Biosorption of lanthanum, europium and ytterbium by *Sargassum polycystum* biomass

by

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A thesis submitted to the Faculty of Graduate Studies and Research
in partial fulfillment of the requirements
of the degree of Doctor of Philosophy

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Your file Votre référence
ISBN: 978-0-494-27770-6
Our file Notre référence
ISBN: 978-0-494-27770-6

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ABSTRACT

Biosorption of the lanthanides: La^{3+} (Lanthanum), Eu^{3+} (Europium) and Yb^{3+} (Ytterbium) from single and multi-component batch and column systems using *Sargassum polycystum* biomass was studied. Ground and dried biomass was used in batch experiments with particle size 0.5-2.0 mm, while natural size cut and wet was used for packing the column. The ion exchange mechanism was confirmed by the exchange of ions observed during the process. The metal binding increased with pH and the maximum metal uptake capacity for pH 3, 4 and 5 ranged approximately between (0.8 - 0.9) $mmol.g^{-1}$ for La, (0.8 -0.9) $mmol.g^{-1}$ for Eu, and (0.7 - 0.9) $mmol.g^{-1}$ for Yb. The metal affinity sequence established was Eu>La>Yb, and the maximum metal uptakes obtained from multi-metal mixture were 0.41, 0.29, and 0.28 $mmol.g^{-1}$ for Eu, La, and Yb, respectively. The presence of the counterion sulphate reduced La uptake due to the formation of complexes, while the presence of nitrate and chloride did not interfere with the lanthanum removal. The La uptake in such systems varied from 0.6 to 1.0 mmol g^{-1}. Several eluting agents at different concentrations were tested to desorb the lanthanides and 95 to 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. Desorption levels ranged between 85 and 95%, and 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. Batch and sorption column studies of La and Eu in the presence of protons in binary and ternary systems were performed. The equilibrium isotherms were determined for the binary systems, La/H and Eu/H, for a total normality of 3meq g^{-1}, and resulted in separation factors of 2.7 and 4.7, respectively, demonstrating a higher selectivity of the biomass towards europium. Continuous-flow column experiments with single metals and protonated biomass were used to estimate the intra-particle mass transfer coefficient for La (6.0 10^{-4} min^{-1}) and Eu (3.7 10^{-4} min^{-1}). These values were then used in mathematical models predicting reasonably well the breakthrough curves obtained for La and Eu with an equivalent feed mixture. A series of consecutive sorption/desorption runs demonstrated that the metal could be recovered and the biomass reused in multiple cycles with no apparent loss in metal uptake capacity when 0.1N HCl was used for desorption.

RÉSUMÉ

Une étude a été réalisée sur la biosorption des lanthanides: La^{3+} (Lanthanum), Eu^{3+} (Europium) et Yb^{3+} (Ytterbium) avec de la biomasse *Sargassum polycystum* sur des systèmes en discontinus et en continus et en présence avec une ou plusieurs composantes à la fois. Le mécanisme d'échange d'ions a été confirmé durant ces études. La fixation des métaux par le biomasse a augmenté avec le pH et la capacité maximale de fixation pour les pHs de 3, 4, et 5 ont été de 0.8 à 0.9 $mmol.g^{-1}$ pour La, de 0.8 à 0.9 $mmol.g^{-1}$ pour Eu, et de 0.7 à 0.9 $mmol.g^{-1}$ pour Yb. L'affinité du biomasse pour les métaux est Eu>La>Yb et l'absorption maximale pour les systèmes avec plusieurs composantes a été de 0.29, 0.41, et 0.28 $mmol.g^{-1}$ pour La, Eu et Yb, respectivement. La présence de sulfate comme ion opposé a diminué l'absorption de La à cause de la formation d'un complexe avec cette ion. Toutefois, ni la présence de nitrate et de chlore n'a eu un impact sur l'absorption du La; l'absorption de La dans un tels systèmes a été de 0.6 à 1.0 mmol g^{-1}. Plusieurs agents d'élution à différentes concentrations ont été étudiées pour la désorption des lanthanides; avec 0.3 mol. L^{-1} HCl, la désorption a été de 95% à 100% pour tous les métaux. Avec d'autres agents d'élution, la désorption de La a été de: 70% avec 2 $mol.L^{-1}$ $CaCl_2$; 83.7% avec 0.5 $mol.L^{-1}$ EDTA; et 88.4% avec 0.023 $mol.L^{-1}$ d'acide diglycolique. Généralement, la désorption des métaux a été de 85% à 95% et a diminué inversement à l'affinité d'absorption du métal: 94.0%, 86.3%, et 75.2% pour Yb, La, et Eu respectivement, avec 0.1 N HCl comme agent d'élution. Des études de La et Eu avec des protons dans des systèmes binaires et trinaires a été réalisée avec des essais en discontinus et en continus. Les isothermes d'équilibre ont été déterminées pour les systèmes binaires de La/H et Eu/H avec une normalité totale de 3 meq g^{-1} et donne des facteurs de séparation de 2.7 et 4.7 respectivement, ce qui montre une sélectivité plus élevée pour l'Europium. Des essais dans une colonne à débit continu avec un seul métal et de la biomasse protonnée a été réalisés pour estimer le coefficient de transfert de masse entre les particules pour La ($6.0x10^{-4}$ min^{-1}) et Eu ($3.7x10^{-4}$ min^{-1}). Ces valeurs ont été utilisées dans des modèles mathématiques pour calculer les courbes d'épuisement de La et Eu dans un même système. Une série d'essai avec plusieurs cycles d'absorptions et désorptions avec la même biomasse a été réalisé et démontre que la biomasse peut être réutilisée sans perdre sa capacité d'absorption; la désorption a été réalisé avec 0.1N HCl.

PUBLICATIONS

List of Publications

Results of Chapter 3 have been published as refereed paper:

Diniz, V. and Volesky, V. 2005. Biosorption of La, Eu and Yb using *Sargassum* biomass. *Wat. Res.* **39**:239-247.

Results of Chapter 4 have been published as refereed paper:

Diniz V. and Volesky, B. 2005. Effect of counterions on lanthanum biosorption by *Sargassum Polycystum*. *Wat. Res.* **39**: 2229-2236.

Results of Chapter 5 have been published as refereed paper:

Diniz V. and Volesky, B. 2006. Desorption of La, Eu and Yb from *Sargassum*. *Sep. Purif. Technol.* **50**: 71-76.

Results of Chapter 6 will be submitted as refereed paper:

Diniz V. and Volesky, B. 2006. Fixed-bed studies on lanthanum and europium biosorption by *Sargassum*. *Sep. Purif. Technol.* (to be submitted)

CONTRIBUTIONS OF CO-AUTHORS

Professor B. Volesky, the supervisor of this dissertation, co-authored all resulting publications. Except for Prof. Volesky's invaluable supervision in the biosorption research area and correction of the manuscripts, I proposed the research objectives, established the methodologies, conducted the experiments and eventually wrote drafts of manuscripts describing the results obtained.

Dr. M.E. Weber and Dr. J.H. Vera also contributed with invaluable discussions and suggestions.

Nadia Bibi, an undergraduate student, also contributed to part of the experimental results related to the equilibrium isotherms obtained in manuscript 4 (Chapter 6).

ACKNOWLEDGMENTS

I would like first to thank God and my family for their love. Their belief in my potential is far larger than mine and their continuous support and encouragement has pushed me forward to accomplish this challenging task.

I especially thank my fiancé for his love and understanding, and for believing always that I can accomplish anything I put effort into and cheering for me always. His presence in my life has been a light in the day.

I also would like to thank Dr. Volesky for his invaluable supervision and insight during many aspects of this work. His input, particularly regarding the written and oral presentations of the research results, was very helpful and instructive. I really appreciated the opportunity which was given to me for developing the work towards the progression and completion of this thesis.

Many thanks are also given to the Brazilian foundation, CAPES – Coordenadoria de Aperfeiçoamento de Estudo de Nível Superior, which sponsored my Ph.D. studies at McGill.

Special thanks I give to professors Dr. Martin E. Weber and Dr. Juan H. Vera for their insight and valuable discussions. Their kind attention was much appreciated.

In addition, I would like to thank all staff personnel from the Department of Chemical Engineeering, who directly or indirectly provided me with attentive and professional support. Among them I especially cite: Mr. Ed Siliauskas for training and

assisting me with the ICP analysis, Mr. Luciano Cusmich for computer and network related issues, Mr. Alain Gagnon and his staff for making the columns I used in my work, and all secretaries.

I could not forget all the friends I made along my studies at McGill whose support would always light a candle in a tough day.

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LIST OF SYMBOLS

α_H^M	separation factor between metal and proton	
B_i	calcium concentration from the initial blank	[meq L^{-1}]
B_f	calcium concentration from the final blank	[meq L^{-1}]
Log β	stability constant	
C	final metal concentration	[mmol L^{-1}]
C_i	Initial metal concentration in batch experiments (manuscript 1 – Chapter 3)	[mmol L^{-1}]
C_f	Final metal concentration in batch experiments	[mmol L^{-1}]
C_i	element concentration in column experiments and equilibrium in batch experiments (manuscript 4 – Chapter 6)	[meq L^{-1}]
C°	total normality	[meq L^{-1}]
ε_b	bed void fraction	
ξ	dimensionless bed size	
f	flow rate	
$[H]_{add}$	Hydrogen concentration of added solution for pH adjustment	[mol L^{-1}]
$[H]_i$	Hydrogen concentration of initial solution	[mol L^{-1}]
$[H]_f$	Hydrogen concentration of final solution	[mol L^{-1}]
k	slope	
k_{s_M}	mass transfer coefficient in the solid	[min^{-1}]
K	Langmuir adsorption constant	[L $mmol^{-1}$]
K_i	Equilibrium constant for species i	[L meq^{-1}]

K_j^i	Separation factor of species I with respect to species j	
K_i^0	Frendlich parameter for single species	
K_{ij}	extended Frendlich parameter for species i with respect to species j	
K_{ji}	extended Frendlich parameter for species j with respect to species i	
L	total bed length	[cm]
L/S	solid to liquid ratio	[L g^{-1}]
m	dry mass of sorbent	[g]
n_i^0	Frendlich parameter for single species	[L g^{-1}]
n_{ii}	Extended Freundlich parameter for two species to be used in species i equation	
n_{jj}	Extended Freundlich parameter for two species to be used in species j equation	
n_{ij}	Extended Freundlich parameter for two species to be used in species i equation	
n_{ji}	Extended Freundlich parameter for two species to be used in species j equation	
$[M]_t$	solute concentration in the outlet solution at time t	[meq L^{-1}]
$[M]_0$	solute concentration in the inlet solution	[meq L^{-1}]
$[M]_e$	equilibrium solid-phase concentration of sorbate	[meq L^{-1}]
q	metal uptake	[mmol g^{-1}]

q_i	metal uptake of species I	[meq L^{-1}]
Q	metal binding capacity	[meq g^{-1}]
q_M	metal uptake	[mmol g^{-1}]
q_H	proton uptake	[mmol g^{-1}]
ρ_b	bed packing density	[g L^{-1}]
S/L	solid to liquid ratio	[g L^{-1}]
t	time	[min^{-1}]
τ	dimensionless time variable	
u	superficial velocity	[cm min^{-1}]
V_i	Initial solution volume	[L]
V_f	Final solution volume	[L]
v	intersticial velocity	[cm min^{-1}]
x_M	metal equivalent fraction in the liquid	
x_i	element equivalent fraction in the liquid	
y_i	element equivalent fraction in the solid	
y_M	metal equivalent fraction in the solid	
y^*_M	metal equilibrium equivalent fraction in the solid	
z	bed axial variable	[cm]
z_i	ionic charge of species i	

CHAPTER 1

INTRODUCTION

There are many indications that biosorption could be an efficient and cost-effective process for the removal and recovery of heavy metal ions from industrial effluents such as those originating from mining or electroplating operations. The technology based on biosorption can be applied in the treatment of wastewater containing toxic metals like lead, cadmium, copper, nickel, uranium, zinc and such designated generally as heavy metals. Environmental issues have been the main driving force for developing and optimizing an effective process in this regard.

Two general and major lines of examining biosorption have been established, equilibrium and dynamic, corresponding to the fundamentals of sorption operation. Static, batch, or equilibrium studies are usually carried out first before proceeding to investigating more involved and more difficult to interpret dynamic sorption systems.

The initial information on sorption properties of materials (sorbents) is usually based on batch equilibrium studies resulting in sorption isotherms that may or may not take into account the effects of pH, ionic strength, and presence of other metals. The early attempts for modeling of isotherms made by Langmuir and Freundlich, were expanded as Multi-component Langmuirian approach, eventually also considering the ion exchange phenomenon. The latter has been confirmed as the main mechanism in metal biosorption. While many modeling attempts have been made to model the sorption process, they do not reflect the physico-chemical parameters of the sorption process, and therefore, would have to be considered as purely empirical. More recently, more involved fixed-bed sorption column studies have been given a considerable attention due to the necessity of applying the biosorption process using this particular and most effective operational mode. Experimental and modeling work best goes hand in hand whereby modeling can make the experimental work more effective and, in turn, model improvements are based on well guided experimental studies.

Once again, different modeling approaches have been used to model the breakthrough curves generated by fixed-bed columns which are the most common and effective way for maximizing adsorption and ion exchange processes performance. Although the biosorption process has been studied for more than half a century, reliable user-friendly models capable of simulating and predicting the biosorption process are urgently needed for designing and optimizing the biosorption process and making it available for application to the industry.

Industrial growth and newly developed technologies dictate the path where academic and industrial research should follow. Increasing demand for rare earth metals, which include yttrium, scandium and the fifteen lanthanides, due to the need of catalytic converters for the automobile industry and also to the need of more compact and advanced computer devices among other applications, makes these elements a very promising metal group for industrial growth. Along with that, stricter environmental regulations will certainly follow. In addition, the need for pure individual elements makes the separation of these elements, which is a challenging and difficult task, very attractive.

Brown seaweed such as *Sargassum sp.* has proven to have high affinity for metal cations from aqueous solutions. This type of algae has in its cell wall structure alginate which is rich in carboxylate groups responsible for attaching the metal ions to the binding sites. Carboxyl groups are hard bases and lanthanides are hard acids according to the Pearson terminology hence this reaction is a promising one. In the present study, *Sargassum polycystum* was chosen due to its large availability in the Philippines and because all *Sargassum sp.* species present about the same metal uptake levels and characteristics with few variations. The objective of this thesis was to evaluate the biosorption performance of three lanthanides which could represent the series for metal removal and selectivity. For this reason, a light metal from the beginning of the series, La, an intermediate metal from the middle of the series, Eu, and, a heavy metal from the end of the series, Yb, were chosen. Batch dynamic and equilibrium experiments as well as column dynamics were performed to investigate the metal uptake levels and the reversibility of this biosorption reaction using suitable eluting agents. Modeling of equilibrium and column experiments was also studied for simulating and predicting the breakthrough curves generated by a fixed-bed column packed with the biosorbent.

This thesis is presented in *manuscript* format in accordance wih the outline provided by the Faculty of Graduate Studies and Research at McGill University. Consequently, the work is divided amongst four original scientific research papers either in preparation, previously published or submitted to various journals in the field. As a requirement of the thesis office, the texts of previously submitted journals must be reproduced in their entirety. In order to maintain a constant style, they are all presented with the same style. Although all manuscripts have an extensive literature review, another Chapter(2) was written to give a general and updated introduction to the topic of my thesis. Also as a requirement to manuscript-based theses, connecting texts that form logical bridges from one chapter (paper) to the next are present as forewords to the chapters containing original research articles (chapters 3 to 6). Also required for manuscript-based theses, a section entitled "Contribution of authors" is included prior to the introduction.

Chapter 3 deals specifically with the sorption of the three lanthanides under study, La-Eu-Yb, using *Sargassum Polycystum* biomass. Equilibrium isotherms were built to account for the effect of pH. Single and multi-component metal systems were studied to verify possible affinity differences. Metal solutions were prepared with nitrate salts to avoid formation of complexes at this stage. Calcium loaded biomass was used as most of binding sites are occupied by Ca because of the sea environment. The mechanism of the lanthanides biosorption was also examined.

Chapter 4 deals with the effect of counterions on La biosorption. More specifically, the objective of this work was to verify the impact if any of the presence of ions sulphate and chloride by using metal salts of the respective anions. These anions are commonly present in industrial processes and their effect on metal removal had to be assessed. The effect of pH under these new conditions was also studied. In order to explain the differences obtained, speciation of La in such systems was studied. The effect of the type of mineral acid for pH adjustment was accounted for as well because it would impact the speciation of the ion.

Chapter 5 deals with the desorption of the three lanthanides, La-Eu-Yb, using several inorganic and organic eluting agents to verify the reversibility of the biosorption of these metals. Effects of concentration levels of the respective elutants as well as of the liquid to solid ratio were studied. The reversibility of the sorption reaction plays an important role not only on the recovery of the elements previously sorbed onto the biomass, but also on the regeneration of the bisorbent for multiple use.

Chapter 6 deals with the fixed-bed column dynamics of binary and ternary systems considering the presence of lanthanum (La), europium (Eu) and protons (H). Isotherms under constant normality were built to account for the ion exchange mechanism and to follow the column dynamics. An ion exchange equilibrium model was proposed using hydrogen ions as the common ion and separation factors concept which resembles the liquid-vapor equilibrium. Dynamic column model neglecting axial dispersion and assuming intra-particle mass transfer resistance as rate control was proposed to model the breakthrough curves of the metals La and Eu from the binary pairs with protons, and then used to predict the behavior of the ternary mixture with equivalent metal fractions in the feed solution. Metal analysis and pH measurements also confirmed the results obtained and the model was validated for longer fixed-bed columns as well. The objective of this section was to model the breakthrough curves for one and two metal systems using protonated biomass for packing the column. The intention was to calibrate both the equilibrium and column models for the binary pairs and then to apply these parameters to predict the breakthrough curves of a ternary mixture, i.e., two metal in the feed solution and the protons loaded onto the packed biosorbent.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

This chapter gives a general overview of this thesis topic from several angles, namely the biosorption process equilibrium, its dynamic operation and process performance modeling. Among the best performing biosorbents for metal cations is the brown seaweed *Sargassum*. Its species have been studied in more detail due to their exceptional cation removal capacity and excellent mechanical and chemical properties. The biosorption of rare earth elements has been studied because of their economic importance. The increasing demand for their oxides and high purity makes this group of elements one of interest for cost-effective recovery including environmental concerns. The characteristics, properties and applications of these elements are also described in this chapter. An overview of the removal of lanthanides through biosorption and other techniques is presented. The feasibility of a biosorption system is based on batch equilibrium performance as well as on a fixed-bed column dynamics. As the behavior of both are best described through the use of mathematical models, this chapter will also discuss the different approaches used to model the equilibrium isotherms and column breakthrough curves.

2.2. Rare earths

A very good future is foreseen for the rare earth elements that comprise Y, Sc and Lanthanides (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu). The demand for these elements has been rapidly increasing and the need for individual elements of high purity grows with new technologies employing them, especially in catalysis and optics fields (Hedrick, 2003; Denning, 2001; Hedrick, 1997; Lutz, 1996). Rare earths bearing effluents could also come from nuclear industry (Volesky, 2001). There are good indications that the biosorption process could be considered as an alternative technology for removing and recovering rare earth elements from aqueous solutions (Palmieri et al., 2003; Philip et al., 2000; Texier et al., 1997).

