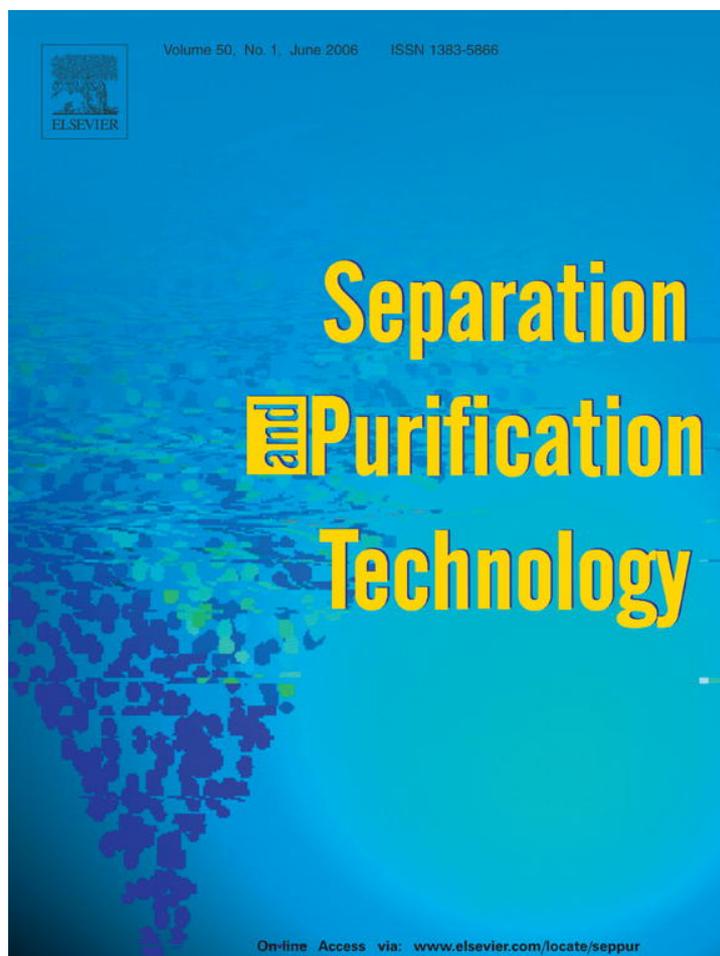


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Desorption of lanthanum, europium and ytterbium from *Sargassum*

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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 HNO₃. 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 CaCl₂, 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 HNO₃. 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.

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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 CaNO₃ (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(NO₃)₃·6H₂O, La₂(SO₄)₃·6H₂O, LaCl₃·6H₂O (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 HNO₃). 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.

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

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.

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

where $[H]_{\text{add}}$ 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

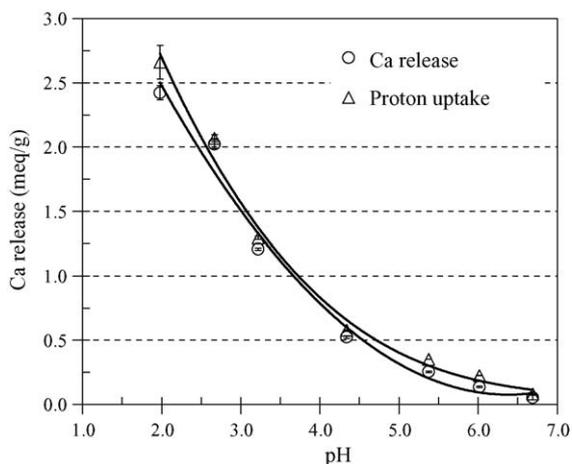


Fig. 1. Release of calcium from biomass and removal of protons at different levels of pH.

released from the biomass and the amount of protons removed from the solution. It can be seen that the total number of ions removed and released were practically the same thus confirming the ion exchange mechanism occurring during the process. The number of calcium ions desorbed from the biomass increased sharply as pH decreased, reaching 2.42 ± 0.06 mequiv. g^{-1} at pH 2. The experiments were also performed at higher acidic concentrations using 0.1 mol L^{-1} HCl, resulting in a calcium release of 2.79 ± 0.02 mequiv. g^{-1} . This number is very much in accordance with the maximum uptake of lanthanides reported in previous work [14]. Table 1 summarizes the release of calcium ions at different concentrations of nitric acid and 100 mmol L^{-1} HCl. The balance of protons at higher acid concentrations could no longer be calculated according to pH due to a large error because the proton removal becomes insignificant compared to the high concentration of hydrogen ions in solution. The results obtained confirmed that the ion exchange was the mechanism of the biosorption process using brown seaweed biomass. In addition, desorption of calcium ions was demonstrated using mineral acids such as hydrochloric and nitric acid.

