

Biosorption of La, Eu and Yb using *Sargassum* biomass

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Abstract

Biosorption of the lanthanides: Lanthanum (La^{3+}), Europium (Eu^{3+}) and Ytterbium (Yb^{3+}) from single-component and multi-component batch systems using *Sargassum polycystum* Ca-loaded biomass was studied. The ion exchange sorption mechanism was confirmed by the release of calcium ions from the biomass that matched the total number of metal and protons removed from the solution. The metal binding increased with pH due to the decrease of proton concentration in the system, as they also compete for the binding sites. The maximum metal uptake capacity for pH 3, 4 and 5 ranged approximately between $(0.8\text{--}0.9)\text{mmol g}^{-1}$ for La $(0.8\text{--}0.9)\text{mmol g}^{-1}$ for Eu, and $(0.7\text{--}0.9)\text{mmol g}^{-1}$ for Yb. Biosorption from multi-component mixtures was examined at pH 4 using equimolar initial concentrations of the metals. The metal affinity sequence established was $\text{Eu} > \text{La} > \text{Yb}$, and the maximum metal uptake obtained was 0.29, 0.41, 0.28 mmol g^{-1} for La, Eu and Yb, respectively.

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1. Introduction

Biosorption studies have mainly been focusing on the removal of heavy metal ions from industrial effluents, the detoxification of these solutions prior to disposal as the primary goal (Matheickal and Yu, 1999; Schiewer and Volesky, 2000; Vieira and Volesky, 2000; Williams et al., 1998; Yu et al., 1999). Cost-effective biosorption technology can utilize naturally abundant biomass, such as seaweeds, and of these *Sargassum* has been identified for its high cation sorption potential (Fourest and Volesky, 1996; Kratochvil et al., 1998; Schiewer, 1996; Yang, 2000; Yang and Volesky, 1999a, b). Further studies of this biosorbent revealed the ion-exchange nature of the high metal uptakes by *Sargassum*, for

example, of cadmium (Yang and Volesky, 1999b), chromium (Kratochvil et al., 1998), copper/lead (Matheickal and Yu, 1999) and uranium (Yang and Volesky, 1999a). *Sargassum* contains high amounts of alginate, well locked within its cellular structures, with abundant carboxylic groups capable of capturing cations present in solution. It is especially the guluronic acid in alginate that offers these functional groups (Siegel and Siegel, 1973) for ion exchange. As the alginate matrix is present as a gel phase, this material is easily penetrable for small metallic cations making it thus a suitable biosorbent with a high sorption potential (Yang and Volesky, 1999b).

While rare earths are relatively abundant in the Earth's crust, they do not represent a common toxic threat. However, the concentrations of these elements in ores that could be feasibly mined are generally lower than for most other metals. Undiscovered resources are thought to be very large relative to expected demand. Mining production is around 80,000 tons, while the

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reserves are around 100,000,000 tons (Hedrick, 2001). US reports agree that in the year 2000, the rare earths were mainly used in automotive catalytic converters (22%), glass polishing and ceramics (39%), permanent magnets (16%), petroleum refining catalysts (12%), metallurgical additives and alloys (9%), rare-earth phosphors for lighting, televisions, computer monitors, radar, and X-ray intensifying film (1%), with miscellaneous uses at 1%. The use of rare earths is expected to increase as future demand for automobiles, electronics, computers and portable equipment grows. Future growth is forecast for rare earths in rechargeable batteries, fiber optics, medical applications as magnetic resonance imaging contrast agents, scintillation detectors, medical isotopes and dental and surgical lasers (Hedrick, 2000).

The interest in the rare earths started with the Manhattan Project during World War II. It was confirmed that radioactive isotopes, including rare earths, were formed during uranium fission. In the production plutonium, it was observed that synthetic organic ion exchange resins could adsorb some of the uranium fission products that could be individually eluted from the adsorbent using chemical reagents under controlled conditions. However, the usage of individual rare earths became only possible in the 1950s when separation and metallurgical technologies improved. With lowering prices of rare earth elements the demand for them started to accelerate (Hedrick, 1998). The rare earths include scandium, yttrium and the fifteen lanthanides (Hedrick, 2000, 2001; Jones et al., 1996). The prices for REEs depend on their purity and quality. Price fluctuations are usually due to supply and demand, environmental legislation and economic factors, especially inflation and energy costs (Hedrick, 2000). Table 1 lists approximately the average prices for rare earths in 1998. The high prices for most of these elements and the rapid current expansion of their applications result in increased pressures on the production of these elements and minimizing industrial production losses has thus become an important objective. Research emphasis has been focusing on the progressively more cost-effective removal and recovery of rare earths for industrial process.