Rare earths are relatively abundant in the Earth's crust. However, the concentrations of these elements in ores that could be economically mined are lower than for most other metal-bearing ores. The world resources are based on more abundant bastnasite (China and USA) and on monazite (Australia, Brazil, China, India, Malaysia, South Africa, Sri Lanka, Thailand and USA), the second largest in occurence. Undiscovered resources are thought to be very large relative to the expected demand. Mining production is around 80,000 tons per year, while the reserves of rare earth elements are estimated at around 100,000,000 tons.

2.2.1. Applications

In 2004, the demand for rare earth oxides and other refined products increased for use in automotive catalytic converters, fiber optics, lasers, oxygen sensors, phosphors for fluorescent lighting, color television, electronic thermometers, X-ray intensifying screens, pigments, and superconductors among others (Hedrick, 2005). The use of rare earths is expected to increase as future demand for automobiles, electronics, computers and portable equipment grows. China is the world's principal rare-earth supplier with approximately 43% of world reserves. The economic growth in developing countries may provide potential new markets and demands particularly in Southeast Asia and Eastern Europe (Hedrick, 2000, 2003).

Markets for individual high-purity products were responsible for growth in the rare-earth industry between 1986 and 1998. The demand was greatest for neodymium metal used in high-strength neodymium-iron-boron (NIB) permanent magnet alloys and its alloying agent dysprosium. Lanthanum demand also increased because of lanthanum-nickel metal hydride rechargeable batteries used for cordless tools, camcorders, cellular phones and laptop computers (Hedrick, 2001; Lutz, 1996).

The new technologies explore the magnetic or optical properties of the rare earths. Permanent-magnet materials (NIB and samarium-cobalt) can be found in cars and in voice coil motors for computer disk drives that would not be so small, fast and store so much data without rare-earth based magnets. For other applications the magneto-optic property of terbium-iron-cobalt alloys is used in magneto-optical storage systems, which can store 15 to 20 times more information than the conventional magnetic hard disk.

Another alloy family, terbium-dysprosium-iron, called terfenol, is applied to sonar devices, micropositioners, and liquid control valves. Europium oxide and yttrium are used as phosphors and were responsible for the improvement in color TV images. Trichromatic fluorescent lamps that mix three colors of light produced by rare-earth phosphors are much more efficient than conventional fluorescent tubes. Lasers and optical fibers also exploit rare earths with the main application of neodymium and yttrium in Nd:YAG (yttrium aluminum garnet) that is the most common laser in use today. Optical amplifiers can be made with erbium. Environmental concerns also play an increasing role in conjunction with rare earth elements. The rechargeable metal-hydride batteries that employ $LaNi_5$ are replacing the ones that contain cadmium, a toxic heavy metal. In addition, catalytic converters use cerium to reduce harmful automobile emissions, and chemical and pharmaceutical companies have developed a family of pigments that include cerium sulfide, replacing heavy-metal-based pigments used for coloring plastics and other materials (Lutz, 1996). There is a large market for lanthanide ions in color display screens and fluorescent light tubes. Modern tubes rely entirely on lanthanide dopants in oxide hosts (Denning, 2001).

Usage of individual rare earths was only possible after the 1950's when separation and metallurgical technologies improved. The demand started increasing as the cost of individual earths became lower (Hedrick, 1998). REE prices depend on their purity and quality. Price fluctuations are usually due to the supply and demand factors, environmental legislation and economic factors, especially inflation and energy costs

(Hedrick, 2000). Prices are high especially for europium, terbium, holmium and lutetium as Table 1 shows.

Table 2.1: Rare-earth oxide prices

Product (oxide)	Purity (%)	Standard package quantity (Kg)	Price (US$/Kg)
Scandium	99.99	1	6,000.00
Yttrium	99.99	50	88.00
Lanthanum	99.99	25	23.00
Cerium	96.00	25	19.20
Praseodymium	96.00	20	36.80
Neodymium	95.00	20	28.50
Samarium	99.90	25	360.00
Europium	99.99	1	990.00[1]
Gadolinium	99.99	3	130.00
Terbium	99.99	5	535.00
Dysprosium	99.00	3	120.00
Holmium	99.90	10	440.00[2]
Erbium	96.00	2	155.00
Thulium	99.90	5	2,300.00
Ytterbium	99.00	10	340.00
Lutetium	99.99	2	3,500.00

[1] Price for quantity greater than 40 Kg is $900.00/Kg

[2] Price for quantity less than 10 Kg is $485.00/Kg

Source: (Hedrick, 2003)

The interest in the rare earths started with the Manhattan Project that was created during World War II for the development of the atomic bomb. It was discovered that radioactive isotopes, including rare earths, were formed during uranium fission. In order to produce plutonium, it was observed that synthetic organic ion exchange resins could adsorb some of the uranium fission products, which could be differentially eluted from the adsorbent using chemical reagents under controlled conditions (Ettre, 1999).

2.2.2. Chemical properties

To explain the similarities of the rare earth metals, one needs to look at the structure of their atoms. 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. With the exception of Ce^{4+} and Eu^{2+}, all lanthanides occur in Nature as Ln^{3+} (Henderson, 1996). The divalent ions are not sufficiently stable (Topp, 1965). These ions are characterized by large ionic radii, which mean 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 and are very electropositive, so their bonding characteristics are largely ionic (Henderson, 1996; Krumholz, 1964), although yttrium is much more prone to covalency due to its inert gas structure. The ions have low polarizability due to their high z/r ratio. They are usually found in solids with CN (coordination number) 8, while the smaller Sc^{3+}

is found in CN 6. However, lanthanides and yttrium tend to bind the water molecules, and the most common form obtained is $Ln(H_2O)_6^{3+}$ (Brookins, 1989).

The hydrolysis of these ions is slight and there is an increase in hydration with 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 $Ln(OH)^{2+}$, $Ln(OH)_3(aq)$, and $Ln(OH)_4^-$ decrease significantly. At acidic to neutral pH media, the dominant form in water may be Ln^{3+}. Several complexes are important and pH-specific. At very low pH, Ln^{3+} and $LnSO_4^+$ are ionic species of importance. The halide complexes of the lanthanides are only of minor importance, even at low pH (Brookins, 1989). At neutral to slightly basic pH range, the carbonate complexes are dominant, $Ln(CO_3)^+$ and $Ln(CO_3)_2^-$. The light lanthanides prefer the former and the heavier the latter. At pH approaching 10, hydrolysis becomes important for trivalent ions, $Ln(OH)^{2+}$ and $Ln(OH)_3$ (Brookins, 1989).

The Lanthanides are hard acids in the terminology of Pearson (Brookins, 1989) and will bond preferentially with hard bases that contain oxygen as donor atoms. On the other hand, these ions will bond more weakly with soft bases, such as those with donor S or P. Correspondingly, the dominant ligands contain at least one donor oxygen atom, and kinetically, rare earths react quickly to form complexes. Table 2 shows some of the lanthanide properties.

Table 2.2: Some characteristics of rare earths

Symbol	Element	Atomic Number	Molecular Weight	Ionic radii (CN = 6) (nm)	Electronic Configuration
Y	Yttrium	39	88.91	10.19	$[Kr]4d^1 5s^2$
La	Lanthanum	57	138.9	11.60	$[Xe]5d^1 6s^2$
Ce	Cerium	58	140.1	11.43	$[Xe]4f^2 6s^2$
Pr	Praseodymium	59	140.9	11.26	$[Xe]4f^3 6s^2$
Nd	Neodymium	60	144.2	11.09	$[Xe]4f^4 6s^2$
Sm	Samarium	61	147.0	10.79	$[Xe]4f^5 6s^2$
Pm	Promethium	62	150.4		$[Xe]4f^6 6s^2$
Eu	Europium	63	152.0	10.66	$[Xe]4f^7 6s^2$
Gd	Gadolinium	64	157.3	10.53	$[Xe]4f^7 5d^1 6s^2$
Tb	Terbium	65	158.9	10.40	$[Xe]4f^9 6s^2$
Dy	Dysprosium	66	162.5	10.27	$[Xe]4f^{10} 6s^2$
Ho	Holmium	67	164.9	10.15	$[Xe]4f^{11} 6s^2$
Er	Erbium	68	167.3	10.04	$[Xe]4f^{12} 6s^2$
Tm	Thulium	69	168.9	9.94	$[Xe]4f^{13} 6s^2$
Yb	Ytterbium	70	173.0	9.85	$[Xe]4f^{14} 6s^2$
Lu	Lutetium	71	175.0	9.77	$[Xe]4f^{14} 5d^1 6s^2$

For Ce^{4+} and Eu^{2+} the ionic radii are 9.7 and 12.5 nm respectively.

Source: (Henderson, 1996).

2.2.3. Mass extraction and separation

The main raw mineral materials from which rare earths are extracted are monazite and bastnasite. The two main methods of mineral breakdown are the traditional sulfuric acid and the caustic soda. After solubilization in sulfuric acid, neutralizing to pH 1.05 with ammonia first precipitates thorium. Rare earths are precipitated by careful neutralization to pH 2.3. Finally, uranium can be recovered by neutralizing to pH 6. Rare earths can also be recovered during solvent extraction of thorium and uranium (Bril, 1964) get recent references . A greater variety of monazite ores can be handled with sulfuric acid rather than with caustic soda. The main advantages of the caustic soda process are higher yields, cleaner separations and production of technical grade trisodium phosphate, although the cost is slightly higher than for the sulfuric acid process. However, caustic soda is preferred when further beneficiation of the rare earth group is considered (Bril, 1964).

The solvent extraction technique has been extensively used to remove and separate rare earth metals. It makes use of the ability of certain organic solvents in retaining selectively some elements while keeping others in the aqueous phase. Separation of Samarium (Sm), Europium(Eu) and Gadolinium(Gd) has been studied by photoreductive stripping in solvent extraction process. Equimolar mixtures of the three elements resulted in a 93% Eu-containing solution (Hirai and Komasawa, 1995). Other studies have attempted to recover Lanthanum(La) (Saleh et al., 2002) and other lanthanides (Kim et al., 1997).

An attempt to recover europium from chloride solutions consisted of reducing Eu^{III} to Eu^{II} by a zinc amalgam, followed by the precipitation of Eu^{II} sulphate in an inert atmosphere (CO_2). Initial concentrations ranged from 0.5 to 5.0 $g.L^{-1}$ of Eu_2O_3 and resulted in a constant residual concentration of 0.1 $g.L^{-1}$ of Eu_2O_3 (Morais and Ciminelli, 1998). Biosorption, on the other hand, could be effectively used to remove cost-effectively this residual low metal content, which would be expensive to recover through conventional processes such as ion exchange resins.

2.3. Biosorption

Biosorption can be defined as a passive metal sequestration process by certain types of biomaterials. The advantage of this technique relies on the fact that it can utilize raw materials that are both abundant and readily available in Nature such as seaweeds or industrial wastes generated by fermentation processes. Seaweed has the advantage of having good chemical and mechanical properties that make it suitable for sorption operations. On the other hand, industrial wastes would have to be processed to withstand the sorption operating conditions (Volesky, 2001). Biosorption processes can make use of (inactivated, dead) microorganisms such as fungi or bacteria, as well as certain abundant biomolecules such as chitin, among others (Bailey et al., 1999; Schiewer and Volesky, 2000; Vieira and Volesky, 2000; Yu et al., 1999). Even keratinous materials such as human hair have been used to sequester Cu^{2+}, Hg^{+}, Ag^{+}, Pb^{2+}, Cd^{2+}, Cu^{2+}, Cu^{+}, Cr^{6+}, Cr^{3+}, and Ni^{2+} (Tan et al., 1985).

Biosorption has been extensively studied, especially in the last decade (Volesky, 1999; Volesky and Holan, 1995). The review of the field of biosorption confirms relatively high uptake capacities of particularly heavy metals including Cr (III,VI), Co, Ni, Cu, Zn, Cd, Ag, Au, Pb, Th, and U by several specific types of biomass under different conditions (Veglio and Beolchini, 1997). Another review of chitosan-based sorbents, containing amino functional groups, reported on metal removal capacities and mechanisms involved (Guibal, 2004).

Biosorption has been focusing mainly on the removal of heavy metal ions from industrial effluents as it was seen as an alternative method for detoxification of such effluents for safe disposal to the environment (Matheickal and Yu, 1999; Schiewer and Volesky, 2000; Vieira and Volesky, 2000; Williams et al., 1998; Yu et al., 1999). This process represents a inexpensive technology that can utilize naturally abundant biomass for the removal of cations from aqueous solutions (Fourest and Volesky, 1996; Kratochvil et al., 1998; Schiewer, 1996; Yang, 2000; Yang and Volesky, 1999a, 1999b).

2.3.1. Types of sorbents

Many other types of sorbents have also been used to remove and recover metal ions from solution such as natural and synthetic zeolites, activated carbon, fungi, bacteria, yeast, and crab shells among others. The functional groups present in the sorbent cell wall structure play an important role in the applicability of such sorbent materials for the removal of metal ions. Therefore, some sorbents are more efficient in removing metal cations from solution while others remove metal anion complexes more preferably.

Crab shells have the ability to remove metal anion complexes from aqueous solutions due to their amino functional groups that become positively charged under acidic conditions (Niu and Volesky, 2001a; 2001b; 2003).

Biosorption with yeast biomass could not be considered successful neither for scandium at pH lower than 4.5, nor for samarium and lanthanum at pH lower than 5. X-ray analysis indicated that rare earth elements were accumulated mainly on the surface structures (Korenevsky et al., 1999).

Natural and synthetic zeolites have been used to sequester heavy metal ions such as Cr, Ni, Zn, Cu and Cd from electroplating wastewater. The synthetic ones demonstrated ten times better metal uptake capacities than those observed with the natural materials (Álvarez-Ayuso et al., 2003). However, metal uptake levels were lower than those of *Sargassum* species for the same metals. In addition, lateritic minerals have also been used to remove cadmium from aqueous solutions at the minimum pH of 5.4 by ion exchange with protons present in the silanol (-SiOH) group (Ahmad et al., 2003).

Although many types of biomaterials have the ability to remove ions from aqueous solution, most of them do not possess proper mechanical and chemical properties. Different biomass immobilization techniques have been examined to improve its mechanical strength. Among them are adsorption on inert supports, entrapment in a polymeric matrix and cells cross-linking (Vèglio and Beolchini, 1997). For example, sphagnum peat moss immobilized in porous polysulfone beads removed zinc and lead among other metals (Trujillo et al., 1991).. In addition, synthetic biosorbents have also been developed that could operate over a broader pH range and without the weight loss observed in natural biomaterials.

Many biomaterials need to be immobilized in solid structures to improve their mechanical strength, rigidity and porosity necessary for using them in process operations typical of chemical engineering. Some of these techniques include adsorption on inert supports, entrapment in a polymeric matrix and cell cross-linking (Veglio and Beolchini, 1997).

Many biosorption tests have been conducted over the last two decades assessing the biomass metal uptake. Only more recent few examples of metal uptake capacities for several sorbents are described in Table 2.3.

Table 2.3: Metal sorption studies

Sorbent	*Metal*	*pH*	*Metal Uptake* [meq g^{-1}]	*Reference*
Sphaerotilus natans (bacteria)	Cu Pb	5 5	1.3 1.3	(Beolchini et al., 2005)
Penicillium chrysogenum	Zn Ni Cr(III)	5 5 5	0.8 0.7 1.6	(Tan and Cheng, 2003)
Sugar beet pulp	Cd Pb	5 initial	0.4 0.7	(Reddad et al., 2003)
Peat	Cr Cu Cd	4	1.2 0.8 0.4	(Ma and Tobin, 2003)
Amberlite IR-120 resin	Cr(III)		3.9	(Alguacil et al., 2004)

2.3.2. Biosorption of rare earths

Removal of lanthanides through sorption processes has been studied using different types of sorbents such as seaweed, bacteria, yeast and activated carbon.

Studies reported uptakes of neodymium for the following biosorbents at pH 1.5: 10.5 mmol g^{-1} for the microalga *Monoraphidium* sp., 2.2 mmol g^{-1} for yeast biomass, 1.2 mmol g^{-1} for *Penicillium* sp., and 0.4 mmol g^{-1} for activated carbon (Palmieri et al., 2000). Other biosorption studies have been performed using different types of biomasses: microalgae, 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 for the microalgae and yeast, although the final equilibrium concentrations were rather high in the range of g L^{-1}. The uptake capacities of the metals by *Sargassum* sp. ranged from 0.6 to 0.7 mmol g^{-1}, demonstrating the capacity to remove the respective elements from solution. However, it took 60 days for the microalga to be cultivated (Palmieri, 2001). On the other hand, biomaterials such as seaweeds have the advantage of being abundantly and readily available in Nature.

Sargassum fluitans successively removed La in batch systems resulting in 0.73 mmol g^{-1} at pH 5. The presence of sulphate counterion reduced the metal uptake compared to that obtained when chloride was present (Palmieri et al., 2003).

The *Pseudomonas aeruginosa* bacteria have also been studied for the removal of the rare earth elements. The biosorption of La, Eu and Yb was investigated for the ternary and binary systems and the following affinity sequence was observed Eu=Yb>La. The presence of Na, Ca or K did not affect metal sorption, however, the presence of Al greatly suppressed lanthanide removal. The effect of anions such as Cl^-, NO_3^- or SO_4^{2-} did not show a significant impact on metal sorption (Texier et al., 1999). Other sorption studies using the same biomass revealed that the removal of lanthanides such as La, Pr, Nd, Eu and Dy at pH 5 varied from 0.8 to 1.0 mmol g^{-1}. Desorption of the La ion was possible with 0.2 mol L^{-1} HCl, although there was a 20% metal uptake loss in the second cycle. Langmuir, Freundlich and Brunauer-Emmet-Teller (BET) models were used to describe the equilibrium isotherms (Philip et al., 2000). Another work using the same sorbent immobilized in polyacrylamide gel was used to remove La, Eu and Yb through sorption column studies with feed solution concentration of 1 mmol L^{-1} for each metal at pH 5. The affinity sequence observed was Eu>Yb>La. The overshoot of the column-exit La concentration was observed. However, single metal studies with the same metals resulted in similar metal uptake capacities being slightly lower for europium, and biomass-chitosan beads were used for sorption equilibrium experiments (Texier et al., 2000a).

Another bacterium, *Mycobacterium smegmatis,* was used to remove La and Eu. Once again, the biosorbent demonstrated preference for the Eu rather than the La ions . Langmuir and Freundlich models were used to model the equilibrium isotherms as a mono-layer adsorption was believed to be the mechanism involved (Texier et al., 1997).

Table 2.4 summarizes the earlier results obtained for rare earths biosorption.

Table 2.4: Rare earths sorption.