3.2. Biomass weight loss caused by mineral acids

The effect of using mineral acids on the biomass weight loss was also verified. The use of either acid (HCl or HNO_3) resulted in a weight loss between 27 and 30% with small differences observed in the TOC leached from the biomass. A slightly lower weight loss, compared to the other results, was observed when 100 mmol L^{-1} HCl was used. Therefore, 0.2 mol L^{-1} HCl could

Table 1
Calcium ions released at different acidity levels

Acid	Acid concentration (mmol L^{-1})	Calcium released (mequiv. L^{-1})
HNO_3	38	2.58 ± 0.03
	50	2.75 ± 0.06
	196	2.71 ± 0.09
HCl	100	2.79 ± 0.02

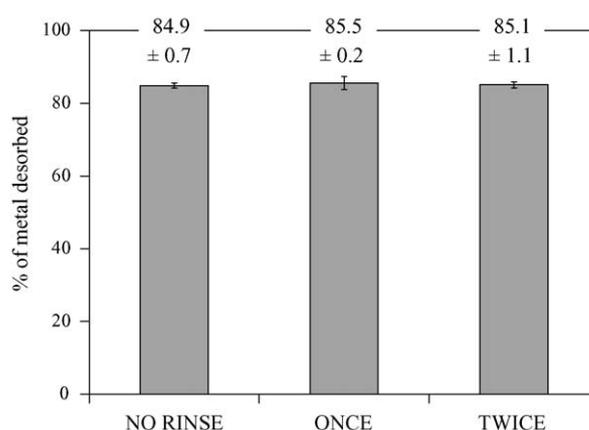


Fig. 2. Effect of washing the biomass after La sorption and before its desorption.

safely be used for desorption purposes without increasing the biomass weight loss.

3.3. Effect of washing the biomass after sorption and before desorption

Fig. 2 describes the effect of washing the La-loaded biomass either once or twice or even not washing it at all – the procedure did not have an impact on the amount of lanthanum eventually desorbed from the biomass. For this reason, only the necessary volume of water for transferring the material to the paper filter was used in the following experiments.

3.4. Desorption of an individual metal system

The objective was to verify the possibility of desorbing the immobilized lanthanide metals from the biomass. Fig. 3 shows the percentage of desorption of each element individually using hydrochloric or nitric acids at different concentrations. They were chosen because mineral acids appear to be the most feasibly applicable eluting agents. The desorption of the selected elements ranged from 65 to 100%. In the batch desorption technique used, it is likely that at weak acidity a new low-pH equilibrium was reached in the desorption system, preventing the complete elution and release of the sorbate metal into the

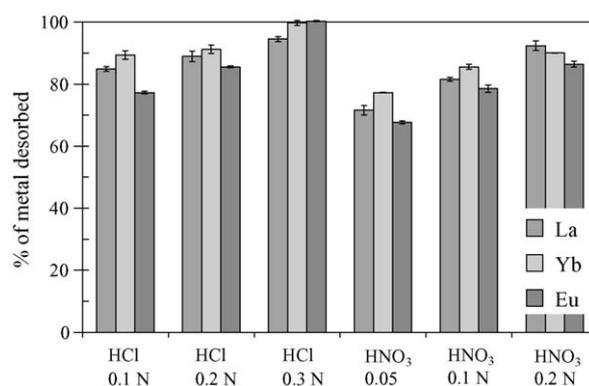


Fig. 3. Desorption of individual elements with different concentrations of mineral acids. Single-element systems containing respectively La, Eu and Yb.

solution. The complete desorption of the elements was achieved at 0.3 mol L^{-1} HCl. As expected, the percentage desorption for all three elements increased with increasing acid concentrations, i.e., elevated proton concentrations. The most common acid concentration of 0.1 mol L^{-1} HCl desorbed from 80 to 90% of the metals.