This study focuses on exploring the biosorption potential in the recovery of a light (La), intermediate (Eu) and a heavy (Yb) rare earth elements using *Sargassum* biomass in single- and multi-component metal systems. The rare earths tend to react promptly with oxygen donor atom groups, such as carboxylic groups present in the cell-wall structure of the selected seaweed biosorbent. In addition, it is important to establish whether metal sorption affinity differences exist among the elements selected so as to provide a basis for the separation and purification of lanthanides through the process of biosorption.

Table 1
Average prices of rare earths in 1998

Compound	Price (US\$/Kg)
Scandium	18,000
Yttrium	450
Lanthanum	350
Cerium	350
Praseodymium	540
Neodymium	450
Samarium	300
Europium	6500
Gadolinium	400
Terbium	1300
Dysprosium	500
Holmium	1200
Erbium	725
Thulium	6500
Ytterbium	1600
Lutetium	7500

Source: Hedrick, 1998.

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 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 50 mmol 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 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

2.2.1. Single-component system

Batch sorption dynamics tests were performed in order to determine the necessary contact time for attaining the sorption system equilibrium with the given biosorbent particle size. Samples of 0.1 g of prepared biomass (as above) were contacted with 0.05 L of solution of known initial metal concentration ranging from 0.4 to 7.2 mmol L⁻¹. The sorption suspension samples (in duplicates) were contacted for a specific length of time varying between 0.5 and 24 h, and then

each supernatant was analyzed for residual metal content by using the ICP atomic emission spectrometer.

Solutions containing the metals were individually prepared using distilled de-ionized water and nitrate salts: $\text{LaNO}_3 \cdot 6\text{H}_2\text{O}$, $\text{EuNO}_3 \cdot 6\text{H}_2\text{O}$, $\text{YbNO}_3 \cdot 6\text{H}_2\text{O}$ (all Alfa Aesar supplied). For the batch equilibrium experiments the initial metal concentrations ranged from 0.7 to 3.6 mmol L^{-1} . 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 ($25\text{--}200 \text{ mmol L}^{-1} \text{ HNO}_3$). The pH was adjusted in order to obtain the final equilibrium pH 3, 4 or 5 for which the equilibrium isotherms were eventually plotted.

2.2.2. Multi-component system

Solutions containing the three selected lanthanides in equimolar concentrations were prepared with the same nitrate salts mentioned above. The pH was adjusted the same way as was done for the single-component experiments to give the final equilibrium pH of 4. All experiments were performed in duplicate.

2.3. Metal analysis

Metal content present in solution for 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

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

where m is the biomass dry weight.

The calcium residual concentration was calculated by the difference between the total number of binding sites (Q) and the amount of calcium released into the solution. Blanks were used with distilled de-ionized water and biomass to account for calcium excess release to be subtracted from the total calcium released when metals were present

$$q = Q - (C_{\text{Ca}} V_f / m). \quad (2)$$

The proton uptake was calculated according to Schiewer and Volesky (1996) 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

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

The total number of binding sites was determined by protonating the biomass with $100 \text{ mmol L}^{-1} \text{ HCl}$, to account for the total calcium actually released by the biomass. The amount of calcium released from blanks was subtracted from the total number of Ca ions released after protonating the biomass.

3. Results and discussion

3.1. Single-component isotherms

The time required to achieve equilibrium was determined through experiments establishing the metal uptake dynamics. The time taken can be from 10 min to half an hour depending mainly on the average particle size and on the concentration of metal in solution. However, the need to adjust pH may extend the time required to attain equilibrium and a time of 24 h was eventually chosen for all equilibrium experiments. During daytime, the pH would be gradually adjusted and equilibrium would be established overnight.