Sorbent	***Metal***	***pH***	***Metal Uptake*** [meq g^{-1}]	***Reference***
Monoraphidium sp	Nd	1.5	31.4	(Palmieri et al., 2000)
Yeast			6.5	
Penicilium sp			1.9	
Activated carbon			1.3	
Monoraphidium sp	Er	5	23.8	(Palmieri and Garcia, 2001)
Saccharomyces sp			6.7	
Penicillium sp			1.9	(Oxides in HCl)
Activated carbon			1.2	
Monoraphidium sp	Yb	5	19.1	(Palmieri and Garcia, 2001)
Saccharomyces sp			5.4	
Penicillium sp			2.0	(Oxides in HCl)
Activated carbon			1.2	
Mycobacterium smegmatis	La	1.5	0.1	(Texier et al., 1997)
	Eu		0.4	
	La mix		0.1	(Nitrate salts)
	Eu mix		0.2	
Pseudomonas aeruginosa	La	5	3.0	(Philip et al., 2000)
	Eu		2.5	
	U		1.2	(Chloride salts)
	Pr		2.8	
	Nd		3.3	
	Dy		3.0	
	La	5	1.2	(Texier et al., 1997)
	Eu		0.9	(Nitrate salts)
	Yb		1.0	
Pseudomonas aeruginosa immobilized in polyacrylamide gel (column)	La	5	0.6	(Texier et al., 2002)
	Eu	initial	0.7	
	Yb		0.6	(Nitrate salts)
Sargassum sp	La	5	2.2	(Palmieri et al., 2002)
		4	1.8	(Chloride salts)
	La	5	1.6	(Sulphate salts)
		4	0.9	
		3	0.6	
		2	0.1	

2.3.3. Brown seaweed and *Sargassum*

Many studies have reported the outstanding uptake capacity of brown seaweed biomasses, especially *Sargassum*, for the removal of heavy metal cations from aqueous solutions.

Among the metals already studied are cadmium (Davis et al., 2000; Yang and Volesky, 1999), chromium (Kratochvil et al., 1998), copper (Davis et al., 2000), lead (Matheickal and Yu, 1999), and uranium (Yang and Volesky, 1999).

Sargassum biomass contains carboxylic groups capable of sequestering cations present in solution. Alginate is the main component of the brown seaweed cell wall structure. It is composed of guluronic acid and mannuronic acid residues of which primarily the former offers the functional groups for metal uptake (Siegel and Siegel, 1973). As the alginate matrix is present as a gel phase, it allows the ions to easily move through this material (Yang and Volesky, 1999).

The presence of guluronic acid blocks in alginates within the thallus of any brown seaweed significantly influences the relative affinity of the biomass for the ions in solution. Furthermore, the alginate content directly correlates with the metal uptake capacity of brown algal biomass such as *Sargassum* (Davis et al., 2003).

Other brown seaweed species such as *Laminaria* do not provide good mechanical stability despite their high metal removal capacities (Fourest and Volesky, 1997).

Its properties make *Sargassum* species an extremely promising biosorbent for binding rare earth metals quite easily as long as the conditions for best uptake, especially pH, are provided. In addition to that, carboxylate groups are considered as hard bases while rare earth elements are considered as hard acids according to the Pearson terminology and this makes for an easy binding reaction between rare earths and carboxylate groups. Some authors have pointed out that the pH for best uptake of the cations should be between 4 and 5, where an uptake plateau is often seen. A study found a metal uptake plateau at pH 4.5 for seaweed biosorption (Matheickal and Yu, 1999).

Another study showed that chromium demonstrated higher affinity towards *Sargassum sp.* than for copper, although the uptake was slower supposedly due to a larger ionic radius caused by hydration (Silva et al., 2003).

2.3.4. Biosorption mechanisms

Several mechanisms could be involved in the biosorption process due to the complexity of the biomaterial molecular structure. Sometimes, more than one physicochemical interaction could be involved in the process such as physical adsorption, ion exchange and complexation. The cell wall structures of these materials could offer metal-binding functional groups such as carboxylate, hydroxyl, sulphate, phosphate and amino groups (Veglio and Beolchini, 1997). These sorption mechanisms were demonstrated to be relatively fast and could be reversed (Kuyucak and Volesky, 1987).

A recent review of heavy metal biosorption by brown algae concluded the ion exchange character of this process. The conformational variability of alginates could be related to the metal uptake levels observed (Davis et al., 2003).

On the other hand, biosorption of mercury by *Pseudomonas aeruginosa* was believed to be not a simple ion exchange process but an affinity-based selective adsorption (Chang and Hong, 1994). The presence of 50 mmol L^{-1} sodium phosphate buffer (pH 7.4) enhanced the metal uptake while reducing that of a cation exchange resin, AG 50W-X8.

Potentiometric titrations of *Pseudomonas aeruginosa* showed that the amount of strong and weak acidic groups was 0.24±0.04 and 0.86±0.02 meq g^{-1}, respectively. Carboxyl and phosphate groups were suggested to play an important role in Eu biosorption (Texier et al., 2000). On the other hand, titration of *Sargassum fluitans* showed that 0.25±0.05 and 2.00±0.05 meq g^{-1} corresponded to the strong and weak acidic groups, respectively. These values corresponded to 0.27±0.03 and 2.25 meq g^{-1} of sulphonate and carboxylate groups, respectively. Alginate represents 45% of the biomass dry weight and it is responsible for the functional carboxyl groups (Fourest and Volesky, 1996).

Mycelium of *Penicillium chrysogenum,* a byproduct of penicillin fermentation, removed heavy metal ions by chelation with amino groups (Tan and Cheng, 2003).

The metal selectivity of *Sargassum* species and alginates was explained in terms of their α-L-Guluronic acid content and conformation. The presence of these G-blocks was proven to enhance selectivity for cadmium or calcium over other monovalent ions and smaller divalent ones (Davis et al., 2003).

Potentiometric titrations carried out on *Sargassum polycystum* biomass indicated the presence of three functional groups. The first one was believed to be the carboxyl group and its dissociation constant, pK_H, was estimated at 3.7±0.1 and the number of binding sites was 2.6±0.1 meq g^{-1}, representing the most abundant group. The second group had a pK_H value of 5.4±0.3 and 0.5±0.1 meq g^{-1} of binding sites, and it was believed to be the phosphonate group. Finally, the third one was believed to be the amine group with pK_H values of 8.8±0.3, representing 0.7±0.1 meq g^{-1} (Yun and Volesky, 2003).

On the other hand, the biosorption mechanism of chitosan-based sorbents is believed to be of chelation for metal cations and of electrostatic attraction on protonated amine groups for metal anions (Guibal, 2004).

Titration of the following species *Petalonia fascia*, *Sargassum hemiphyllum*, *Colponemia sinuosa* and *Ulva fascia*, resulted in a total number of binding sites of 2.9, 2.6, 1.5 and 1.1 meq g^{-1} respectively, which corresponded to the weakly acidic groups. Metal uptake was observed to decrease with increasing ionic strength (Schiewer and Wong, 2000).

2.4. Sorption equilibrium isotherms

Sorption studies often involve the determination of equilibrium isotherms at a specified pH whereby the total metal concentration increases along the curve. The Langmuir adsorption model has been used to model many of the sorption isotherms. This model describes well the process behavior quantitatively although not qualitatively. On the other hand, ion exchange isotherms are usually dimensionless and are determined under a specified total normality along the entire curve. The batch equilibrium isotherms can provide information on the favorability of the biosorption process and can also indicate the affinity differences among the metals.

2.4.1. Modeling equilibrium isotherms

Many different approaches have been used to describe the behavior of sorption equilibrium isotherms. Many sorption isotherm relationships have been derived for adsorption processes based on activated carbon. They were eventually used for biosorption to quantitatively represent the process behavior. The Langmuir model, considering monolayer adsorption, is usually the most frequent way of representing such isotherms. Other models such as Freundlich, which is empirical; BET, which reflects multilayer adsorption; and also the multi-component Langmuir model have also been used to describe sorption isotherms and are summarized in Table 2.5 that also includes the ion exchange occuring with *Sargassum* species. A review of biosorption process simulation tools using some of these models is broadly covered in the book by Volesky (Volesky, 2003). Many of the isotherms that have been determined are related to either same valence systems or to monovalent or divalent metal ions.

Single Langmuirian graphical representations are amongst the most common in the literature. However, adsorption models do not consider the exchange of ions that actually often dominates in the biosorption process. Ion exchange equations are then the best way to describe these systems whereby the total normality of the solution is kept

Table 2.5: Equilibrium isotherm models

Isotherm	*Equation*	*Reference*
Langmuir	$q_i = \frac{QK_iC_i}{1+K_iC_i}$	(Reddad et al., 2003)
Multi-component Langmuir	$q_i = \frac{QK_iC_i}{1+\sum_{i=1}^{n} K_iC_i}$ homovalent species	(Beolchini et al., 2005) (da Silva et al., 2002) (Veglio and Beolchini, 1997) (Sag et al., 2002)
	$q_i = \frac{Q(K_iC_i)^{1/z_i}}{1+\sum_{i=1}^{n}(K_iC_i)^{1/z_i}}$	(Schiewer and Volesky, 1996) (Figueira et al., 2000)
Freundlich	$q_i = K_i^0 C^{1/n_i^0}$	(Sag, 2000) (Silva et al., 2003)
Extended Freundlich Binary	$q_i = \frac{K_i^0 C_i^{n_i^0+n_{ii}}}{C_i^{n_{ii}} + K_{ij}C_j^{n_{ij}}}$ $q_j = \frac{K_j^0 C_j^{n_j^0+n_{jj}}}{C_j^{n_{jj}} + K_{ji}C_i^{n_{ji}}}$	(Sag, 2000) (Silva et al., 2003)
Ion exchange Binary	$y_1 = \frac{K_2^1 x_1}{1+(K_2^1-1)x_1}$	(Tan and Spinner, 1994)
Ternary	$y_i = \frac{K_1^i x_1}{1+(K_1^i-1)x_i+(K_1^{i+1}-1)x_{i+1}}$	

constant and could be applied to any system containing ions with different valences system as concentrations are expressed as equivalent fractions.

Studies using ion exchange resins such as amberlite IR-120 also make use of Langmuir and Freundlich models to describe their processes (Alguacil et al., 2004). Freundlich and competitive Freundlich models were used in other studies involving Cr(VI) and Fe(III) (Sag, 2000).

Another equilibrium model (HIEM – the Hydrolyzed Ion Exchange Model) was developed which considered the hydrolyzed species of the uranyl ion (UO_2^{2+}) in solution accounting for the several complexes formed (Yang and Volesky, 1999). The model used the same approach as outlined earlier by Schiewer and Volesky (1995) where the sorbent would offer only one type of a binding site, a condition acceptable under certain conditions. While the binding stoichiometry involved an unnatural fraction of the metal element (corresponding to 1/z, z = valence, e.g. $M_{1/z}B$), this facilitated the computer calculations.

2.5. Sorption column dynamics

The sorption process design as well as the design of adsorption and ion exchange processes, often employs the continuous flow-through column operating mode. The design of a continuous ion exchange process requires the performance of laboratory and pilot plant experiments and the complete understanding of the results. Some of the difficulties encountered include the validity of assumptions, the lack of diffusion coefficient data and mathematical difficulties associated with multi-component ion exchange systems (Slater, 1979). In general, fixed-bed columns are considered the best operation device for sorption processes as it maximizes the sorbent utilization capacity (Volesky, 2003; Stenzel, 1993). It is not only the generation of experimental breakthrough curves but their in-depth understanding and generalization that constitute the foundation for the successful design and optimization of a continuous dynamic sorption operation.

Membrane reactors containing free microbial cells have also been studied for the removal of heavy metal ions. The Langmuir equilibrium model for single and binary mixtures was used for describing the behavior of Pb and Cu biosorption by bacteria (Beolchini et al., 2005). This type of reactor was also used to adsorb cadmium and lead by sugar beet pulp (Reddad et al., 2003).

2.5.1. Modeling breakthrough curves

The purpose of modeling the breakthrough curves is to be able to predict the behavior of the sorption system as it is reflected in those curves. The breakthrough curve is a product of several key process factors that must be taken into consideration as they function in combination: the metal sorption equilibrium (isotherms), the speciation of metals in solution, the external and internal mass transfer properties and the column fluid flow characteristics (Volesky, 2003). Another important aspect, and an important challenge in the sorption design process, is to predict the behavior of multi-component metal systems. This may lead to solving several partial differential equations that can account for all these factors. Reliable user-friendly mathematical models are needed to model the sorption column dynamic behavior. The system of model equations can simultaneously be solved only by a powerful and preferably user-friendly computer algorithms and software. Some of the programs that have been developed for this unique purpose so far include IMPACT (Jausein et al., 1989) and FEMLAB (2004). The latter provides solution to partial differential equations in a simple and efficient way, being able to solve several coupled equations simultaneously.

The first approach to consider would be to determine and model the equilibrium isotherms directly from the multi-metal system equilibrium data and then using that for the column model. Another better-suited approach would consist of modeling the binary pairs and then use these parameters to model the multi-metal sorption column breakthrough curves.

When considering the column equations, i.e., solid and liquid mass balances, few assumptions can be made to model a breakthrough curve. The first one would be to neglect axial dispersion, which would represent a plug flow regime with uniform velocity across the intersectional area. The second aspect would be to consider local equilibrium, which would assume infinite mass transfer, and metal concentrations on the solid phase would be directly related to the equilibrium isotherm model values.

The conventional Bohart-Adams model was originally developed for adsorption on granulated activated carbon and applied for columns long enough to produce a constant mass transfer zone pattern (Bohart and Adams, 1920). The equilibrium column model (ECM) was developed for multi-component ion exchange systems and neglects both axial dispersion and mass transfer resistance (Helfferich, 1967; Klein et al., 1967). In addition, the mass transfer model (MTM), which includes both axial dispersion and mass transfer resistance, resulted in a more predictive behavior (Tan and Spinner, 1994). Another approach to this model was to combine both external and intra-particle mass transfer resistance into one parameter (Kratochvil et al., 1997). Another useful treatment for sorption designs was the Thomas approach (Sherwood et al., 1980), which assumes that a kinetic driving force is responsible for the rate of adsorption. This adsorption rate is proportional to a kinetic coefficient, to the surface area available for interphase transfer and an overall driving force. This kinetic coefficient could be related to an individual mass transfer coefficient that could represent diffusional resistances in both fluid and solid phases (Sherwood, 1975).

A summary of the models that have been applied to sorption column processes is in Table 2.6.

Table 2.6: Sorption column models

Column Model	**Equilibrium Model**	**System**	**Reference**
Bohart-Adams		Cd	(Volesky and Prasetyo, 1994)
		U	(Jansson-Charrier et al., 1996)
		Lanthanides	(Muraleedharan et al., 1994)
ECM	Ion Exchange	Cu	(Kratochvil and Volesky, 2000)
	Freundlich	Cu, Cd	(Galbadon et al., 2000)
MTCM	Ion Exchange	Cu,Ca,Fe,Zn	(Kratochvil, 1997)
			(Kratochvil et al., 1997)
	Freundlich	Cu, Cd	(Galbadon et al., 2000)
	Multicomponent Langmuir	Cu	(da Silva et al., 2002)
Macrocopic Model	Langmuir	Cr(III)	(Lin and Kiang, 2003)
	Freundlich		

A single-metal system would consist of a feed solution containing only one metal; however, assuming that an ion exchange reaction occurs, there would be another element already bound to the biomass, which could be either protons, H^+, or a light metal ion such as Ca, Na or K. As a matter of fact, such a sorption system is a binary one with a pair of ions present. It is important to point out that the total normality of the solution remains constant along the column because the number of equivalents of ions that are being released equals the number of ions that are being removed.

Table 2.7 shows the parameters obtained for mass transfer coefficients for the metals studied.

Table 2.7: Mass transfer coefficients.

Metal	k_m **[min $^{-1}$]**	***Conditions***	***Reference***
Cu	3.6E-3 – 2.4E-2		(Galbadon et al., 2000)
	1E-3 – 4E-3	$pH_i = 3.5$ Binary multi-component Langmuir (Ca/Cu)	(da Silva et al., 2002)

Some studies (da Silva et al., 2002) determine an equilibrium isotherm based on a specific final pH and then use it to predict the column dynamics behavior. However, while the total normality remains constant along the column, the pH cannot be controlled and may vary along the column as protons can also be exchanged during the process. In most studies the presence of protons is not considered in the sorption isotherm models that are used in the column behavior prediction. It was also observed that metal uptake and isotherm parameters were higher in column experiments than those obtained in batch equilibrium experiments (da Silva et al., 2002; Sag, 2000).

The following macroscopic model was developed as an alternative to a set of partial differential equations which would include the equilibrium resin adsorption capacity and the mass transfer rate (Alguacil et al., 2004):

$$\ln\left(\frac{[M]_t}{[M]_0-[M]_t}\right)=k[M]_0\left(t-\frac{[M]_e m}{[M]_0 f}\right) \tag{1}$$

Where $[M]_t$ is the solute concentration in the outlet solution at time t, $[M]_0$ is the inlet solution concentration, k is the rate constant of adsorption, and $[M]_e$ is the equilibrium solid-phase concentration of sorbate, m is the mass of sorbent, f is the flow rate and finally, t is the time.

This model could be simplified into the following expression:

$$\ln\left(\frac{[M]_t}{[M]_0-[M]_t}\right)=k\left(t-\tau^*\right) \tag{2}$$

Where k represents the slope and τ^* the intercept.

While this model represented well the experimental results, its parameters do not have a physical interpretation making it an empirical model.

Modeling multi-metal systems represents a challenging task especially in solving numerically several coupled partial differential equations that have to be solved simultaneously. For this purpose, some commercial computational software, such as FEMLAB(2004), or proprietary programs like IMPACT (Jausein et al., 1989) have been particularly useful in this task.

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CHAPTER 3

Foreword

In this first article, the objective was to verify the biosorption performance of the brown seaweed *Sargassum Polycystum* biomass in conjunction with lanthanides lanthanum (La), europium (Eu) and ytterbium (Yb). The effect of different pH levels as well as the interference of individual metals with the uptake of another in multi-component mixtures was evaluated. All *Sargassum* species have proven to be very effective in removing metal cations from solution, demonstrating similar metal uptake capacities. This species was chosen due to its ease of supply from the Philippines. Individual lanthanides were selected due to their economic importance, increasing demand for them and, in particular, because they represent a light (La), an intermediate (Eu) and a heavy (Yb) elements in the series. The preliminary study was to indicate how the biosorption of lanthanides might vary along the element series showing the metal removal capacity of the biosorbent and possible affinity differences for the metals chosen. The cell wall structure of *Sargassum* biomass is rich in alginate containing carboxylic groups which are hard bases having good affinity for hard acids such as the lanthanide ions. These basic theoretical considerations favored the choice of the relatively new biosorption system that became the focus of the initial part of this thesis research.

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

Water Research 39 (2005) 239-247

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3.1. Abstract

Biosorption of the lanthanides: La^{3+} (Lanthanum), Eu^{3+} (Europium) and Yb^{3+} (Ytterbium) 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 - 0.9) $mmol.g^{-1}$ for La, (0.8 -0.9) $mmol.g^{-1}$ for Eu, and (0.7 - 0.9) $mmol.g^{-1}$ 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 Eu>La>Yb, and the maximum metal uptake obtained was 0.29, 0.41, 0.28 $mmol.g^{-1}$ for La, Eu and Yb, respectively.

Key-words: biosorption; ion exchange; Lanthanum; Europium; Ytterbium; *Sargassum*

3.2. 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 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, 1999; Yang, 1999). Further studies of this biosorbent revealed the ion-exchange nature of the high metal uptakes by uptakes *Sargassum*, for example, of cadmium (Yang and Volesky, 1999), chromium (Kratochvil et al., 1998), copper/lead (Matheickal and Yu, 1999) and uranium (Yang and Volesky, 1999). *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 smal metallic cations making it thus a suitable biosorbent with a high sorption potential (Yang and Volesky, 1999).

