is responsible for these functional groups [7]. As the alginate matrix is present as a gel phase, it allows this material to be suitable as a biosorbent due to its high porosity, making it easier for the ions to move through this material [3,4].

The desorption process has the purpose of recovering these metals while regenerating the biomass that could be used in subsequent sorption and desorption cycles. The recovered metals could be further used for process application in more concentrated solutions that could be obtained from continuous sorption/desorption cycles in a fixed-bed column reactor. Desorption studies have provided evidence on the reversibility of the metal sorption process using biomass and that HCl constitutes one of the most used elutants [8–11]. In addition, isocratic [12] and gradient [13] elution chromatography has employed nitric acid for rare earths separation.

Sorption studies of these lanthanides – lanthanum, europium and ytterbium – by the brown seaweed *Sargassum polycystum* biomass were already reported in earlier work [14]. The present study focused on desorbing these metals from the biomass by using eluting agents capable of removing all the metals present

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in the *Sargassum* cell wall structure. The goal of this work was to verify the reversibility of the sorption reaction thus the possibility of the desorption process for simultaneously metal recovery and regeneration of the biomass.

2. Materials and methods

2.1. Biomass preparation

The biosorbent used in this work was the brown seaweed, *Sargassum polycystum*, collected in the Philippines. The sun-dried biomass 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 mol L^{-1} $CaNO_3$ (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 the excess of Ca ions. Finally, to increase its shelf-life, the biomass was again dried overnight at 50–55 °C.

2.2. Metal sorption and desorption batch experiments

Sorption experiments were performed in order to load the biomass with the lanthanides La, Eu and Yb. Solutions containing the metals were individually prepared using distilled de-ionized water and nitrate salts: $La(NO_3)_3.6H_2O$, $La_2(SO4)_3.6H_2O$, $LaCl_3.6H_2O$ (all Alfa Aesar supplied). The initial metal concentrations were 3 mmol L^{-1}. 2 g of dry biomass was contacted with 1 L of known-concentration solutions for 24 h and the suspension was agitated using a magnetic stirrer. The pH adjustment was made when necessary with solutions containing a known concentration of nitric acid (0.025–0.2 mmol L^{-1} HNO_3). The pH was adjusted in order to obtain the final equilibrium pH between 4 and 5 in order to achieve approximately the maximum metal sorption uptake possible. The biomass was further filtered out, washed with deionized water and dried overnight at 50–50 °C. For multi-metal loaded biomass, the initial concentrations of individual metals were 1 mmol L^{-1} each, resulting in a total metal concentration of 3 mmol L^{-1}.

The biomass weight loss was examined by weighing 0.5 g of biomass and put into contact with 50 mL of 0.1 and 0.2 mol L^{-1} of nitric and hydrochloric acid. The samples were filtered and dried overnight at 50–55 °C. The total organic carbon of the filtrate was assessed by a Total Organic Carbon Analyzer DC-80, DC-85 and model 183 TOC Boat sampler (Folio Instruments Inc., Rosemount Dohrmann).

Desorption experiments were performed using 0.1 g of metal loaded biomass and 50 mL of eluting solution for 24 h. Blanks were performed to account for excess metal released. Among the eluting agents tested were: hydrochloric (Fisher), nitric (Fisher), oxalic (Alfa Aesar) and diglycolic (Research Chemicals) acids, calcium nitrate (Anachemia), EDTA – disodium salt (Anachemia).

The experiments assessing the effect of liquid to solid ratio were performed varying the mass of the biomass and the volume of eluting agent to provide the ratios of 0.5, 1, 2, 4 and 8 L g^{-1}. Desorption experiments were also performed at a (L/S) ratio of 2 L g^{-1} using 0.025 g of lanthanide loaded biomass in 50 mL of eluting agent.

2.3. Metal analysis

The metal content of liquid samples (La, Eu, Yb and Ca) was determined by an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrell Ash, Model Trace Scan).

2.4. Metals uptake and proton binding

The lanthanide metals uptake by the biomass was calculated from the difference between the initial (C_i) and final concentrations (C_f) in the liquid phase expressed in mmol L^{-1}:

$$q_M(\text{mmol g}^{-1}) = \frac{C_i V_i - C_f V_f}{m} \quad (1)$$

where m is the biomass dry weight (g), V_i the initial volume of solution (L), V_f is the final volume of the solution (L).

The amount of calcium released by the biosorbent was calculated by the difference between the initial and final concentrations of calcium in the respective solutions. Blanks were prepared with distilled de-ionized water and biomass to account for calcium excess release to be subtracted from the total calcium released into the solution.

$$q_{Ca(rel)}(\text{mequiv. g}^{-1}) = \frac{((C_f V_f - C_i V_i) - (B_f - B_i)V_i)}{m} \quad (2)$$

where C_i is the initial concentration of calcium in solution (mequiv. L^{-1}), C_f the final concentration of calcium in solution (mequiv. L^{-1}), B_i the initial concentration of calcium obtained from the initial blank (mequiv. L^{-1}); B_f is the final concentration of calcium obtained from the initial blank (mequiv. L^{-1}).

The proton uptake was calculated according to [15] by the difference between the final and initial pH values and the amount of nitric acid used to adjust the pH of the sorption system.

$$q_H(\text{mequiv. g}^{-1}) = \frac{\{[H]_{add} V_{add} - ([H]_f V_f - [H]_i V_i)\}}{m} \quad (3)$$

where $[H]_{add}$ is the concentration of the acid added for adjusting the pH (mmol L^{-1}); V_{add} the volume of acid used for adjusting the pH [L]; $[H]_f$ the final proton concentration relative to the final pH of solution (mmol L^{-1}); $[H]_i$ is the initial proton concentration relative to the initial pH of solution (mmol L^{-1}).

3. Results and discussion

3.1. Desorption of calcium with pH

In this part of the present work, the amount of calcium released from the biomass was assessed at different levels of pH adjusted with nitric acid. Fig. 1 shows the amount of calcium ions