Figs. 1, 2 and 3 show the equilibrium isotherms for the three lanthanides, La, Eu and Yb, at pH 3, 4 and 5. Sorption isotherms relate the uptake of a certain metal, in mmol g^{-1} , and the final equilibrium metal concentration. In these three figures the metal uptake observed is quite similar for all three metals. However, a slightly lower uptake for ytterbium indicated that there might be at least some differences in affinities among these elements. The maximum uptake capacity for La and Eu can reach up to 1 mmol g^{-1} , while for ytterbium it reached 0.9 mmol g^{-1} . As can be seen, different levels of pH, reflecting the hydrogen ion concentration, affect the uptake of the metal. It is known that protons compete for the binding sites present in the biosorbent material used. As pH represents the negative logarithm of proton concentration, the lower the pH value the higher the proton concentration in the solution. As the metal uptake at pH 5 was only slightly higher than that at pH 4, this may be due to the fact that the concentration of hydrogen ions was already relatively low under these two conditions, and the impact of the proton presence was not as significant as at pH 3. The uptake increased sharply at low metal concentrations until it reached a plateau, indicating that the maximum uptake capacities for La and Eu were approximately 1.0, 0.9 and 0.8 mmol g^{-1} for pH 5, 4 and 3, respectively. However, the Eu sorption isotherm curves were steeper than those for La, demonstrating a higher selectivity for Eu at lower metal concentrations in solution. The isotherms appear to be highly favorable as high metal uptake capacity is achieved at low metal concentrations. Moreover, nearly 80% of the total capacity can be achieved at a final metal concentration lower than 0.25 mmol L^{-1} . Comparing to the metal uptake of these same elements

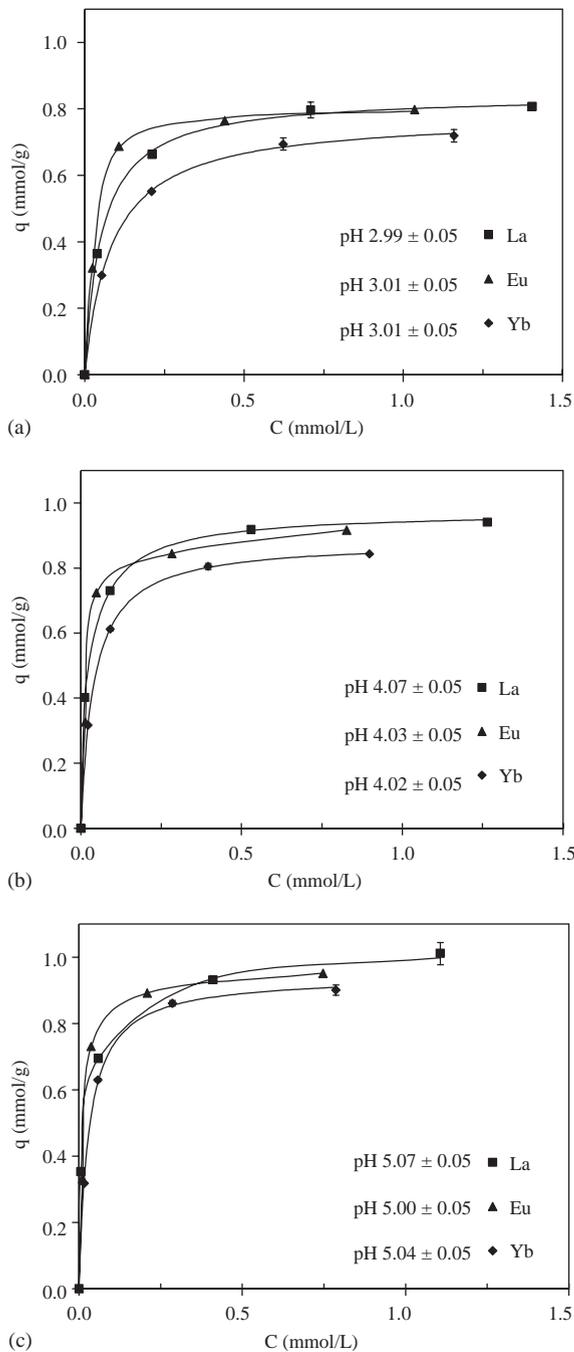


Fig. 1. Effect of La, Eu, Yb for nitrate solutions at different values of pH: (a) pH 3, (b) pH 4, (c) pH 5.

by *Pseudomonas aeruginosa* (Texier et al., 1999) that ranged from 0.3 to 0.4 mmol g⁻¹ under the same pH 5, *Sargassum* represents an interesting alternative for removing these ions from solution. Even at pH 3, metal uptakes of (0.7–0.8) mmol g⁻¹ can be achieved.