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 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 1950's 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 3.1 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

Table 3.1: 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	6,500
Gadolinium	400
Terbium	1,300
Dysprosium	500
Holmium	1,200
Erbium	725
Thulium	6,500
Ytterbium	1,600
Lutetium	7,500

Source: Hedrick, 1998

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.

3.3. Materials and methods

3.3.1. Biomass preparation

The biosorbent used in experiments was the brown seaweed, *Sargassum 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 0.5mm were selected. The biomass was subsequently loaded with calcium in a solution of 50 mmol.L $^{-1}$ $CaNO_3$ (biomass concentration of 10 g.L^{-1}) for 24 hours 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.

3.3.2. Batch equilibrium experiments

3.3.2.1. 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 to 24 hours, 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: $La(NO_3)_3.6H_2O$, $Eu(NO_3)_3.6H_2O$, $Yb(NO_3)_3.6H_2O$ (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 hours 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 to 200 $mmol.L^{-1}$ 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.

3.3.2.2. 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.

3.3.3. 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).

3.3.4. 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:

$$q_M = \{(C_i V_i - C_f V_f)/m\}.(z_M/M_M) \qquad [\text{meq g}^{-1}] \qquad (3)$$

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.

$$q = Q - (C_{Ca} V_f/m).(z_{Ca}/M_{Ca}) \qquad [\text{meq g}^{-1}] \qquad (4)$$

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.

$$q_H = \{[H]_{add}V_{add} - ([H]_f V_f - [H]_i V_i)\}/m \qquad [\text{mmol g}^{-1}] \qquad (5)$$

The total number of binding sites was determined by protonating the biomass with 100 mmol.L^{-1} 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.

3.4. Results and discussion

3.4.1. Single-component isotherms

The time required to achieve equilibrium was determined through experiments establishing the metal uptake dynamics. This time can take from 10 minutes 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 hours was eventually chosen for all equilibrium experiments. During daytime, the pH would be gradually adjusted and equilibrium would be established overnight.

Figure 3.1 shows 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 capacity 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 curves were steeper than La curves, 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 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.

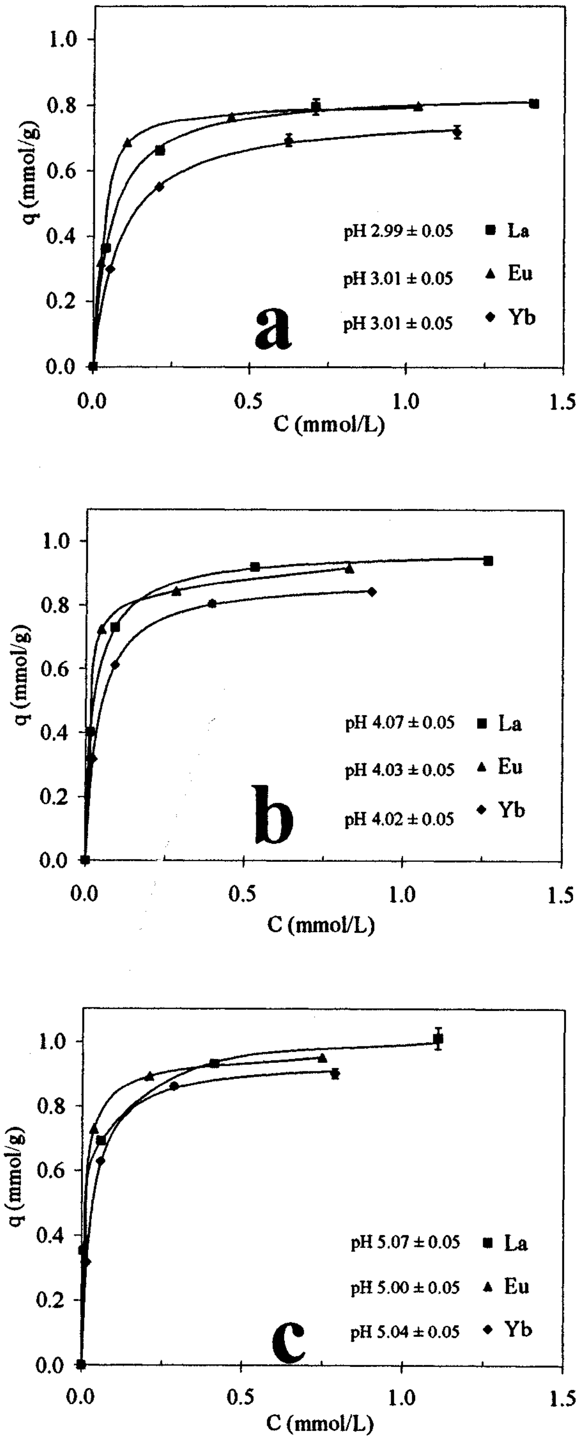

Figure 3.1: Effect of pH on La, Eu and Yb biosorption for nitrate salts solutions: (a) pH 3, (b) pH 4, (c) pH 5.

Various species of *Sargassum* have been reported to remove cations from solution. The uptakes of other metals by other species of *Sargassum* were recently reported to be 0.99 mmol.g^{-1} for cadmium at pH 4 (Yang and Volesky, 1999), 1.18 mmol.g^{-1} for Cu (Kratochvil et al., 1997), 2.38 mmol.g^{-1} for uranium at pH 4 (Yang and Volesky, 1999). 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 *Sargassum hemiphyllum* (Schiewer and Wong, 2000), 2.25 meq.g^{-1} for *Sargassum 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 mequ.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 *Sargassum 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 *Pseudomonas 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 $mg.L^{-1}$.

3.4.2. Ion exchange

The simultaneous release of Ca ions with the uptake of lanthanides and protons point to an ion exchange mechanism being involved (Figure 3.2). 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 1mM showed that 100% of the total lanthanum species was La^{3+}. The concentration of hydrolyzed species $LaOH^{2+}$ is lower than 0.001 mmol L^{-1} at pH 5 and, consequently, not significant. Aqueous hydroxide compound

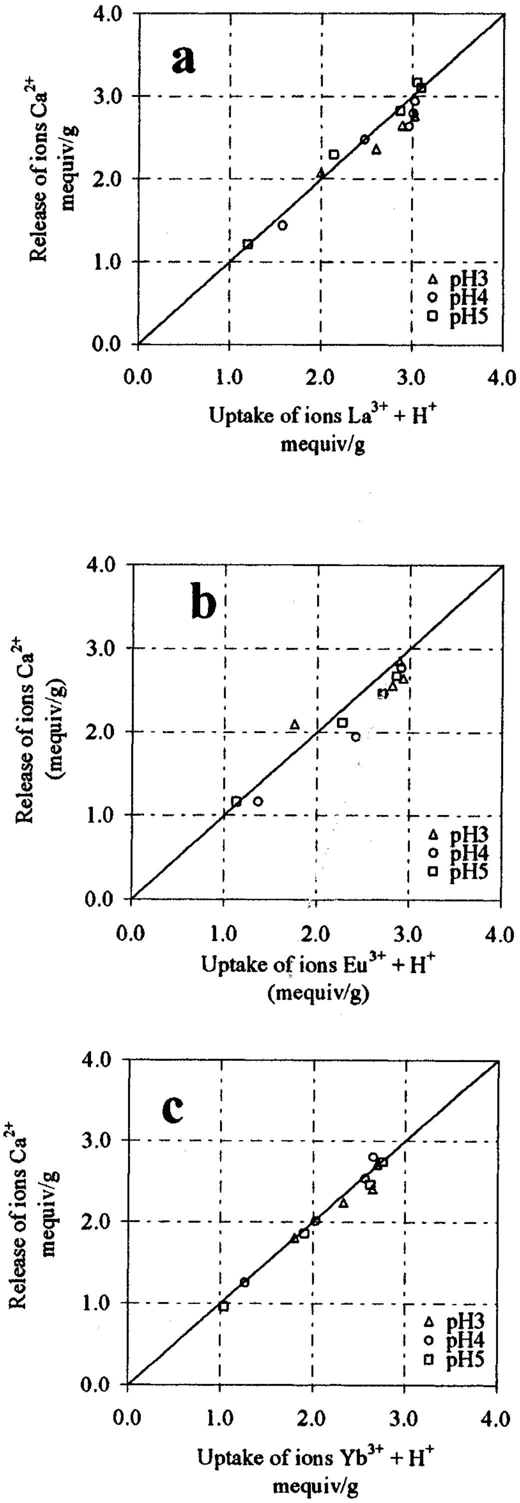

Figure 3.2: Ion exchange for (a) La, (b) Eu, (c) Yb

started forming at pH 7 precipitated at pH 7.5. In addition, La speciation in nitrate solution, according to the program MINEQL+ (version 4.5) (Schecher, 1991), showed that La is present as a free trivalent ion for the pH and metal concentrations examined in this work. This further supports the conclusion that ion exchange was 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 $Ln(H_2O)_6^{3+}$ (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 $Ln(OH)^{2+}$, $Ln(OH)_3(aq)$, and

$Ln(OH)^{4-}$ 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, $Ln(OH)^{2+}$ and $Ln(OH)_3$ (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 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 *Sargassum fluitans* biomass pretreated with $CaCl_2$ or HCl (100mmol.L $^{-1}$) although the weight loss was 24% and 44%, respectively. However, their $CaCl_2$ pretreated biomass was also first protonated with HCl 100mmol.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 ± 0.11 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 *Sargassum 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 *Sargassum fluitans* observed by Yang and Volesky (Yang and Volesky, 1999) 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.

3.4.3. 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. Figure 3.3 shows the single-component isotherms and the total metal uptake from the multi-component system at pH 4. From the graph it can be

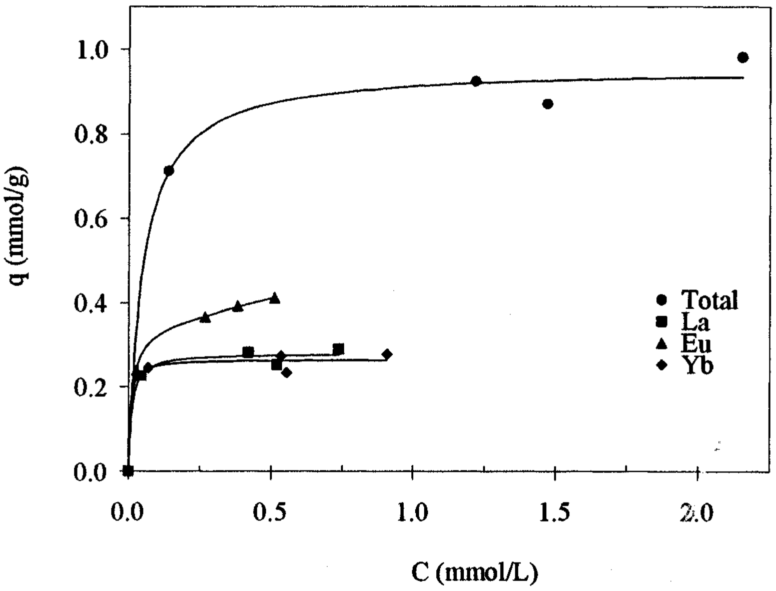

Figure 3.3: Multi-component isotherms at pH 4

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. Figure 3.4 (a,b and c) shows 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 Figure 3.5. 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

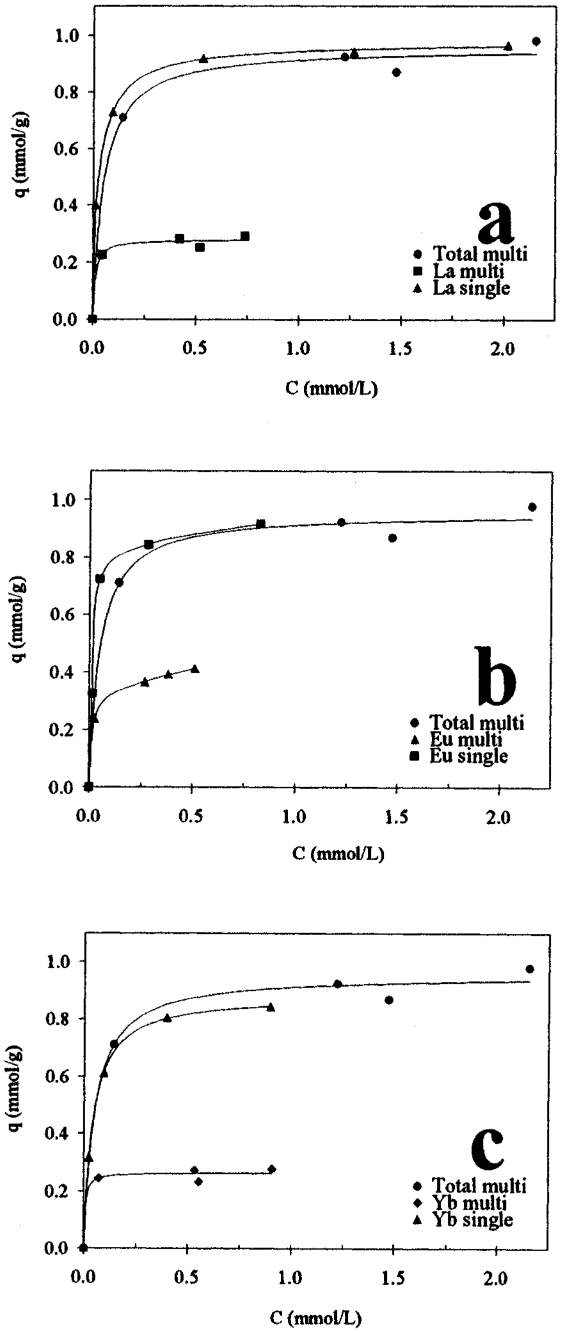

Figure 3.4: Single and multi-component individual isotherms compared to the total uptake of the different metals in the multi-component system for (a) Lanthanum, (b) Europium, and (c) Ytterbium at pH 4.

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 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.

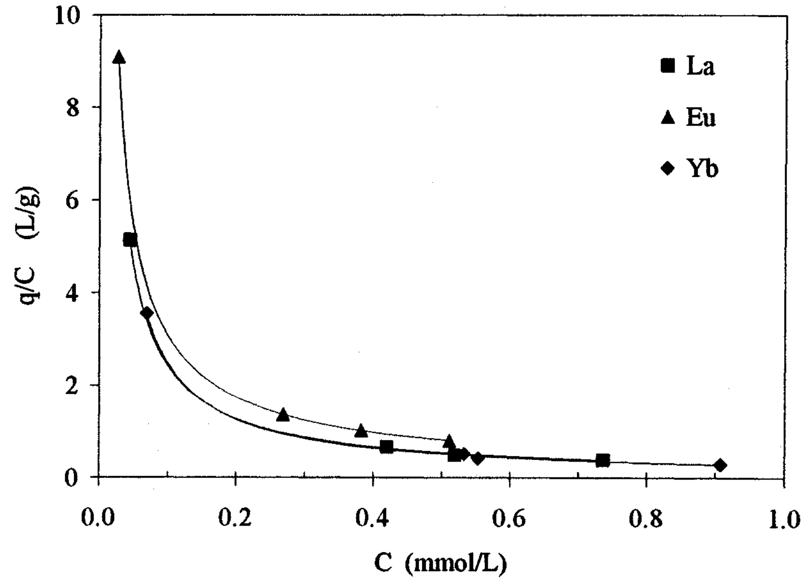

Figure 3.5: Distribution coefficient for lanthanum, europium and ytterbium in multi-component systems.

For another type of biomass, however, during column dynamics experiments in a fixed-bed with *Pseudomonas aeruginosa* immobilized in polyacrylamide gel, it was observed that the affinity sequence for the same lanthanide ions was Eu≥Yb>La (Texier et al., 2002). There are review papers in the literature comparing the biosorption of rare earths using microbial biomass (Andres et al., 2003) and the biochemistry of heavy metal biosorption by brown algae (Davis et al., 2003).

3.5. Conclusions

The *Sargassum* biomass tested in this work removed lanthanide ions from solution immobilizing up to 0.8 to 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 Eu>La>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.

3.6. Acknowledgements

The international CAPES (Brazil) Scholarship to V. Diniz enabled this work.

3.7. References

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CHAPTER 4

Foreword

All the studies reported on in the first article were performed with nitrate metal salts because such systems usually do not form complexes and the metal ions would be in the free valence form. However, it could be expected that in the real-world solutions chloride and sulphate counterions might abound. It is important to know what would be the biosorption behavior of at least one of the lanthanides in such systems. In the previous article, very good biosorption of lanthanides from nitrate systems was noted. In this subsequent piece of work, the study of lanthanum biosorption from chloride and sulphate metal salts at different pH levels was investigated and compared to that observed with the nitrate environment as reported earlier (Chapter 3). Speciation of all the ions present in solution is an important factor assisting in explanation of the results obtained. When isotherms are built for a specific final pH value, the acid used for adjusting the final pH also has an important effect on metal removal. In this work, an acid containing the same counterion present in the metal salt or nitric acid were added for pH adjustment to investigate this effect.

Effect of Counterions on Lanthanum Biosorption by *Sargassum Polycystum*

Water Research 39 (2005) 2229-2236

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4.1. 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, 4 and 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.

Key-words: biosorption, anions, Lanthanum, *Sargassum*, speciation

4.2. 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 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., 1999; Ahuja et al., 1999; 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; Palmieri et al., 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 *Sargassum polycystum* biomass.

4.3. Materials and methods

4.3.1. Biomass preparation

The biosorbent used in experiments was the brown seaweed, *Sargassum 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 0.5mm were selected. The biomass was subsequently loaded with calcium in a solution of 0.05 M $CaNO_3$ (biomass concentration of 10 g L^{-1}) for 24 hours 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.

4.3.2. Batch equilibrium experiments

Solutions containing the metals were individually prepared using distilled de-ionized water and different La salts: $La(NO_3)_3.6H_2O$, $La_2(SO_4)_3.6H_2O$, $LaCl_3.6H_2O$ (all Alfa Aesar supplied). For the batch equilibrium experiments the initial metal concentrations ranged from 100 to 500 mg L^{-1}. 0.1 g of dry biomass was contacted with 0.05 L of known-concentration solutions for 24 hours 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 mol L^{-1} to 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 mol L^{-1} to 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}).

4.3.3. 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).

4.3.4. 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.

4.4. Results and discussion

The earlier work (Diniz and Volesky, 2005) presented equilibrium sorption isotherms for lanthanum using nitrate salt and *Sargassum polycystum* biomass at pH levels of 3, 4 and 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.

4.4.1. 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. Figure 4.1 shows the equilibrium isotherms for solutions prepared with three different types of lanthanum salts, $La(NO_3)_3$, $La_2(SO_4)_3$ and $LaCl_3$ under pH 3, 4 and 5. It can be observed that there is an effect of the type of anion present on the lanthanum uptake. The presence of sulphate notably decreased the metal uptake for all three different levels of pH tested. On the other hand, the presence of chloride does not seem to have a significant effect. The metal removal decreased according to the following sequence: $NO_3^- \cong Cl^- > SO_4^{2-}$.