A pattern could be pointed out in the current desorption results. Europium showed the least percentage of desorption, followed by lanthanum and ytterbium under the same conditions. A previous work [14] described the “affinity sequence” for the biomass as $\text{Eu} > \text{La} > \text{Yb}$. It is obvious that the metals with higher affinity towards the biomass were more difficult to desorb, resulting in an inverted sequence for the “percentage of metal desorbed” $\text{Yb} > \text{La} > \text{Eu}$. However, for higher acid concentrations the same pattern could not be expressed. When the concentration of protons is very high, the relatively small individual metal affinity differences did not play a role any more. The protons just swept the metals away from the biosorbent. In another work, lanthanum could be completely desorbed from *Sargassum fluitans* by 0.24 mol L^{-1} HCl under the liquid to solid ratio of 0.5 L g^{-1} [11], confirming the requirement for a higher proton pressure in order for this to take place.

The (L/S) ratio used in the current experiments was 0.5 L g^{-1} , the same ratio as used in the sorption uptake experiments. Actually, the percentage desorption could have been somewhat larger if a higher (L/S) ratio had been used. However, the aim of this work was to verify the possibility of the desorption of the respective elements and compare the results among them using the same ratio as used in sorption experiments. The best way to perform these experiments would be using the “tea bag” technique where the (L/S) ratio could be infinitely high to allow for a complete desorption without any restrictions related to the (liquid) volume. The “tea bag” test simulates the process taking place in a dynamic fixed-bed column whereby a fresh eluting agent feeds the column continuously. In the “tea bag” technique, the metal content of the solids is assessed since the metal content in the “vast” amount of liquid would practically not change. The best results could eventually be used for further tea bag experiments for optimizing the process and verify if eventually 100% desorption could be achieved. On the other hand, a very large volume could lead to large errors. Eventually, only repeated actual dynamic column experiments would be really able to tell if all metal could be completely desorbed from the biomass.

In addition, organic eluting agents were also used for the desorption of lanthanum. Fig. 4 describes the results obtained. All the percentage desorption values were lower than those obtained from nitric and hydrochloric acids under the conditions tested. EDTA and diglycolic acids resulted in lanthanum desorption levels from 85 to 90%. Oxalic acid resulted in very poor desorption values. EDTA constitutes one of the most common organic elutants and has been reported in other works [16]. In column experiments, $96 \pm 4\%$ of lanthanum could be desorbed from *Pseudomonas aeruginosa* using 0.1 mol L^{-1} EDTA [17]. Oxalic and diglycolic acids are mainly used in chromatography for rare earth elements separation [18,19].

Calcium nitrate and chloride solutions were also tested for desorption purposes. High concentrations of these solutions

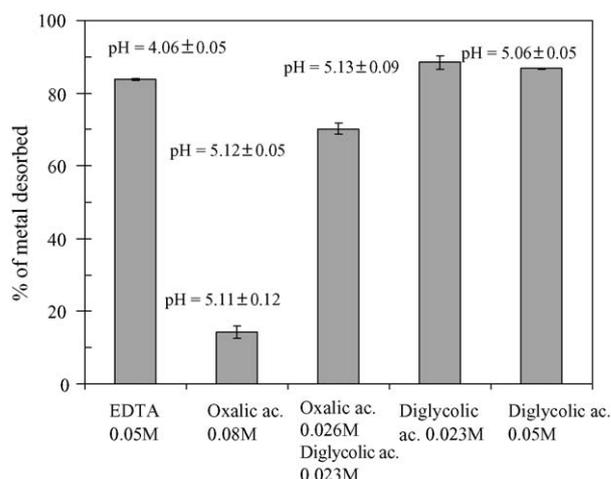


Fig. 4. Single-element system desorption of La using different organic acids.

could only be made upon acidification. Calcium chloride solutions were also tested at higher concentration levels to verify if all the metal present in the biomass could be desorbed and if so, what level of calcium concentration in solution would be necessary to attempt desorbing all the metals from the biomass. The lanthanide ions are characterized by large ionic radii, what means that substitution reactions usually involve the large cations such as calcium or strontium. These ions are essentially spherical and form complexes very much like alkaline and alkaline earth ions and are very electropositive, so their bonding characteristics are largely ionic [20]. The affinity of the calcium ions is much lower than that of the lanthanides. Therefore, concentration of calcium ions in solution definitely plays a role. The limitation is the solubility of the calcium salt in aqueous solution. The results are depicted in Fig. 5. It can be seen that calcium chloride solution resulted in a little larger percentage desorption at 50 mmol L^{-1} than nitrate for the same concentration. This could be due to the formation of the monovalent calcium nitrate complex. It was also observed that lanthanum desorption increased with the calcium concentration. However, the maximum desorption obtained was around 50% at 500 mmol L^{-1} CaCl_2 solution. The calcium chloride salt rather than the nitrate one would be