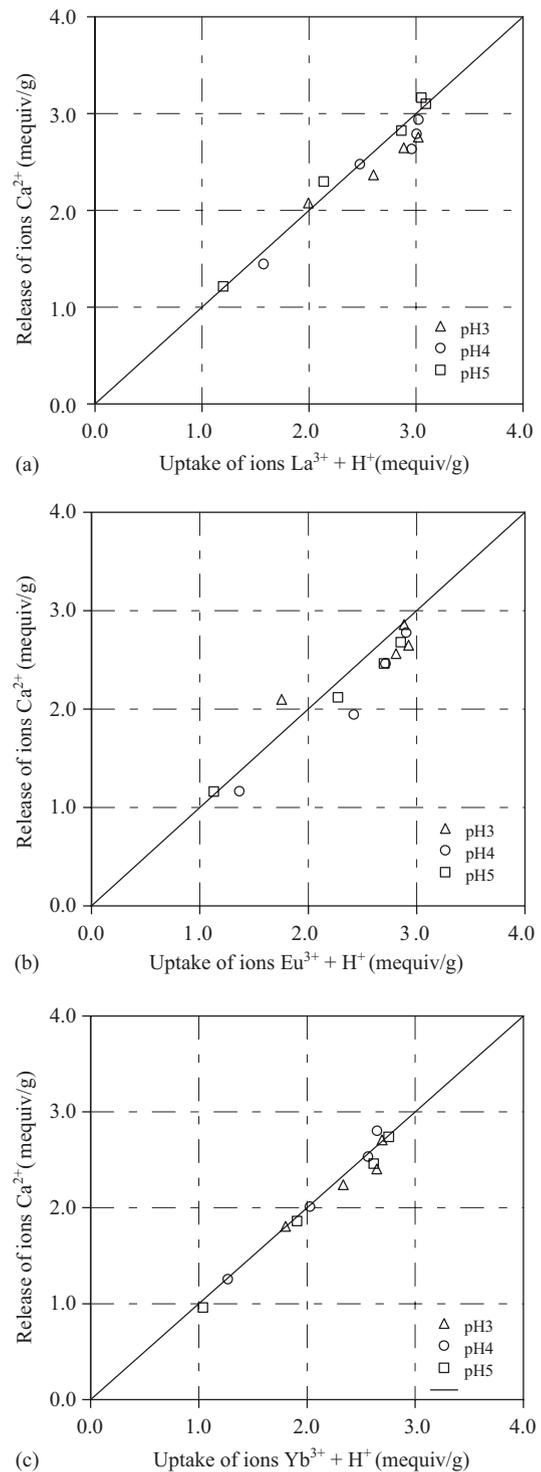


Fig. 2. Ion exchange for (a) La, (b) Eu, (c) Yb.

Various species of *Sargassum* have been reported to remove cations from solution. The uptakes of other metals by other species of *Sargassum* were recently

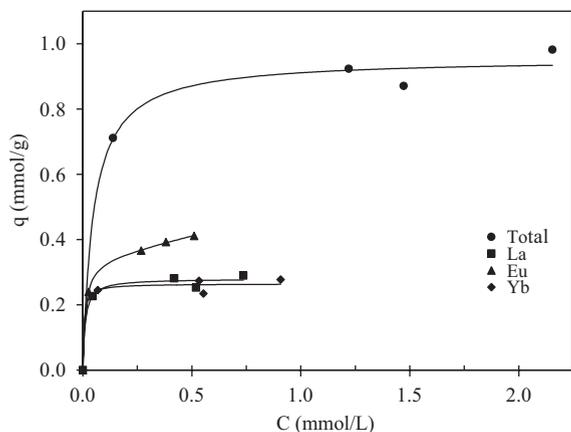


Fig. 3. Multi-component isotherms at pH 4.