The concentration of anions in the system comes from two different sources. The first source is the metal salt used for solution preparation. Consequently, the concentration of anions is equivalent to the concentration of metal in the initial solution. Therefore, the concentration of anions in the system is higher at higher metal concentration levels, i.e., in the plateau region, and smaller at low metal concentrations, i.e., in the linear region of the sorption isotherm. The second source of anions is the mineral acid used to adjust the pH of the solution to the desired levels. The amount of

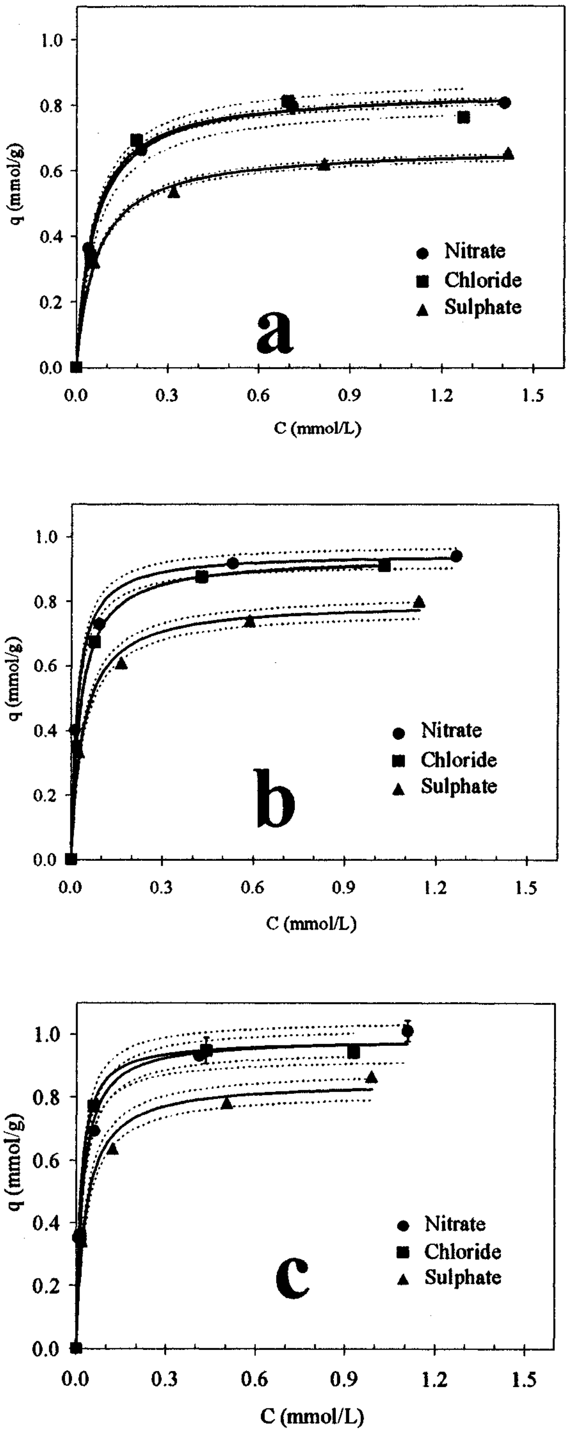


Figure 4.1: Effect of pH on La biosorption for nitrate, sulphate and chloride solutions: (a) pH 3, (b) pH 4, (c) pH 5.

anions that came from the acid added to adjust the pH to 4 and 5 was negligible compared to the concentration of metal in solution, which approximately ranged from 0.1 to 1 mmol.L^{-1}. The hydrogen ions concentration in the system was 0.1 mmol L^{-1} at pH 4 and 0.01 mmol L^{-1} at pH 5, which was much lower than the metal content in the solution.

In a previous work (Diniz and Volesky, 2005), ion exchange was indicated to be the main mechanism involved during the lanthanum sorption process using a nitrate salt. The active groups involved were the carboxylic groups present in the biomass and the exchangeable ions were calcium, lanthanum and protons. However, the Langmuir model, which represents the adsorption phenomenon, was shown to describe the process quantitatively well (Zouboulis et al., 1997) and for this reason was used for comparative purposes, although it is necessary to realize that it does not represent the mechanism involved in the biosorption process. The calculated R^2 values and standard errors are summarized in Table 4.1 while the respective adjustable parameters are reported in Tables 4.2 and 4.3. Experimental errors were low and always below 0.02 while larger errors were caused by model inadequacy. All R^2 values obtained were above 97.8% and demonstrated significant regression. From the results it can be inferred that the maximum metal uptake was identical for both nitrate and chloride systems. It was slightly lower for sulphate systems for all levels of pH tested. The sorption constant K obtained must be considered as reflecting an "apparent affinity" due to the non-Langmuirian nature of the sorption system. These apparent sorption affinities showed large variation in some cases, reflecting part of the inadequacy of the Langmuir model for the present sorption process. Despite the variation it can be concluded that the sorption

Table 4.1: Estimated values of R^2 and standard error.

	NO_3^-	SO_4^{2-} (HNO_3)	SO_4^{2-} (H_2SO_4)	Cl^- (HNO_3)	Cl^- (HCl)
pH 3	$R^2 = 99.87$ $q = q \pm 0.02$	$R^2 = 99.80$ $q = q \pm 0.02$	$R^2 = 99.63$ $q = q \pm 0.04$	$R^2 = 98.80$ $q = q \pm 0.07$	$R^2 = 99.71$ $q = q \pm 0.03$
pH 4	$R^2 = 99.31$ $q = q \pm 0.06$	$R^2 = 99.40$ $q = q \pm 0.05$	-----	$R^2 = 100.0$ $q = q \pm 0.005$	-----
pH 5	$R^2 = 97.77$ $q = q \pm 0.11$	$R^2 = 99.10$ $q = q \pm 0.06$	$R^2 = 99.49$ $q = q \pm 0.03$	$R^2 = 99.20$ $q = q \pm 0.07$	$R^2 = 99.51$ $q = q \pm 0.05$

constant increased with pH, although it was quite similar for pH 4 and 5. In addition, it was obviously lower for the sulphate systems. Therefore, the following sequence of affinity could be drawn for the systems studied: $NO_3^- = Cl^- > SO_4^{2-}$.

Kuyucak and Volesky studied the effect of counterions on cobalt biosorption using the brown seaweed *Ascophyllum nodosum* at pH 2 and 4.5. Nitrate (NO_3^-) ions seemed to strongly inhibit cobalt removal reducing the metal uptake capacity by 35% at pH 4.5. The presence of carbonate (CO_3^{2-}) also suppressed the cobalt removal by 4%, while the presence of phosphate and sulphate did not have an impact on the metal removal. The effect of all the anions tested was less pronounced under pH 2 (Kuyucak and Volesky, 1989). The presence of nitrate or sulphate ions also reduced cobalt biosorption by biomass of *Oscillatoria anguistissima* (Ahuja et al., 1999). However,

Table 4.2: Maximum metal uptake capacity by Langmuir model: $q = \frac{QKC}{1+KC}$

	Q (mmol.g^{-1})				
	NO_3^-	SO_4^{2-} (HNO_3)	SO_4^{2-} (H_2SO_4)	Cl^- (HNO_3)	Cl^- (HCl)
pH 3	0.84±0.01	0.67±0.02	0.65±0.02	0.85±0.06	0.79±0.03
pH 4	0.95±0.06	0.80±0.04	-----	0.94±0.00	-----
pH 5	0.98±0.16	0.85±0.06	0.91±0.05	0.99±0.10	0.93±0.06

Table 4.3: Apparent affinity constant by Langmuir model: $q = \frac{QKC}{1+KC}$

	K (L.mmol^{-1})				
	NO_3^-	SO_4^{2-} (HNO_3)	SO_4^{2-} (H_2SO_4)	Cl^- (HNO_3)	Cl^- (HCl)
pH 3	19.0±3.7	15.3±5.6	6.3±1.3	17.0±10.7	25.9±3.2
pH 4	51.3±12.1	25.5±4.7	----	33.5±0.2	-----
pH 5	69.4±31.6	32.5±7.9	9.9±1.8	48.0±11.2	67.0±13.0

other studies on the removal of zinc using *Oscillatoria anguistissima* (Ahuja et al., 1999) demonstrated that nitrate ions did not affect zinc uptake, while especially sulphate and also chloride ions contributed to reducing the metal uptake. Similar results were observed for lanthanum biosorption using another seaweed biomass (Palmieri et al., 2003). The maximum lanthanum uptake for *Pseudomonas auruginosa* reached 1 mmol g^{-1} at pH5 from a chloride salt solution (Philip et al., 2000).

Another work (Pulsawat et al., 2003) studied the effect of chloride, nitrate and sulphate ions on manganese removal using extracellular polymeric substance from *Rhizobium etli*. It was observed that the metal removal decreased in the following order SO_4^{2-} (2.26 meq g^{-1}) > NO_3^- (1.93 meq g^{-1}) > Cl^- (0.76 meq g^{-1}). While sulphate and nitrate produced similar results, chloride strongly inhibited the metal uptake. However, there was no discussion concerning the metal speciation in solution and how it could affect the metal removal. The values of pH tested ranged from 5.2 to 5.8, which could promote the formation of monovalent chloride complexes and even anionic chloride complexes contributing thus to the reduction of metal uptake. A more thorough study of metal speciation in these systems is necessary to explain the differences in metal uptake. Another work involved sorption studies of europium salts including nitrate, chloride and sulphate using *Pseudomonas aeruginosa* (Texier et al., 2000). The presence of these anions did not inhibit quantitatively the metal binding. However, there was evidence that chemical moieties of these anions were present in the chemical structure surrounding europium in the bacterial cell wall. It was also verified that the carboxyl and phosphate groups were responsible for the europium uptake (Texier et al., 2000).

One possible explanation of the differences and similarities obtained as the results of the present work when compared to those in the literature seems to rest in the speciation of metals in solution. A closer examination, considering the possibility of metal complex formation with counterions in solution, revealed a significant effect on the overall metal uptake by the biomass. The speciation of cobalt in solution is different from that of lanthanum and, on the other hand, zinc may behave more similarly to lanthanum. It should be pointed out that the type of biosorbent material could also affect the behavior observed. The formation of complexes with valences lower than the free metal ion reduce the total metal affinity as multivalent ions usually show higher selectivity than the monovalent ones.

4.4.2. Effect of NO_3^- and Cl^- from pH adjustment on La sorption

The adjustment of the pH can be done in different ways. In this study, results depicted in Figure 6(a,b,c) were based on adjusting pH with nitric acid. This was done in order to keep the total concentration of sulphate and chloride constant for each point of the isotherm. The addition of sulphate or chloride would contribute even more to the formation of complexes and precipitate. Other isotherms were derived at pH 3 and 5 for chloride systems with the pH being adjusted with hydrochloric acid. Figure 4.2 shows both isotherms at pH 3 and 5 where pH was adjusted with either nitric or hydrochloric acids. The figure shows that the isotherms were similar for both levels of pH.

Tables 4.2 and 4.3 show the Langmuir model parameters obtained from the chloride isotherms. Overall, nitrate and chloride solutions produced similar isotherms with practically no difference in both the metal uptake and the sorption affinity constant.

4.4.3. Effect of SO_4^{2-} and NO_3^- for pH adjustment on La sorption

The effect of adjusting the pH of lanthanum sulphate solutions with either nitric or sulphuric acid on the La uptake was verified in this study. The addition of sulphuric acid increases the total concentration of sulphate ions in the solution. That, in turn, affects the speciation of the metal in the liquid phase. It is important to point out that when adding nitric acid to adjust the pH, the only source of sulphate ions is the lanthanum sulphate salt. On the other hand, adjusting the pH using sulphuric acid increases the total sulphate concentration in the liquid, contributing even more to the formation of complexes. Figure 4.3 shows the isotherms for lanthanum sulphate solutions at pH 3 and 5. It can be clearly seen that the apparent affinities reflected by the slope of the curves at low metal concentrations were lower when using sulphuric acid rather than nitric acid. However, the maximum uptake capacity was similar with both acids, especially at pH 5. The difference is more pronounced for lower metal concentrations in the solution, especially at pH 3 when the amount of sulphuric acid added to adjust the pH is much higher than the amount added at pH 5. The parameters obtained by fitting the isotherms with the Langmuir model are summarized in Tables 4.2 and 4.3. The values of the apparent affinity constant K are much lower for the sulphuric

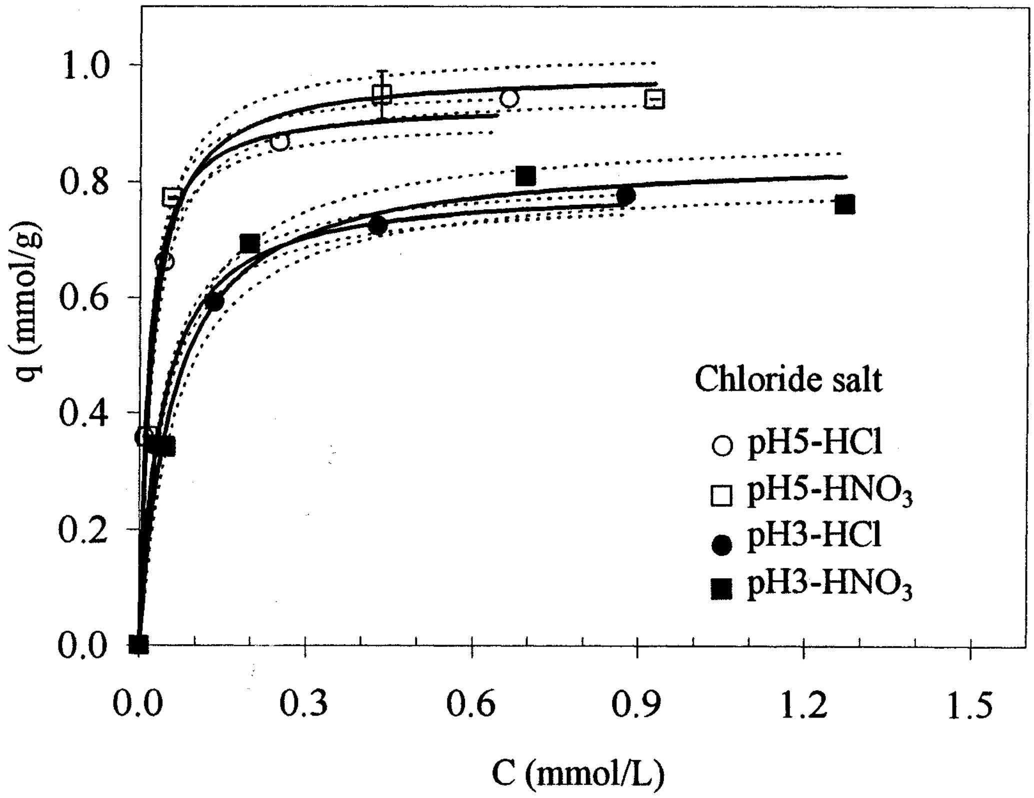


Figure 4.2: Effect of adjusting pH with HCl and HNO_3 for chloride systems at pH 3 and 5.

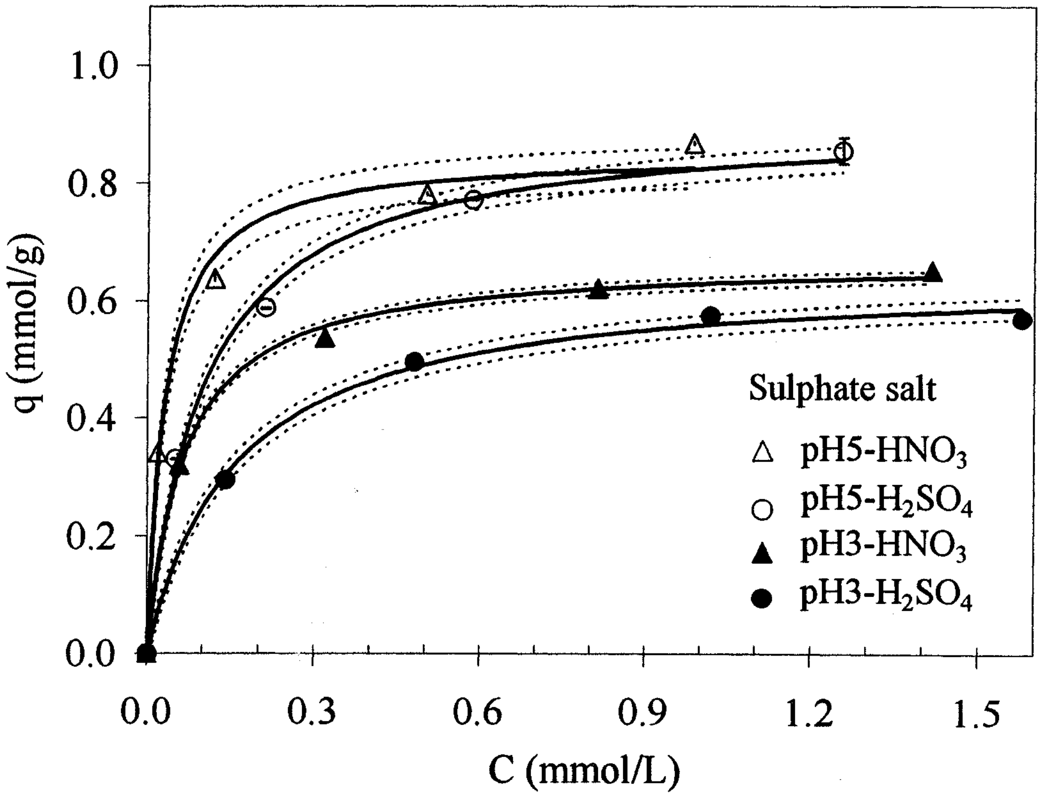


Figure 4.3: Effect of adjusting pH with H_2SO_4 and HNO_3 for sulphate systems at pH 3 and 5.

acid addition compared to the nitric acid addition, indicating a much less steep isotherm curve and, consequently, lower selectivity. The maximum La uptake capacity was similar at pH 5 and lower for the sulphuric acid addition at pH 3. From the results it can be inferred that the addition of sulphuric acid inhibits the lanthanum removal from the solution as it increases the total concentration of sulphate ions in the system. Studying the speciation of the ions in solution provided a reasonable explanation for the differences observed from the isotherms obtained for lanthanum sulphate salts.

4.4.4. Speciation of La in the presence of NO_3^-, Cl^- and SO_4^{2-}

A closer look into the solution chemistry of the La sorption system could assist in explaining the results obtained, especially those involving complexation and/or precipitation, and to verify the metal uptake mechanisms occurring during the biosorption process. A good knowledge of the real metal deposition mechanism(s) serves as a basis for composing mathematical process models that eventually could reliably predict the biosorption process performance. Metal speciation in solution can explain the differences observed in the lanthanum uptake due to the presence of a specific anion. The speciation was calculated using the software Mineql+ (Schecher, 1998). The usefulness of this program has already been demonstrated in other biosorption works (Diniz and Volesky, 2004; Yang and Volesky, 1999a,b). Table 4.4 describes the main possible reactions that can occur in the systems under study, and their respective overall stability constants. Some complexes and precipitates have a high potential to occur, including sulphate and chloride complexes.