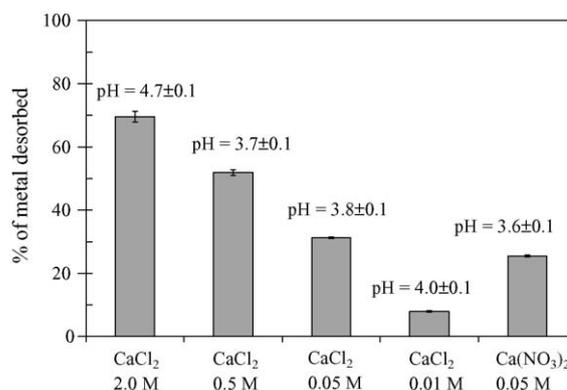


Fig. 5. Single-element system desorption of La using different concentrations of calcium nitrate and chloride solutions.

best suited for desorption purposes. The pH of the calcium solutions was kept below 4 to avoid any precipitation with carbonate due to the very high calcium concentration. Increasing the total calcium concentration up to 2000 mmol L^{-1} , the total lanthanum desorbed corresponded to 69.6%. Slightly better results were obtained for the chloride solutions than the nitrate ones for the same level of concentration, 0.05 mol L, resulting in lanthanum desorption values of 25.5 and 31.2%, respectively.

Cadmium desorption from another species of *Sargassum* biomass showed that 0.1 mol L^{-1} HCl was a more powerful metal-desorbing agent being able to elute 100% of the sorbed cadmium from *S. filipendula*. In addition, CaCl_2 and CaNO_3 solutions of 1% (w/v) at L/S ratio of 1 L g^{-1} could desorb around 95% of the metal. It was also verified that lower initial pH around 3 improved the percentage metal elution. Moreover, there was no significant difference between calcium chloride and nitrate solutions on cadmium elution. However, chloride solutions were preferable to nitrate ones due to polluting and cost-effectiveness reasons as chlorides are less expensive and more easily tolerated than nitrates [9]. The elution of cadmium was much more easily obtained than that of the lanthanides. Three times more concentrated hydrochloric acid solutions had to be used in order to elute all the metals from the biomass. It can be inferred that the affinity of the biomass for the lanthanides is stronger than that for cadmium.

Sodium carbonate at 1.0 mmol L^{-1} was able to desorb 76% of cobalt from the cyanobacterium *Oscillatoria angustissima*. Other elutants at different concentrations were tested such as 10 mmol L^{-1} EDTA, 2 mmol L^{-1} CaCl_2 , 100 mmol L^{-1} HCl at different concentrations, but they all produced lower desorption values of 66, 18 and 29%, respectively [16]. The concentrations of calcium chloride and EDTA tested were very low compared to the values tested in this work. Moreover, the time allowed for desorption experiments was only 90 min which in many cases was not enough to allow equilibrium to be attained.

3.5. Effect of liquid to solid ratio on metal desorption

The objective of this study was to verify the effect of using larger volumes of eluting agent on the amount of metal desorbed from the biomass. Fig. 6 shows that the percentage of metal

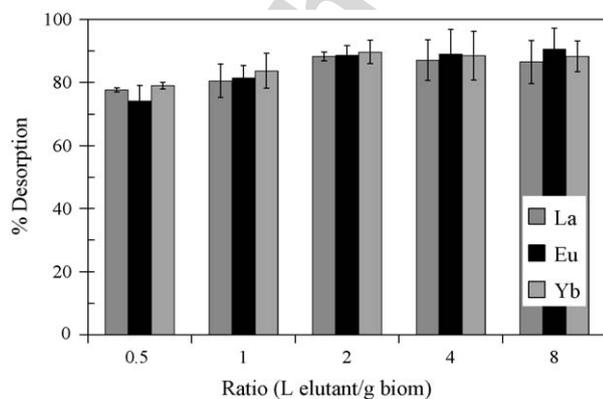


Fig. 6. Effect of liquid to solid ratio on the percentage of desorption for La, Eu and Yb in each respective single-element system.