reported to be 0.99 mmol g^{-1} for cadmium at pH 4 (Yang and Volesky, 1999b), 1.18 mmol g^{-1} for Cu (Kratochvil et al., 1997), 2.38 mmol g^{-1} for uranium at pH 4 (Yang and Volesky, 1999a). It should be pointed out that the biosorbents used were pre-treated differently and that could affect the total number of binding sites for attaching the metals. The total number of binding sites was 2.6 meq g^{-1} for protonated *S. hemiphyllyum* (Schiewer and Wong, 2000), 2.25 meq g^{-1} for *S. fluitans* (Fourest and Volesky, 1996). In another work, *Sargassum* biomass was protonated to be further loaded with calcium; the number of binding sites decreased from 2.23 to 1.80 meq g^{-1} (Figueira et al., 2000). Underestimation of the total uptake capacity for non-protonated biomass may be the result of the decrease in the number of titrable acidic groups due to the protonation treatment that may have destroyed some. This could explain the higher-than-expected metal uptake capacity observed for *S. polycystum* tested in this work. Moreover, as these were all different *Sargassum* species and, at unspecified point in their life-cycle, they may have somewhat different numbers of total binding sites as the alginate content and its composition may vary.

Other brown seaweed types, like *Durvillaea potatorum* and *Ecklonia radiata*, loaded with calcium in their pretreatment, were able to remove 3.10 and 2.60 meq g^{-1} of Pb^{2+} , respectively (Matheickal and Yu, 1999). It can be inferred that pre-treatments using a calcium salt produced higher uptake capacities when compared to an acidic one usually with 0.1 M concentration. For the bacterial type of biomass of *P. aeruginosa* it was suggested that phosphate and carboxyl groups were responsible for binding europium and that the total number of binding sites would be 0.24 and 0.86 meq g^{-1} , respectively (Texier et al., 2000).

Using other techniques, an attempt to recover europium from chloride solutions consisted of reducing Eu^{3+} to Eu^{2+} by a zinc amalgam, followed by the precipitation of Eu^{2+} sulphate in an atmosphere of CO_2 . Initial concentrations ranged from 0.5 to 5.0 g L^{-1} of E_2O_3 and resulted in a constant residual concentration of 0.1 g L^{-1} of Eu_2O_3 (Morais and Ciminelli, 1998). This indicated an opportunity for using biosorption technology, as it can work well for less concentrated solutions from 0 to 100 mg L^{-1} .

3.2. Ion exchange

The simultaneous release of Ca ions with the uptake of lanthanides and protons point to an ion exchange mechanism being involved (Fig. 2). Considering that lanthanides are trivalent ions and that neither complexation nor hydrolysis occurs, it can be seen that the ion exchange was stoichiometric. As the concentrations in the sorption systems examined were low, the solutions can be considered as dilute and hydrolysis of rare earths is not expected to occur below pH 5. In addition, nitrate anions have a low tendency to form complexes. According to Kusaka et al. (1998), the speciation of lanthanum for a total concentration of 1 mM showed that 100% of the total lanthanum species was La^{3+} . The concentration of hydrolyzed species LaOH^{2+} is lower than $0.001 \text{ mmol L}^{-1}$ and, consequently, not significant. In addition, La speciation in nitrate solution, according to the program MINEQL+ (version 4.5) (Schecher, 1991), is only as a trivalent metal for the pH and metal concentrations examined in this work. This further supports the conclusion that ion exchange is the main sorption uptake mechanism in the system studied.

To explain the sorption behavior similarities of the rare earth metals, one needs to look at their electronic structure. All of them have three electrons in the outermost shell and these electrons determine their chemical behavior. The difference is in the inner shell—4f, with systematic filling of f orbital, while 5d, 6s and 6p are empty (Brookins, 1989; Henderson, 1996). Their divalent ions are not sufficiently stable (Topp, 1965) and are characterized by large ionic radii; the most common form is the trivalent ionic form. This means that substitution reactions usually involve the large cations such as calcium or strontium and, in conjunction with their high valence, they tend to be segregated from other trivalent ions. The ionic radii of the lanthanides decrease from La^{3+} to Lu^{3+} . These ions are essentially spherical and form complexes very much like alkaline and alkaline earth ions. They are very electropositive, so their bonding characteristics are largely ionic (Henderson, 1996). The lanthanides and yttrium tend to bind the water molecules and the most common form obtained is $\text{Ln}(\text{H}_2\text{O})_6^{3+}$ (Brookins, 1989). The hydrolysis of these ions is slight and there is an increase in hydration with