Table 4.4: Overall metal stability constant values

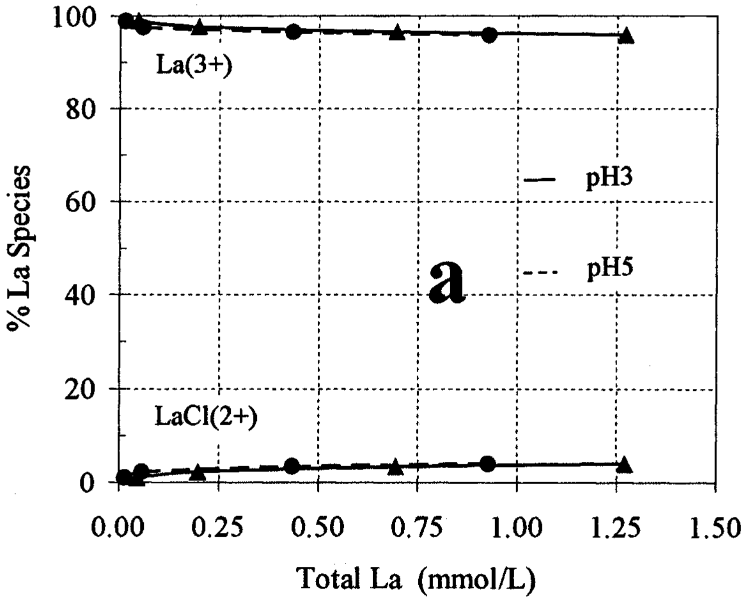
Reaction	*Log β*
$La^{3+} + OH^{-} \leftrightarrow [LaOH]^{2+}$	-9.000
$La^{3+} + 3OH^{-} \leftrightarrow La(OH)_3$	-21.291
$La^{3+} + Cl^{-} \leftrightarrow [LaCl]^{2+}$	0.700
$La^{3+} + SO_4^{2-} \leftrightarrow [LaSO_4]^{+}$	3.300
$Ca^{2+} + SO_4^{2-} \leftrightarrow [CaSO_4]_{aq}$	2.360
$Ca^{2+} + OH^{-} \leftrightarrow [CaOH]^{+}$	-12.697
$Ca^{2+} + NO_3^{-} \leftrightarrow [CaNO_3]^{+}$	0.500

Source : (Schecher, 1998)

The total final concentrations of all species present in solution were used as input to the MINEQL program. The species included lanthanum, nitrate, sulphate, chloride, protons, hydroxyls, and calcium. As the ionic strength is known to suppress metal removal (Zouboulis et al., 1997), it was also computed and ranged from 0.004 to 0.024 mol L^{-1} along the curves and the values obtained increased with the metal concentration and were similar for all different salt systems at the same final metal concentration. Therefore, the curves obtained at the same pH levels could be compared. The data obtained from the isotherms in Figures 4.1, 4.2 and 4.3, were used for the calculations, considering the pH and the total concentration of both anions and cations present in the system, including the calcium released from the biomass during the ion exchange process. According to previous work (Diniz and Volesky, 2005), Lanthanum was always present as a trivalent ion in nitrate systems .

Figures 4.4 and 4.5 show the speciation for each specific anion - sulphate and chloride, respectively - in the presence of lanthanum. Every curve shows the speciation at a certain pH varying the total concentration of metal and the anion type present in the experiments.

The La speciation in the chloride system can be seen from Figure 4.4(a,b). Most of the lanthanum present in the liquid is in the free trivalent form. Some of the La was complexed with chloride producing a divalent cation whose percentage in solution varied from 1 to 4%. The formation of this complex could explain the slight decrease in the metal uptake observed in chloride systems when compared to the nitrate ones, being even more pronounced when hydrochloric acid was added.



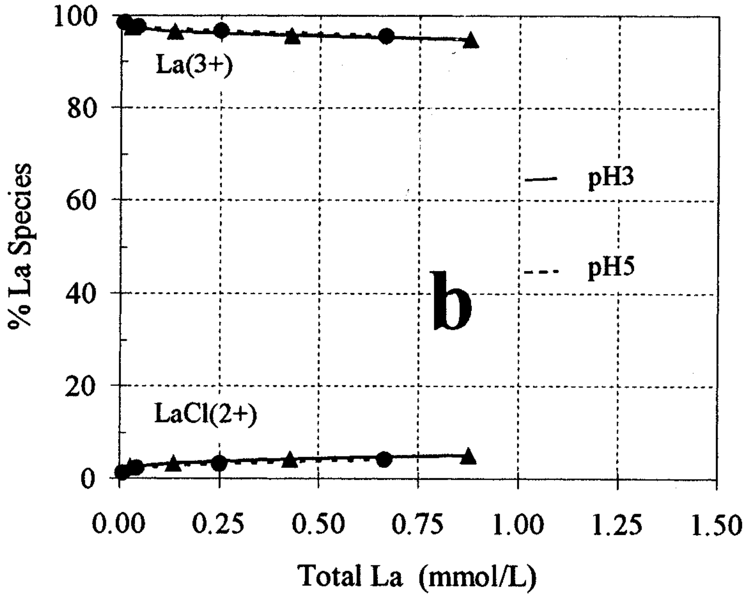
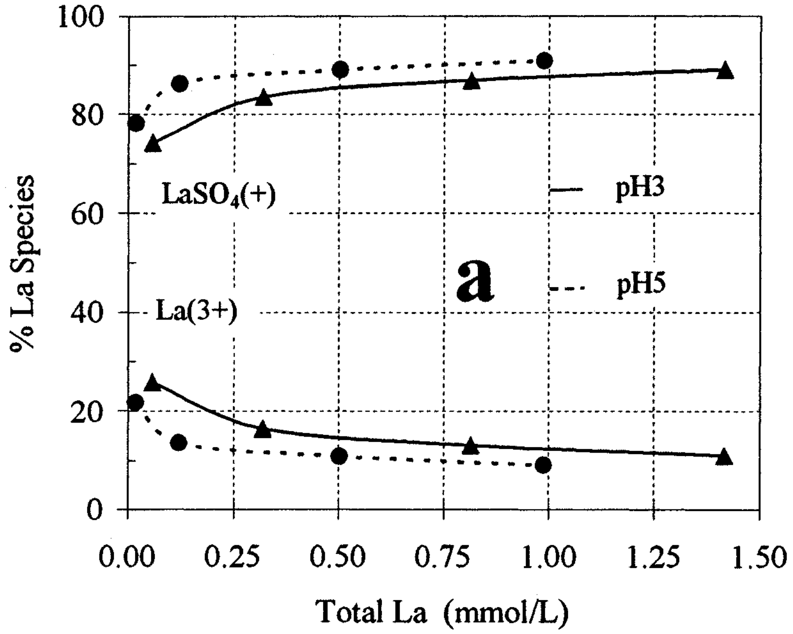


Figure 4.4: Speciation of La in chloride systems representing the conditions obtained from the isotherms under pH 3, 4 and 5. The pH was adjusted with (a) HNO_3 and (b) HCl respectively.

Figure 4.5(a,b) shows that a monovalent cation complex is formed with lanthanum and sulphate. The percentage of this complex increases with metal concentration. Needless to say, with increasing metal concentration, the concentration of the corresponding anion also increases. The behavior was similar for all pH values tested. From the results it can be inferred that the monovalent lanthanum sulphate complex formed has a lower apparent affinity towards the biomass. This was responsible for the decreased metal uptake from solution as seen in the isotherms. The same trend was observed for all levels of the pH tested. When sulphuric acid was added to adjust the pH, the percentage of the monovalent lanthanum sulphate complex increased due to the addition of sulphate ions into the solution, confirming thus that this complex has a lower apparent affinity to the biomass than the free trivalent lanthanum cation. The total metal uptake from solution was thus correspondingly reduced. Figure 4.6 shows the metal speciation in the presence of equivalent concentrations of either sulphate or chloride ions. They simulated the presence of species under initial experimental conditions.

Palmieri's study (Palmieri et al., 2003) suggested that fewer disturbances on the inner coordination sphere caused by chloride anions would improve the interaction with carboxylate groups present in the biomass. However, the metal speciation in solution was not even discussed in this work. Results of the present work are indicative of its importance.



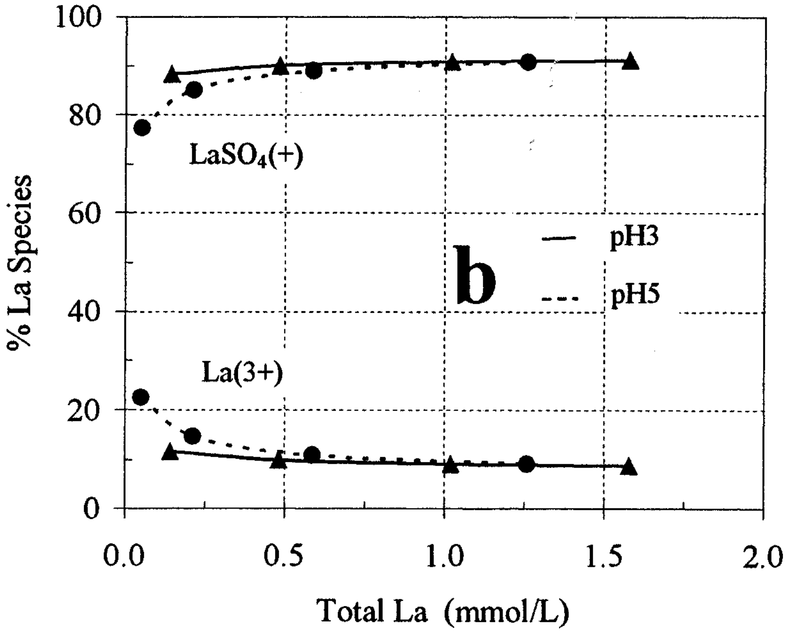


Figure 4.5: Speciation of La in sulphate systems representing the conditions obtained from the isotherms under pH 3, 4 and 5. The pH was adjusted with (a) HNO_3 and (b) H_2SO_4 respectively.

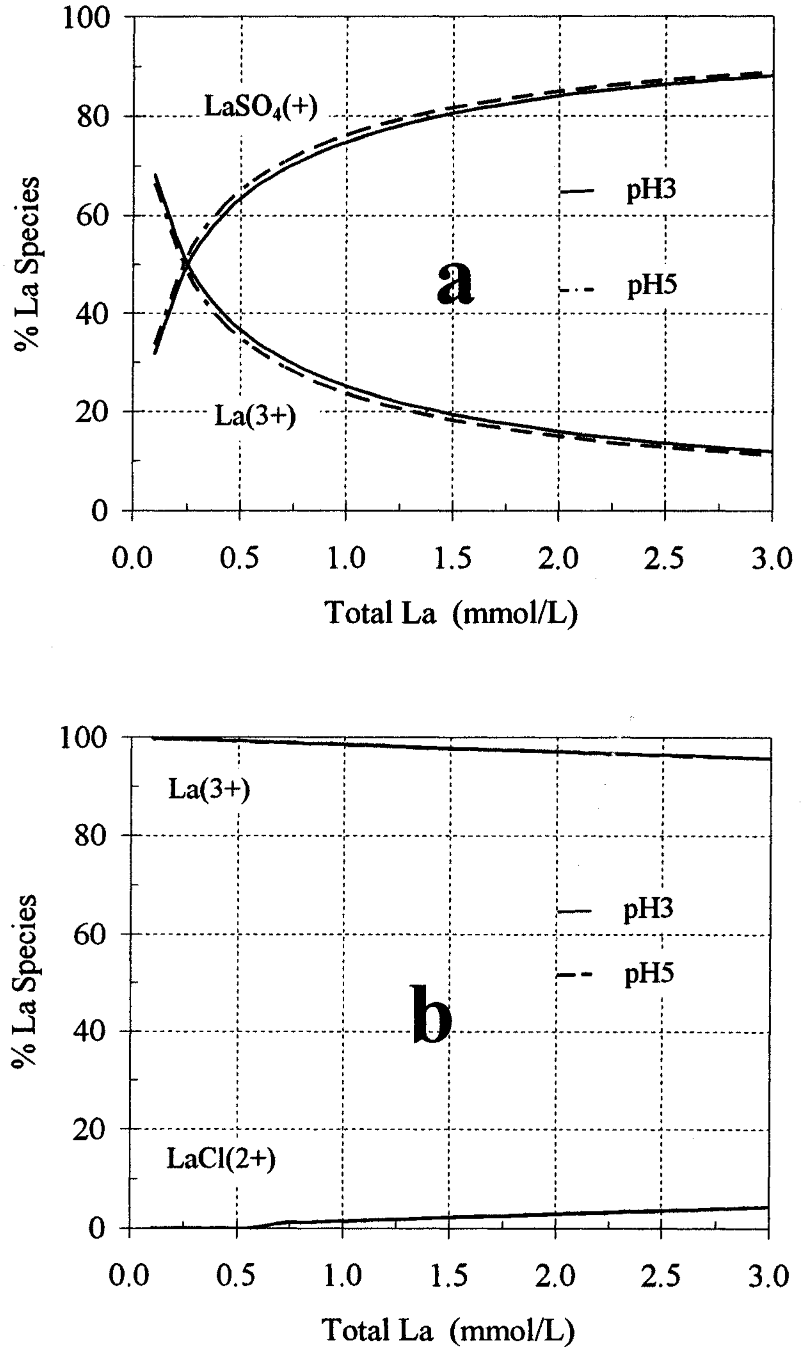


Figure 4.6: Speciation of La at pH 3 and 5 in the presence of equivalent concentrations of either (a) sulphate or (b) chloride ions.

4.5. Conclusions

Lanthanum could be removed from aqueous solutions by Sargassum polycystum biomass. Different metal removal capacities and relative biosorption affinities were observed when different La salts were applied. While nitrate and chloride salts resulted in similar biosorption behavior, sulphate salts inhibited the metal uptake. The metal speciation in solution provided a plausible explanation for the differences observed. Complexation of the metal and sulphate ions, resulting in a less-sorbing monovalent complex, reduced the total lanthanum removal. The addition of sulphuric acid for pH adjustment lowered the metal uptake as it increased the amount of the less-sorbing monovalent lanthanum sulphate complex. This effect was more pronounced at lower pH values when more acid was added to maintain constant pH. Although the R^2 values calculated for fitting the data with the Langmuir model were good, the model could not be considered adequate for describing some sorption behaviour observed. However, it estimated well the maximum metal uptake capacity and showed the differences among the metal-biomass apparent affinities.

4.6. Acknowledgements

The international CAPES (Brazil) Scholarship to V. Diniz enabled this work.

Valuable suggestions by Dr. Demopoulos were greatly appreciated.

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CHAPTER 5

Foreword

The work reported on in the previous article demonstrated that biosorption of the respective lanthanides by *Sargassum polycystum* biomass is a feasible and promising process independent on the type of counterion preset in the system. However, the reversibility of the sorption reactions deserves a special attention as it would provide the basis for the recovery of the elements sequestered by the biosorbent. The desorption should be accompanied by biomass regeneration for multiple uses. The objective of this third stage of work was to verify the possibility of the suitable release of the biomass-sequestered lanthanides. Different eluting agents were tested from mineral to organic acids in order to assess the effectiveness of the lanthanide desorption process that would result in more concentrated solutions amenable to metal recovery operations particularly desirable for the more expensive europium. In addition, these more concentrated desorbing solutions could alternatively also be more effectively processed by other techniques for eventual safe disposal of the wastewater solution.

Desorption of Lanthanum, Europium and Ytterbium from *Sargassum*

Separation and Purification Technology 50 (2006) 71-76

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5.1. 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 meq.g^{-1} at pH 2 and 2.8 meq.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 to 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.

Key-words: desorption, lanthanum, europium, ytterbium, *Sargassum*

5.2. 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 (Volesky, 2003). 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 (Davis et al., 2003).

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 (Yang and Volesky, 1999), chromium (Kratochvil et al., 1998), copper and lead (Matheickal and Yu, 1999), uranium (Yang and Volesky, 1999), 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 (Siegel and Siegel, 1973). 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 (Yang and Volesky, 1999).

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 (Aldor et al., 1995; Davis et al., 2000; Holan et al., 1993; Palmieri et al., 2002). In addition, isocratic (Nesterenko and Jones, 1997) and gradient (Inoue et al., 1996) 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 (Diniz and Volesky, 2004). The present study focused on desorbing these metals from the biomass by using eluting agents capable of removing all the metals present 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.

5.3. Materials and methods

5.3.1 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 0.5mm 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 hours 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.

5.3.2 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 hours 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 to 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 0.5g of biomass and put into contact with 50mL 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 0.1g of metal loaded biomass and 50mL of eluting solution for 24 hours. 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 0.025g of lanthanide loaded biomass in 50 mL of eluting agent.

5.3.3 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).

5.3.4 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} :

$$q_M = (C_i V_i - C_f V_f)/m \qquad [\text{mmol g}^{-1}] \qquad (6)$$

Where:

m is the biomass dry weight [g]

V_i is 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.

$$q_{Ca(rel)} = ((C_f V_f - C_i V_i) - (B_f - B_i) V_i)/m \qquad [\text{meq g}^{-1}] \qquad (7)$$

Where:

C_i is the initial concentration of calcium in solution [meq L^{-1}]

C_f is the final concentration of calcium in solution [meq L^{-1}]

B_i is the initial concentration of calcium obtained from the initial blank [meq L^{-1}]

B_f is the final concentration of calcium obtained from the initial blank [meq L^{-1}]

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.

$$q_{\mathrm{H}} = \{[\mathrm{H}]_{add} V_{add} - ([\mathrm{H}]_f V_f - [\mathrm{H}]_i V_i)\}/m \qquad [\text{meq g}^{-1}] \qquad (8)$$

Where:

$[\mathrm{H}]_{add}$ is the concentration of the acid added for adjusting the pH [mmol L^{-1}]

V_{add} is the volume of acid used for adjusting the pH [L]

$[\mathrm{H}]_f$ is the final proton concentration relative to the final pH of solution [mmol L^{-1}]

$[\mathrm{H}]_i$ is the initial proton concentration relative to the initial pH of solution [mmol L^{-1}]

5.4 Results and Discussion

5.4.1 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. Figure 5.1 shows the amount of calcium ions 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±0.06meq.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 meq.g^{-1}. This number is very much in accordance with the maximum uptake of lanthanides reported in previous work (Diniz and Volesky, 2005). Table 5.1 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.