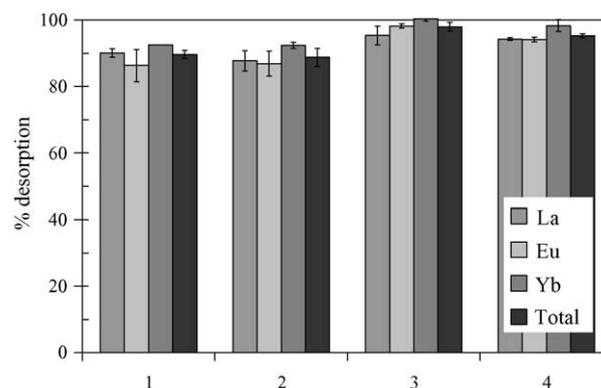


Fig. 7. Desorption of La, Eu and Yb from biomass loaded with all three elements.

desorbed increased with the (L/S) ratio until it reached a plateau whereby the maximum desorption capacity was achieved at a ratio of 2 L g^{-1} . Therefore, this was the value of (L/S) chosen for experiments above which no more metal would be released from the biosorbent. The amount of metal desorbed reached up to 90–95% in average but reaching up to almost 100% considering the error involved.

3.6. Desorption of mixed metal system

Desorption experiments were also performed with mixed metal loaded system. The three lanthanides La, Eu and Yb loaded onto the biomass were subsequently eluted by 100 mmol L^{-1} HNO_3 at a (L/S) ratio of 0.5 L g^{-1} . Fig. 7 shows the results obtained for desorption of the multi-component system containing all three lanthanides at different metal sorption levels. Table 2 describes the individual and total metal loadings. It can be seen that the metal removal ranged between 85 and 100%. The percentage removal seemed to increase with metal load achieving 100% at maximum metal uptake.

Table 3 shows the desorption levels of individual and mixed system using 0.2 mmol L^{-1} HCl at a ratio of 2 L g^{-1} . It can be observed that almost all metals were desorbed from the individual metal loaded biomass. However, for the mixed metal loaded biomass, not all of the metals present in the biomass were eluted. Ytterbium was almost totally eluted, although lanthanum and europium were desorbed by 86.3 and 75.2%, respectively. It should be pointed out that the amount desorbed of the metals in the mixed system was in accordance with the affinity sequence observed from sorption experiments [14].

Table 2
Metal sorption loadings for mixed metal desorption (Fig. 7)

q (mmol g^{-1})	La	Eu	Yb	Total
1	0.23	0.24	0.24	0.71
2	0.28	0.37	0.28	0.93
3	0.30	0.42	0.28	1.00
4	0.25	0.39	0.23	0.88

Table 3
Desorption of individual and mixed system using 0.2 mol L⁻¹ HCl at L/S of 2 L g⁻¹

		La	Eu	Yb
Individual system	% Desorption	99.8 ± 6.4	94.1 ± 9.7	95.9 ± 2.7
	Loading (mmol g ⁻¹)	0.90	1.07	1.04
Mixed system	% Desorption	86.3 ± 1.3	75.2 ± 0.6	94.05 ± 0.2
	Loading (mmol g ⁻¹)	0.28	0.44	0.33

4. Conclusions

The release of calcium ions while protons were removed from the aqueous solution confirmed that ion exchange was the main mechanism occurring during the desorption process. The calcium release achieved 2.5 mequiv. g⁻¹ at pH 2 and 2.8 mequiv. g⁻¹ while using 0.1 mol L⁻¹ HNO₃.

Washing the biomass after the sorption process either once or twice or even not washing it at all did not result in any difference on the percentage of metal recovered from the biomass.

When comparing different organic and inorganic elutants at the same L/S of sorption experiments, 0.5 L g⁻¹, the desorption of La, Eu and Yb was best achieved using mineral acids such as hydrochloric and nitric acids, resulting in 95–100% with 0.3 mol L⁻¹ HCl, and 0.1 mol L⁻¹ with HCl.

The metal recovery from the biomass was improved by increasing the L/S ratio and reached a plateau region at 2 L g⁻¹. Desorption of the metals ranged from 85 to 95% with 0.1 mol L⁻¹ HNO₃, which had resulted in 80–90% at 0.5 L g⁻¹, and complete metal desorption from single metal systems was achieved with 0.2N HCl.

The desorption levels decreased with increasing metal sorption affinity and for the mixed metal loaded system the following values were obtained, 94.0, 86.3 and 75.2% for Yb, La and Eu, respectively when the eluting agent was 0.2N HCl.

Desorption levels are closely related to the affinity of the sorbed ions onto the biomass. Elements that present a very high selectivity index will be more difficult to desorb. Mineral acids are still the most feasible and effective eluting agents. Lower pH resulted in higher desorption levels.

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