the atomic number. The size of the hydrated ion increases from lanthanum to lutetium, and hydrolysis seems to be negligible below pH 5.0 (Topp, 1965). Therefore, lanthanide species do not readily hydrolyze. The stepwise formational constants for $\text{Ln}(\text{OH})^{2+}$, $\text{Ln}(\text{OH})_3(\text{aq})$, and $\text{Ln}(\text{OH})_4^-$ decrease significantly. At acidic to neutral pH, the dominant form in water may be Ln^{3+} . At pH approaching 10, hydrolysis becomes important for trivalent ions, $\text{Ln}(\text{OH})^{2+}$ and $\text{Ln}(\text{OH})_3$ (Brookins, 1989). The lanthanides are considered to be hard acids in the terminology of Pearson (Brookins, 1989) and will bond preferentially with hard bases that contain oxygen as donor atoms. This means that these ions will bond more weakly with soft bases, such as those with donor S or P. Therefore, the dominant ligands contain at least one oxygen donor atom like that in the carboxylic group.

Other similar studies reported uptakes of neodymium by the following sorbents at pH 1.5: microalgae (*Monoraphidium* sp.) $10.48 \text{ mmol g}^{-1}$, yeast (2.17 mmol g^{-1}), *Penicillium* sp. (1.23 mmol g^{-1}) and activated carbon (0.42 mmol g^{-1}) (Palmieri et al., 2000). Most recently, biosorption studies (Palmieri, 2001) have been performed using different types of biomasses: microalga, yeast, *Sargassum* sp. and fungus and the metal uptake decreased in the respective order. They all demonstrated a good capacity to retain erbium and ytterbium, especially the microalgae and yeast, although the final equilibrium concentrations were very high in the range of g L^{-1} . While *Monoraphidium* sp. sorbed very well, it took 60 days for the cells to be cultivated. That can hardly be compared with *Sargassum* seaweed that is readily available and possesses good swelling and mechanical properties suitable for sorption application purposes. A lower metal uptake was observed for *Sargassum* sp. when removing erbium (0.63 mmol g^{-1}) and ytterbium (0.66 mmol g^{-1}) at pH 5 (Palmieri, 2001). However, it could be a different species of *Sargassum* with a lower number of binding sites.

It is important to note that not only different types of brown seaweed but also different species of *Sargassum* could contain a different number of either binding sites or maximum metal uptake capacity. In addition, different types of biomass pretreatment may also affect these parameters. Kratochvil et al. (1997) verified that there was no metal uptake difference between *S. fluitans* biomass pretreated with CaCl_2 or HCl (100 mmol L^{-1}) although the weight loss was 24% and 44%, respectively. However, their CaCl_2 pretreated biomass was also first protonated with HCl 100 mmol L^{-1} and the weight loss was determined relative to the original weight before this protonation. It has been postulated that treating the biomass with hydrochloric acid may have destroyed some binding sites.

The total amount of calcium released when the metal uptake reached the isotherm plateaus at values of pH

examined in the present study for lanthanum, europium and ytterbium was 2.90, 2.80 and 2.75 meq g^{-1} , respectively. These values agreed with the total number of calcium ions ($2.98 \pm 0.11 \text{ meq g}^{-1}$) released from the biomass after protonation. This means that the metal uptake by the biomass almost reached the total number of binding sites. It was observed that the total maximum uptake of metal and protons remained the same at different values of pH tested, while the individual uptake of metal ions and protons varied with the metal final equilibrium concentration. Progressively lower metal uptake at lower final metal concentrations was compensated for by a higher proton binding. Conversely, a higher final metal concentration resulted in higher metal uptakes with proportionately lower proton binding. The uptake of protons varied from 2% to 45%, while the metal uptakes observed were from 55% to almost 100% of total species removed from solution. The number of binding sites, as obtained by this method, seems to be higher than those reported in the literature. This may be due to the commonly practiced pre-treatment protonation of the biomass that destroyed a portion of binding sites. Moreover, the affinity of the biomass for trivalent ions appears to be very high, resulting in the maximum uptake capacity between pH 4 and 5 at 1 mmol L^{-1} total metal concentration. Kratochvil et al. (1997) verified the effect of different biomass pre-treatments and obtained the total Cu uptake of 2.36 meq g^{-1} for *S. fluitans* calcium pre-loaded biomass. This agreed quite well with the indications of 2.25 meq g^{-1} of total binding sites in the same biomass obtained upon titrating it (Fourest and Volesky, 1996). It is worth noting that the uranium uptake by *S. fluitans* observed by Yang and Volesky (1999a) was higher (2.38 mmol g^{-1}) than the total number of binding sites for that species. This was explained by the peculiar hydrolysis of uranium in solution.