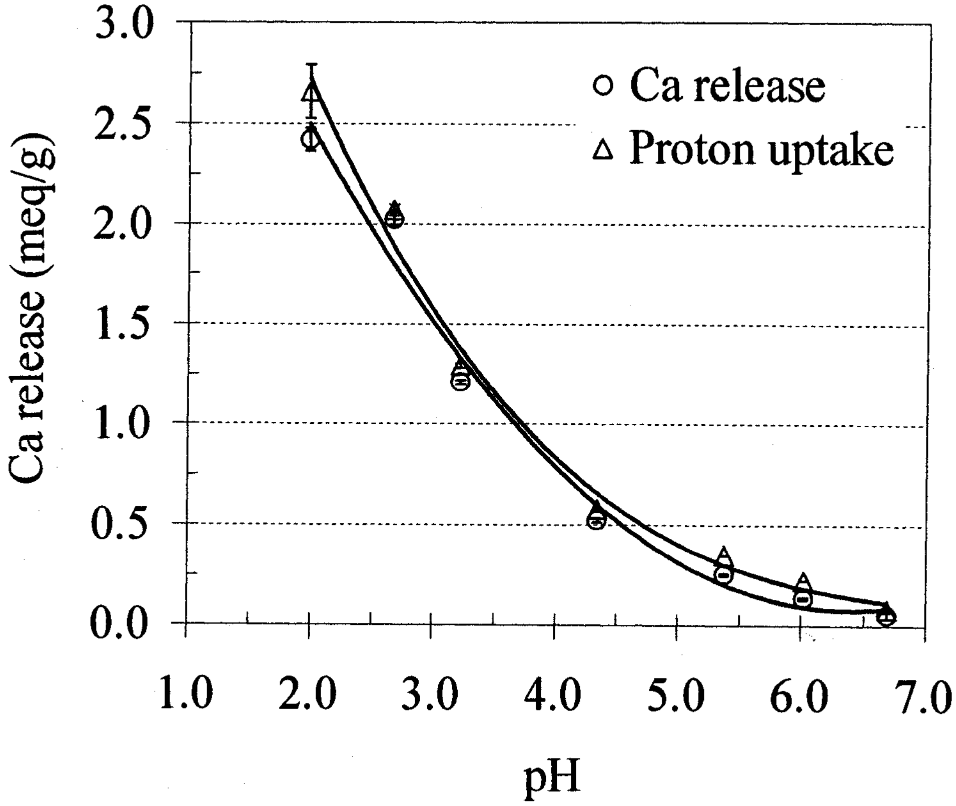

Figure 5.1: Release of calcium from biomass and removal of protons at different pH levels.

Table 5.1: Calcium ions released at different acidity levels.

Acid	Acid Concentration (mmol L^{-1})	Calcium Released (meq g^{-1})
HNO_3	38	2.58 ± 0.03
	50	2.75 ± 0.06
	196	2.71 ± 0.09
HCl	100	2.79 ± 0.02

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

5.4.3 Effect of washing the biomass after sorption and before desorption

Figure 5.2 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.

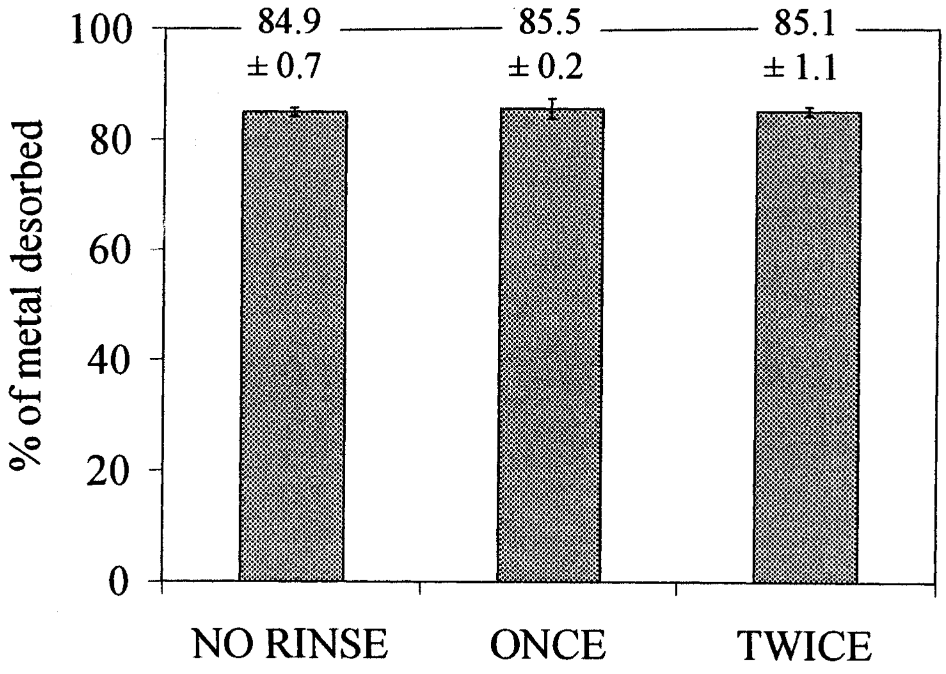

Figure 5.2: Effect of washing the biomass after La sorption and before its desorption.

5.4.4 Desorption of an individual metal system

The objective of this work was to verify the possibility of desorbing the immobilized lanthanide metals from the biomass. Figure 5.3 shows the percentages 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 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 (Diniz and Volesky, 2004) described the "affinity sequence" for the biomass as Eu>La>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" Yb>La>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}

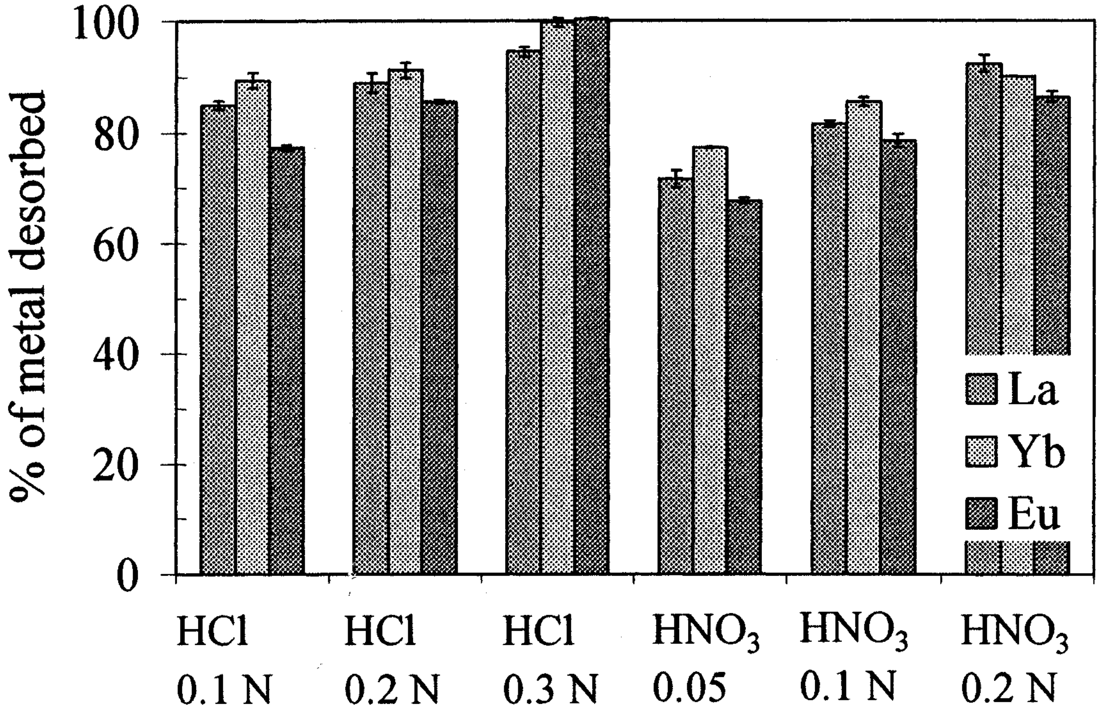

Figure 5.3: Desorption of individual elements with different concentrations of mineral acids. Single-element systems containing respectively La, Eu and Yb.

HCl under the liquid to solid ratio of 0.5 L.g^{-1} (Palmieri et al., 2002), confirming the requirement for a higher proton concentration in order for the desorption to take place.

The (L/S) ratio used in the current experiments was 0.5L.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. Figure 5.4 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 (Ahuja et al., 1999). In column experiments, 96±4% of Lanthanum could be desorbed from *Pseudomonas aeruginosa* using 0.1mol.L^{-1} EDTA (Texier et al., 2002). Oxalic and diglycolic acids are mainly used in chromatography for rare earth elements separation (Bruzzoniti et al., 1996 and 1997).

Calcium nitrate and chloride solutions were also tested for desorption purposes. High concentrations of these solutions could only be made upon acidification. Calcium chloride solutions were also tested at higher concentration levels to verify if all the metal

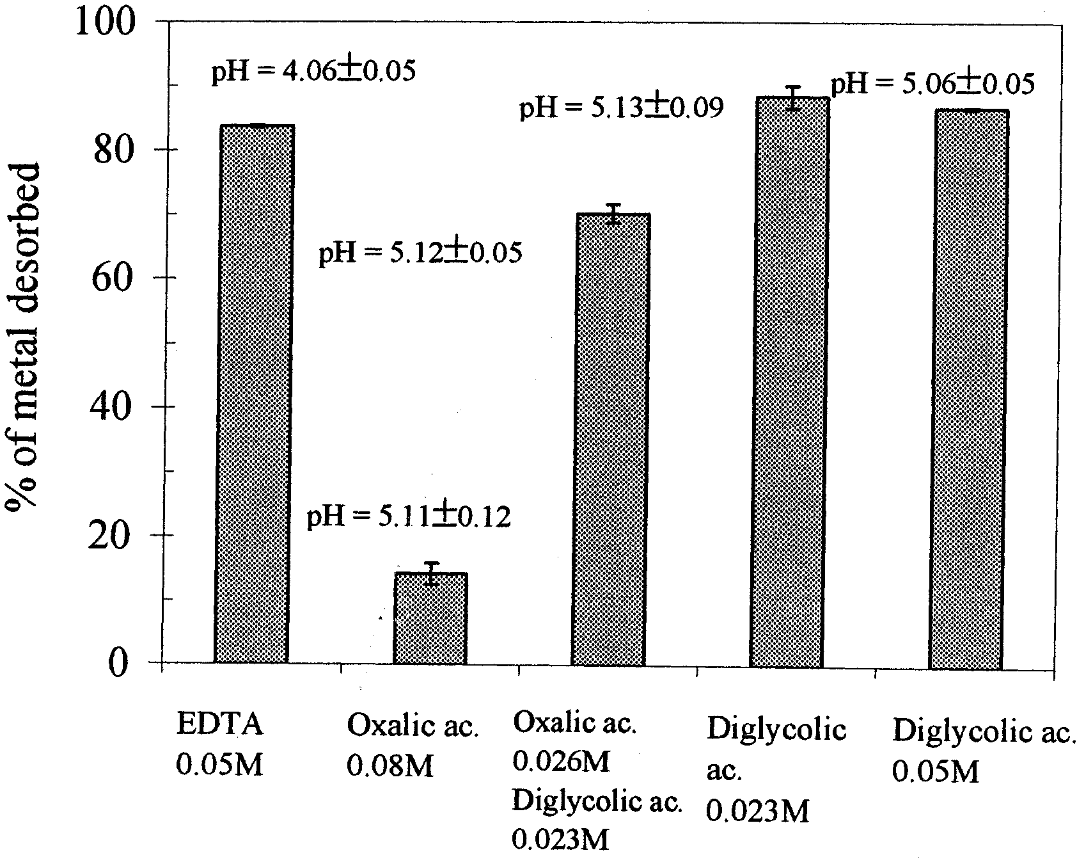

Figure 5.4: Single-element system desorption of La using different organic acids.

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 (Henderson, 1996). 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 Figure 5.5. 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 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 $Ca(NO_3)_2$ 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

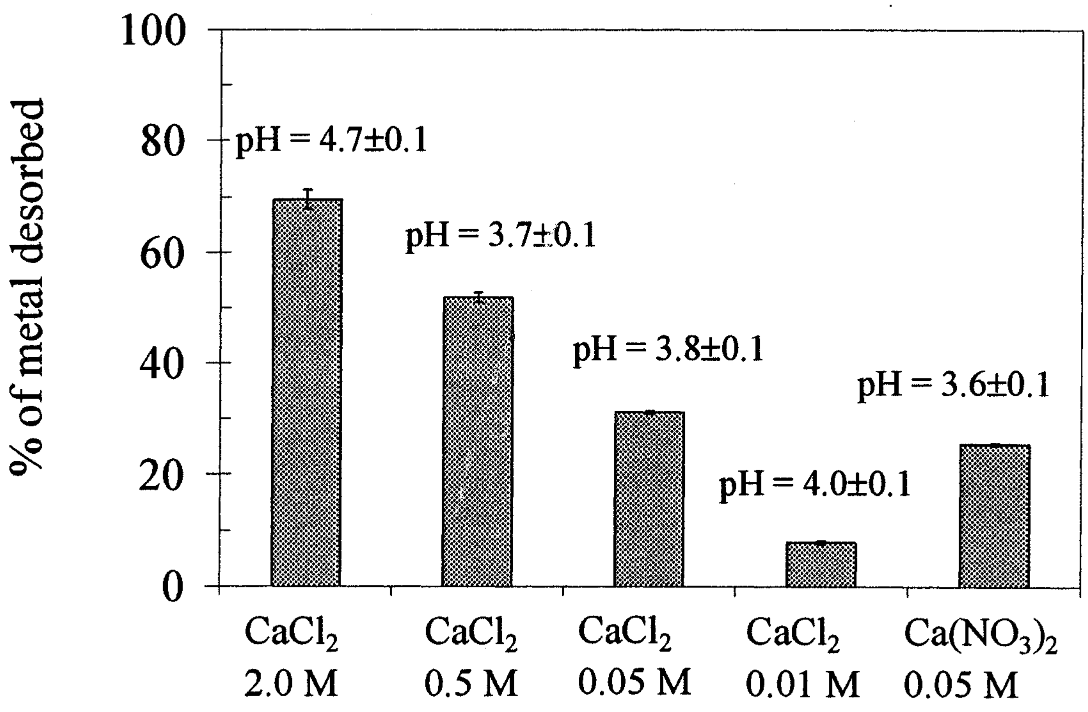

Figure 5.5: Single-element system desorption of La using different concentrations of calcium nitrate and chloride solutions.

nitrates (Davis et al., 2000). 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 anguistissima.* Other elutants at different concentrations were tested such as 10mmol.L^{-1} EDTA, 2mmol.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 (Ahuja et al., 1999). 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 minutes which in many cases was not enough to allow equilibrium to be attained.

5.4.5 Effect of liquid to solid ratio on metal desorption.

The objective of this study was to verify the effect of using larger volumes of 0.1 N HNO_3 on the amount of metal desorbed from the biomass. Figure 5.6 shows that the percentage of metal 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.

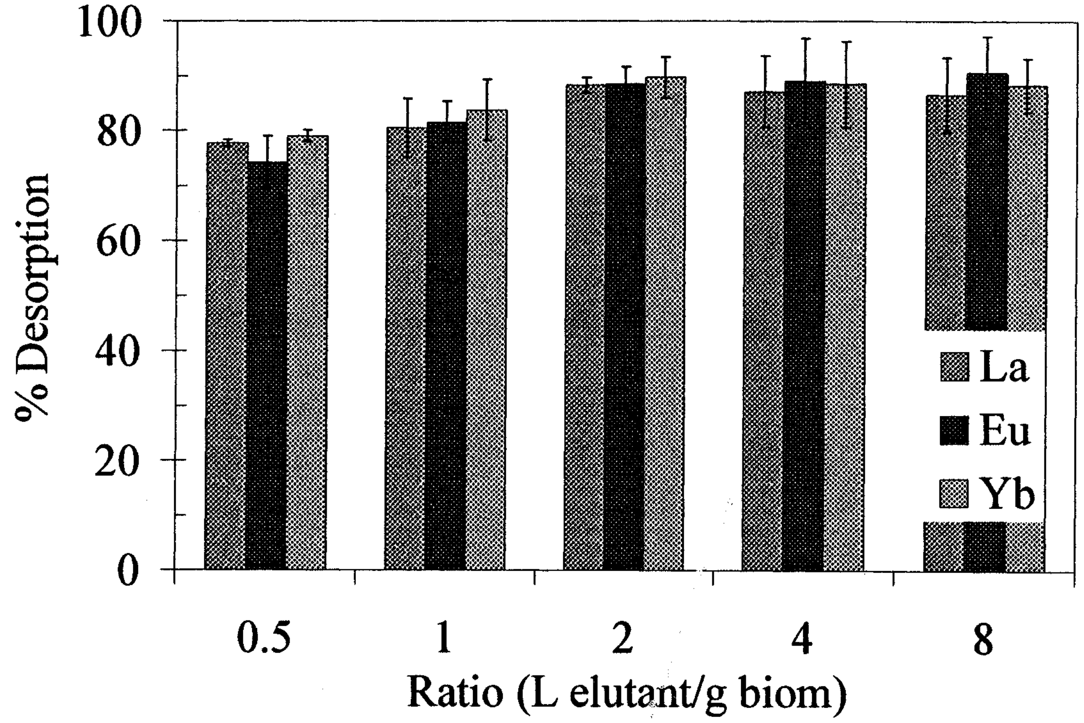

Figure 5.6: Effect of liquid to solid ratio on the percentage of desorption for La, Eu and Yb in each respective single-element system.

5.4.6 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}. Figure 5.7 shows the results obtained for desorption of the multi-component system containing all three lanthanides at different metal sorption levels. Table 5.2 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 5.3 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 (Diniz and Volesky, 2004).

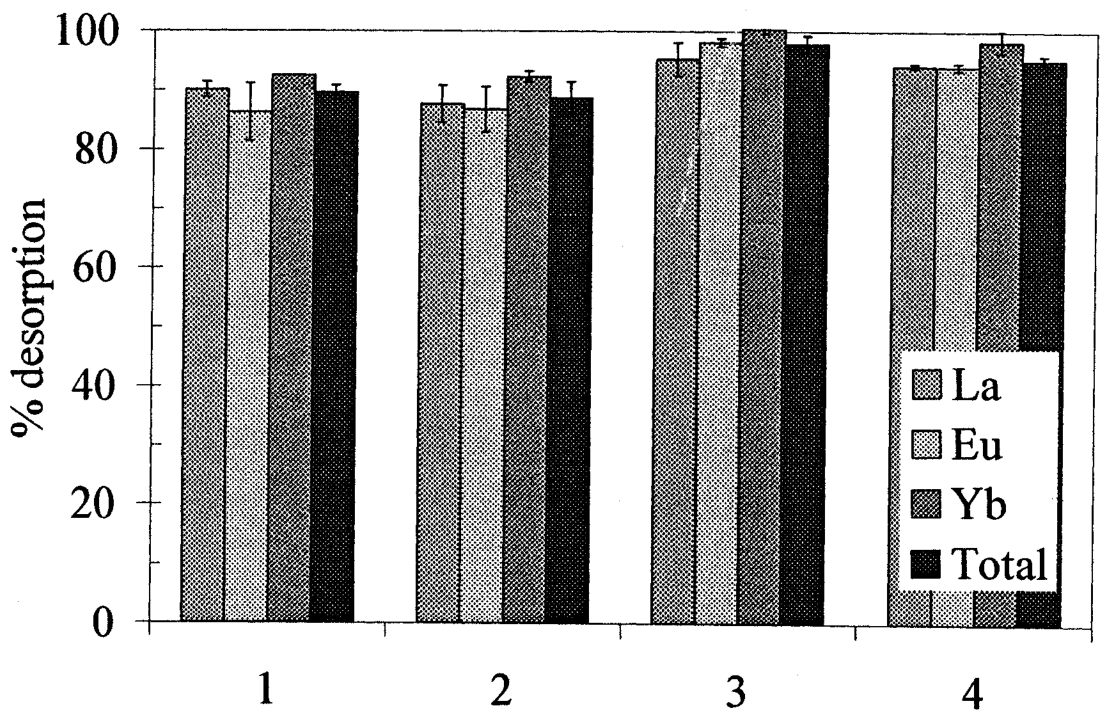

Figure 5.7: Desorption of La, Eu and Yb from biomass loaded with all three elements.