3.3. Multi-component isotherms

When lanthanum, europium and ytterbium were present in the same solution, the total metal uptake was distributed among the three elements. The total metal uptake of (La + Eu + Yb), from the multi-component system indicated a behavior reflecting the single-component isotherms. Fig. 3 shows the single-component isotherms and the total metal uptake from the multi-component system at pH 4. From the graph it can be seen that the uptake of lanthanum and ytterbium ions reached a plateau at very low concentrations, while the europium uptake did not. The total uptake capacity, which increases with the total metal final equilibrium concentration, increased with the removal of europium ions. It can be inferred that the affinity of the biomass for europium is larger than for the other two lanthanides. The maximum metal uptakes of 0.29, 0.41,

0.28 mmol g⁻¹, respectively, could be calculated for La, Eu and Yb. Figs. 4a–c show the single- and multi-component isotherms for La, Eu and Yb, respectively. The total uptake of all metals in the multi-component system is also plotted. It can be seen that the single isotherms are very similar to the total uptake. When all elements are together, they compete for the binding sites, decreasing the individual element uptake capacity that could be obtained when other competing ions are not present in the system.

The distribution coefficient between the solid and liquid phases for each metal for the multi-component system is plotted against the final equilibrium metal concentration in Fig. 5. This parameter is the ratio between the sorbate concentration in the solid phase (q) and its concentration in the liquid phase (C). The higher the distribution coefficient, the higher the affinity of the metal towards the biomass. The same affinity sequence was observed for each equimolar initial concentration applied and it was Eu > La > Yb. The values of the distribution coefficients were greater for low metal concentrations: 9.09, 5.13 and 3.56, for Eu, La and Yb, respectively. The same trend could be observed for higher metal equilibrium concentrations, although the values were much smaller: 0.81, 0.39 and 0.31 for Eu, La and Yb, respectively. The ratio between the distribution coefficients for each pair of metals remained approximately constant for all concentration ranges examined in this work. While a similar behavior can be seen for lanthanum and europium in their single-component isotherms, the europium curve appears to be somewhat steeper, indicating a higher affinity between Eu and the biosorbent. Modeling of the single-component isotherm curves leads to the determination of equilibrium constants that also assist in verification of the metal affinity differences and in explaining the slight selectivity trend observed during the multi-component equilibrium experiments. The properties of the lanthanides tend to feature usually a gradual change along the series but this aspect alone could not explain the affinity trend as observed for the present experiments. One plausible explanation for the affinity sequence obtained is the parameter called water structure. It can be defined as the average number of hydrogen bonds in which a water molecule participates, in ice it is 4, in dilute water vapor it is zero and in liquid water at room temperature it is approximately 1.55. The structure of water in the vicinity of the solute is affected by its presence. Some ions are structure breakers whereas others are structure makers. Ions with numbers lower than 0.1 are structure breakers, whereas ions with numbers higher than 0.1 are called structure makers. The higher this number is the larger is their electrostatic field and the water structure around them will tend to be centrally oriented (Yizhak, 1997). As observed in the present experiments, the water structure parameter for the lanthanides examined

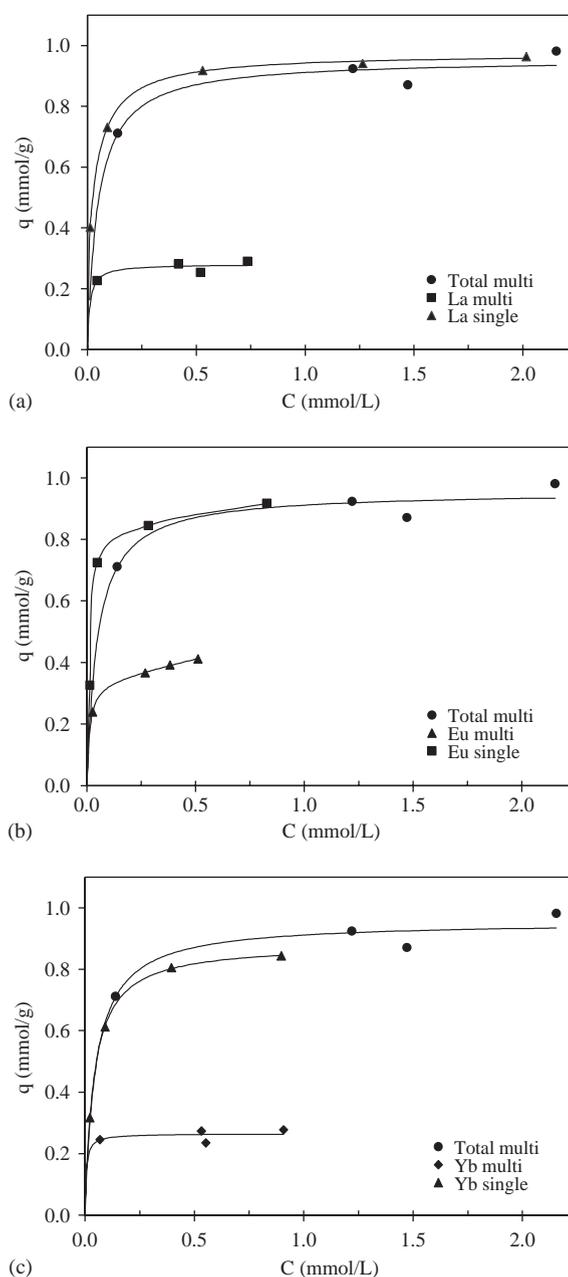


Fig. 4. Single- and multi-component individual isotherms compared to the total uptake of the different metals in the multi-component system for (a) lanthanum, (b) europium, and (c) ytterbium at pH 4.

showed the same trend with values of 0.75, 0.78 and 0.81 for europium, lanthanum and ytterbium, respectively. The lower the value of the water structure parameter, i.e., the less of a structure maker an ion was, the higher the affinity of the metal towards the biosorbent.

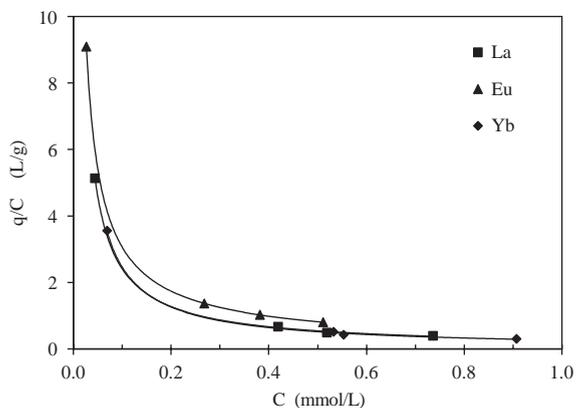


Fig. 5. q/C coefficient distribution for lanthanum, europium and ytterbium in multi-component systems.

For another type of biomass, however, during column dynamics experiments in a fixed-bed with *P. aeruginosa* immobilized in polyacrylamide gel, it was observed that the affinity sequence for the same lanthanide ions was $\text{Eu} \geq \text{Yb} > \text{La}$ (Texier et al., 2002).

There are review papers in the literature comparing the biosorption of rare earths using microbial biomass (Andrès et al., 2003) and the biochemistry of heavy metal biosorption by brown algae (Davis et al., 2003).

4. Conclusions

The *Sargassum* biomass tested in this work removed lanthanide ions from solution immobilizing up to 0.8–1 mmol of metal per gram of dry biomass (3 meq g^{-1}). Ion exchange was confirmed to be the main mechanism responsible for this behavior. The total number of ions removed from solution, of trivalent lanthanide(s) and protons, matched the total number of calcium ions released from the biomass into the solution in terms of meq/g . The single-component isotherms for ytterbium indicated its lower affinity for the biosorbent used. The multi-component system also examined eventually confirmed the metal affinity sequence in the order of $\text{Eu} > \text{La} > \text{Yb}$. In addition, the water structure parameter could be used to explain the affinity sequence observed in the multi-component system tested in this work.

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