Table 5.2: Metal sorption loadings for mixed metal desorption (Figure 5.7)

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 5.3: Desorption of individual and mixed systems 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

5.5 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 meq.g^{-1} at pH 2 and 2.8 meq.g^{-1} while using 0.1 mol.L^{-1} HNO_3.

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 to 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} HNO_3, which had resulted in 80 to 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.

5.6 Acknowledgements

The international CAPES (Brazil) Scholarship to V. Diniz enabled this work.

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CHAPTER 6

Foreword

The previous chapters gave indications that biosorption of lanthanides appeared very encouraging and quite independent of the counterion types present in solution. It was also shown that biosorption was somewhat selective for the given lanthanides. It appears that biosorption is based on a reversible ion exchange reaction, enabling effective desorption accompanied by biomass regeneration. In the next natural step toward technology and process development, a reactor should be chosen in which the sorption and desorption reaction would most effectively take place. Among the existing reactor types, fixed-bed columns represent the most common device applied in adsorption and ion exchange processes. With the industrial application in mind, experimental and modeling studies are essentially important to assess process feasibility and to optimize its design. An ion exchange process will always have at least two elements involved and any single metal system represents actually a binary one with the hydrogen ion also present when the biomass is protonated. Earlier results showed that HCl could be used for effective metal desorption and regeneration of the biomass that became uniformly protonated. Hence protonated biomass was used for packing the column for continuous-flow sorption studies. The main objective of the final stage of the work, reported on in this article, was to examine the fixed-bed column biosorption of lanthanum (La) and europium (Eu). As any reasonable interpretation of these types of results requires modeling of the system performance, this type of more theoretical work is also incorporated in this section with the aim of predicting the breakthrough curves for process applications. Binary batch equilibrium and column studies with metal and proton pairs serve to derive the model parameters required for model-prediction of the multi-component metal sorption system behavior. Initially the model is validated for a ternary mixture, i.e., two metals and protons, and eventually for a ternary mixture in longer columns. Modeling multi-component metal systems represents a challenging task due not only to the complexity of the process, but because it also requires modern, powerful and reliable computer algorithms and software.

Fixed-bed biosorption studies on lanthanum and europium by *Sargassum*

To be submitted to Separation and Purification Technology

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6.1. Abstract

Biosorption of La^{3+} (Lanthanum) and Eu^{3+} (Europium) through batch and column experiments using protonated *Sargassum polycystum* biomass was studied. The ion exchange sorption mechanism was confirmed by the release of protons and by the total normality of the solution, which remained constant during the process. Equilibrium isotherms were determined for the binary systems, La/H and Eu/H for a total normality of 3meq g^{-1}, which produced separation factors that were used into the column model, 2.7 and 4.7 respectively, demonstrating a higher affinity of the biomass towards europium. Column runs with a single metal feed were used to estimate the intra-particle mass transfer coefficient for La and Eu which were 6.0 10^{-4} min^{-1} and 3.7 10^{-4} min^{-1} respectively. The parameters obtained from the single metal runs were then used to predict the breakthrough curves obtained for lanthanum and europium resulting from an equivalent feed mixture of both elements into the column. Modeling batch and column binary systems with proton as one of the elements, was able to predict reasonably well the behavior of a ternary system containing protons. Series of consecutive sorption/desorption runs showed that the metal could be recovered and the biomass reused in multiple cycles by using 0.1 N HCl.

Key-words: lanthanides, modeling, seaweed, ion exchange, column

6.2. Introduction

Biosorption studies have utilized biomass types such as seaweeds (Davis et al. 2003), bacteria, fungi and yeasts not only due to their metal removal capacity but also to their availability in Nature or as industrial by-products (Veglio', 1997; Andrès et al., 2003). More recently, a broader selection of biomass types has been examined such as human hair (Tan et al., 1985), crab shells (Niu and Volesky, 2001a; 2001b; 2003) and chitosan-based sorbents (Guibal, 2004). Moreover, biomass immobilized in solid structures, for example, sphagnum peat moss in porous polysulfone beads, demonstrated improved mechanical strength and rigidity (Veglio' and Beolchini, 1997; Trujillo et al., 1991). The brown seaweed, *Sargassum*, has been shown to remove very effectively heavy metal cations from metal-bearing effluents and possess high mechanical and chemical stability. Biosorption studies have paid attention mainly to batch equilibrium experiments for deriving and modeling the characteristic sorption isotherms. With ion exchange being the main mechanism involved in the biosorption process, most of the isotherms have been derived under constant pH and the Langmuir and Freundlich equations have been used to describe single metal sorption systems; multicomponent Langmuir then for multimetal systems. However, none of these two models reflects the ion exchange mechanism involved. Moreover, as ions are exchanged during the biosorption process, the total normality of the solution, in terms of the number of equivalents, remains constant. When this concept is respected, the isotherms should be derived under constant total normality in the sorption system. The pH would not need to be adjusted and could vary along the isotherm curve. For the dynamic biosorption column system used in practice, the pH can not be effectively controlled inside the column and it will just vary along, reflecting the ion exchange and speciation of the ions present in the solution. The constant-normality type of isotherm would better reflect the actual situation inside a biosorption column. The isotherm should be derived based on the same total normality of the solution that feeds the column.

An isotherm derived at a constant pH is based on an increasing total normality as the metal is exchanged. While in most cases the isotherms are derived under a constant pH, ion exchange isotherms should be determined under a constant total normality in order to maintain the electroneutrality of the solution.

More recently, fixed bed studies and respective modeling using different types of biomass and metal systems have been given a considerable attention (da Silva et al., 2002; Figueira et al., 2000; Kratochvil and Volesky, 2000; Kratochvil et al., 1997; Trujillo et al., 1991). Empirical and mechanistic models have been used to describe the breakthrough curves obtained mainly for single metal systems. Only a few multi-metal systems were also examined. Modeling multi-component metal systems in a predictive and reliable way represents an important challenge and different approaches have been used. While some column modeling neglected axial dispersion and assumeed nonequilibrium conditions (Tan and Spinner, 1994; Trujillo et al., 1991), other attempts considered local equilibrium and also neglected axial dispersion (Helfferich, 1967; Klein et al., 1967). Usually, multi-component data provide the basis for multi-component system modeling. However, every time a new element is introduced, the whole system should be studied again.

Fixed bed studies constitute the most preferable approach among researchers and attempts have been made to model the breakthrough curves. During column runs, the pH is not controlled. The ions are exchanged and the total normality of the solution remains constant. For a system involving protons, the pH will likely change because protons are being removed or released to the solution. The equilibrium batch system should be able to represent such a system whereby the total normality of the solution is kept constant. Therefore, equilibrium isotherms were built with a constant normality by varying the final equivalent fractions of the elements present in both liquid and solid phase. This equilibrium isotherm model can then be used for predicting the behavior of a breakthrough curve with the column being fed at the same total normality.

Ion exchange reactions for most engineering applications, resemble those of adsorption so closely that ion exchange can be considered to be a special case of adsorption, and for that matter operation techniques used for adsorption are also used for ion exchange. These include fluidized- and fixed-bed, continuous countercurrent and stagewise operations. Among them the fixed-bed percolation system were the most common. Early applications of ion exchangers were limited to water-softening problems. In 1935, synthetic ones were introduced such as insoluble polymeric resins containing sulfonic, carboxylic, or phenolic groups, for which different cations would have a different affinity (Treybal, 1987).

The rate of ion exchange depends on the following processes: (a) diffusion of ions from the bulk of the liquid to the external surface of the exchanger particle or sorbent in this case, (b) intra-particle diffusion of ions through the solid to the binding sites, (c) exchange of the ions, (d) diffusion of the released ions to the surface of the solid, and (e) diffusion of the released ions from the surface to the bulk (Treybal, 1987). In the biosorption process using *Sargassum sp.* as a sorbent, intra-particle mass transfer resistance appears to be dominant (Kratochvil et al., 1997).

The high prices for most of these Rare Earth 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 focused on the modeling of the breakthrough curves obtained from the binary pairs with protons being the common element. Moreover, the behavior of the ternary system based on the parameters estimated from the binary pairs could be predicted reasonably well. In addition, the impact of consecutive sorption/desorption cycles was also studied.

6.3. Materials and methods

6.3.1. Biomass preparation

6.3.1.1. Batch equilibrium experiments

The biosorbent used was the brown seaweed, *Sargassum polycystum*, collected at the Philippines. The sun-dried material was washed with tap water, distilled water and distilled deionized 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 0.5mm were selected. The biomass was subsequently protonated with 0.1 N HCl (biomass concentration of 10 g.L^{-1}) for 4 hours under gentle agitation. Later, the biomass was washed with distilled de-ionized water to remove excess H ions until the mixture reached approximately pH 5. Finally, the biomass was again dried overnight at (50-55) °C. Part of the protonated biomass was used for metal loading and both proton and metal loaded biomass were used in the experiments to obtain data points throughout the whole concentration range. 2g of protonated biomass was put into contact with 1 L of a solution containing 4 meq L^{-1} of either La or Eu for 24 hours and gentle agitation.

6.3.1.2. Column runs

For column experiments, the biomass was not ground and it was washed with tap water and distilled water. After drying overnight (at max. temperature of 55°C), 30 g of biomass was subsequently protonated in 3 L of 0.1 N HCl (biomass concentration of 10 g.L^{-1}) for 4 hours under gentle agitation. Later, the biomass was washed with distilled de-ionized water to remove excess H ions and was again dried overnight (55°C). The column packing density of 123 g L^{-1} corresponded to 15.1 g of dry protonated biomass for the 25 cm bed depth (30.2 g for the 50 cm). . Distilled water was used in column experiments for both biomass and solution preparation.

6.3.2. Batch equilibrium experiments - Binary pairs (La/H, Eu/H)

Batch sorption tests were performed at constant total normality to build the equilibrium isotherms for both elements La and Eu present in a binary pair containing hydrogen ions. Samples of 0.025 g of prepared biomass (as above) were contacted with 0.05 L of solution of known total normality of 3 meq L^{-1} with equivalent fractions of both metal and protons ranging from values close to zero to values close to 1, whereby the sum of the equivalent fractions was equal to one. The sorption suspension samples (in duplicates) were contacted for 24 hours on a rotatory shaker at 150 rpm, filtered in 0.2 μm membrane and analyzed for residual metal content by using an ICP atomic emission spectrometer (ICP-AES, Thermo Jarrell Ash, Model Trace Scan). The pH was not adjusted in order to keep constant the total normality throughout the experiment.

Solutions containing the metals were individually prepared using distilled de-ionized water and nitrate salts: $La(NO_3)_3.6H_2O$, $Eu(NO_3)_3.6H_2O$ (all Alfa Aesar supplied).

6.3.3. Column runs

After weighing the biomass, the column was packed by wetting the biomass and breaking it into pieces of approximately 2 cm and inserted into the column one at a time.

The bed void fraction was determined by packing the column with different packing densities and measuring the liquid volume obtained after discharging and allowing some air to run through the column to be able to remove all possible water. This value was compared to the one obtained by emptying a bed full of liquid when no biomass was present in order to account for the volume present in the transfer tubes. Measurements were done in triplicate.

The column internal diameter was 2.5 cm and the length was 25 cm. The volumetric flow-rate was 15 mL min^{-1}, which corresponds to a superficial velocity of 3 cm min^{-1} and an interstitial velocity of 5.2 cm min^{-1}. No increase in pressure was observed during the experiments.

6.4. Model Equations

6.4.1. Equilibrium batch

The biosorption mechanism involving *Sargassum* has been proved to be an ion exchange reaction type between cations already binded to the biomass and the ones present in the aqueous phase (Diniz and Volesky, 2005; Yang, 2000; Yang and Volesky, 1999). In the case where the hydrogen ions are initially attached to the sorbent binding sites which are the monovalent carboxylate functional groups, and the lanthanides are present in solution, the reaction can be represented as follows :

$$La^{3+} + 3HB \leftrightarrow LaB_3 + 3H^+ \quad (9)$$

The total number of equivalents of ions released by the biosorbent is equal to the number of equivalents of ions removed from solution (Diniz and Volesky, 2005). Therefore, the total normality, which represents the sum of the concentrations in meq L^{-1} of all competing cations which can be exchanged during the reaction, remains the same when equilibrium is achieved. Considering a system containing one metal and protons, the total normality is expressed by:

$$C^{\circ} = C_M + C_H \tag{10}$$

Where C°, C_M and C_H are all expressed in meq L^{-1}.

The metal concentration in meq L^{-1} can be obtained by dividing the concentration in mg L^{-1} by its molecular weight and multiplying by the ion valence. In addition, if ions are exchanged during the process, the exchangeable binding sites are always occupied by the competing ions, thus the total number of exchangeable binding sites is the sum of the concentrations in the solid phase of the elements involved and can be represented as follows:

$$q_M + q_H = Q \tag{11}$$

Where q_M, q_H and Q are expressed in meq g^{-1}.

The equivalent fraction of one component in the liquid phase is the ratio between its own concentration and the total normality of the solution, whereas the equivalent fraction in the solid is its concentration in the solid divided by the number of exchangeable binding sites (Klein et al., 1967).

$$x_i = \frac{C_i}{C^o} \tag{12}$$

$$y_i = \frac{q_i}{Q} \tag{13}$$

C° represents the total normality of the solution and Q the total number of exchangeable binding sites, hence the sum of the equivalent fractions on both liquid and solid phases is approximately equal to one, expressed as follows (Klein et al., 1967; Tondeur and Klein, 1967):

$$x_M + x_H = 1 \tag{14}$$

$$y_M + x_H = 1 \tag{15}$$

For a binary system, the separation factor represents in this case the relative selectivity of the metal to the hydrogen ion and is defined by:

$$\alpha_H^M = \frac{y_M x_H}{x_M y_H} \tag{16}$$

This expression is similar to those used by other authors (Tan and Spinner, 1994; Treybal, 1987; Klein et al., 1967, Tondeur and Klein, 1967) to describe the multi-component ion exchange equilibrium relationship. In general, the separation factor at a certain temperature varies with total normality in solution, C°, and also with the metal concentration, C. However, in some cases, α has shown to be essentially constant at fixed C° with varying C (Treybal, 1987). The equivalent hydrogen fraction can be expressed by subtracting the metal fraction from one. Rearranging the above equation by eliminating the hydrogen equivalent fraction, the following expression is obtained:

$$y_M = \frac{\alpha_H^M x_M}{1 + (\alpha_H^M - 1)x_M} \tag{17}$$

For a ternary mixture containing two metals such as La and Eu, and protons whereby the last are the common ions in both binary mixtures, the ion exchange reactions are represented by Eq. 8 and 19:

$$Eu^{3+} + 3HB \leftrightarrow EuB_3 + 3H^+ \tag{19}$$

The separation factors can be expressed exactly the same way as the binary pair (Tan and Spinner, 1994).

$$\alpha_H^{M1} = \frac{y_{M1} x_H}{x_{M1} y_H} \tag{20}$$

$$\alpha_H^{M2} = \frac{y_{M2} x_H}{x_{M2} y_H} \tag{21}$$

Being proton a common ion in both parallel reactions, both equations (20) and (21) are interrelated and the hydrogen ion equivalent fraction can once again be eliminated resulting in the following expression:

$$x_{M_1} + x_{M_2} + x_H = 1 \tag{22}$$

$$y_{M_1} + y_{M_2} + y_H = 1 \tag{23}$$

One expression containing both metal fractions can be obtained by eliminating the proton equivalent fractions and combining equations (22) and (23). The proton equivalent fraction which is the same in both equations can be eliminated to obtain one expression relating both metals present in solution:

$$y_{M_1} = \frac{\alpha_H^{M_1} x_{M_1}}{1+(\alpha_H^{M_1}-1)x_{M_1}+(\alpha_H^{M_2}-1)x_{M_2}} \tag{24}$$

$$y_{M_2} = \frac{\alpha_H^{M_2} x_{M_2}}{1+(\alpha_H^{M_1}-1)x_{M_1}+(\alpha_H^{M_2}-1)x_{M_2}} \tag{25}$$

By combining equations (20) and (21), the selectivity of one metal over the other is obtained by the ratio of both metal separation factors as described next:

$$\frac{x_H}{y_H} = \alpha_H^{M_1}\frac{x_{M_1}}{y_{M_1}} = \alpha_H^{M_2}\frac{x_{M_2}}{y_{M_2}} \tag{26}$$

$$\alpha_{M_2}^{M_1} = \frac{\alpha_H^{M_1}}{\alpha_H^{M_2}} = \frac{y_{M_1}x_{M_2}}{x_{M_1}y_{M_2}} \tag{27}$$

6.4.2. Column model

Doing the mass balance in the liquid and solid phases neglecting the axial dispersion and assuming solid phase rate controlling gives respectively the following equations:

$$\frac{\partial x_M}{\partial \tau} = -\frac{\partial x_M}{\partial \xi} - \frac{\rho_b Q}{\varepsilon_b C^0}\frac{\partial y_M}{\partial \tau} \tag{28}$$

$$\frac{\partial y_M}{\partial \tau} = \frac{k_{s_M} L}{u/\varepsilon_b}(y_M^* - y_M) \tag{29}$$

With boundary conditions:

$$x_M = 1 \tag{30}$$

$$\xi = 0 \tag{31}$$

Initial conditions at $\tau = 0$:

$$x_M = 0 \tag{32}$$

$$y_M = 0 \tag{33}$$

And dimensionless variables:

$$x_i = \frac{C_i}{C^{\circ}} \tag{34}$$

$$y_i = \frac{q_i}{Q} \tag{35}$$

$$\tau = \frac{t}{L/(u/\varepsilon_b)} \tag{36}$$

$$\xi = \frac{z}{L} \tag{37}$$

Being k_{s_i}, the mass transfer coefficient in the solid, and y_M^*, the batch equilibrium relation from the binary or ternary system. In the case of a ternary system, the four mass balances in the solid and liquid phases for both metals should be solved simultaneously using the ternary equilibrium isotherm. The equations were solved using FEMLAB (Comsol) software, which uses the finite elements method.

6.5. Results and discussion

6.5.1. Batch equilibrium

The results obtained for the binary metal/proton equilibrium isotherms for a total normality of 3meq L^{-1} are depicted in Figure 6.1. The equivalent fractions in both solid and liquid phases are on axes y and x, respectively. It can be seen that europium demonstrated a slightly higher affinity compared to the lanthanum one with respect to the hydrogen ion. The separation factors obtained between metal and protons were 2.7 and 4.7 for lanthanum and europium respectively. The separation factor relating europium to lanthanum determined by the ratio of the metal/proton binaries observed was 1.7 which is lower than the ones relating to the proton. Both isotherms could be reasonably well represented by a constant separation factor throughout the entire range studied for a fixed total normality of 3 meq L^{-1}, although the fitting for lanthanum was not as good as compared to europium. In agreement with Tondeur and Klein (1967), ion exchange equilibria, involving the same or different valence ions, could often be characterized by constant separation factors. The estimated number of exchangeable binding sites represents 70% of the maximum lanthanum and europium removal from non-protonated biomass (reported in earlier work by Diniz and Volesky, 2005). This represented a metal uptake reduction of 30%. However, the preceding biomass protonation resulted in biomass weight losses around 27% (Diniz and Volesky, 2006) and this could very well be responsible for the reduction in the number of binding sites observed in this work.

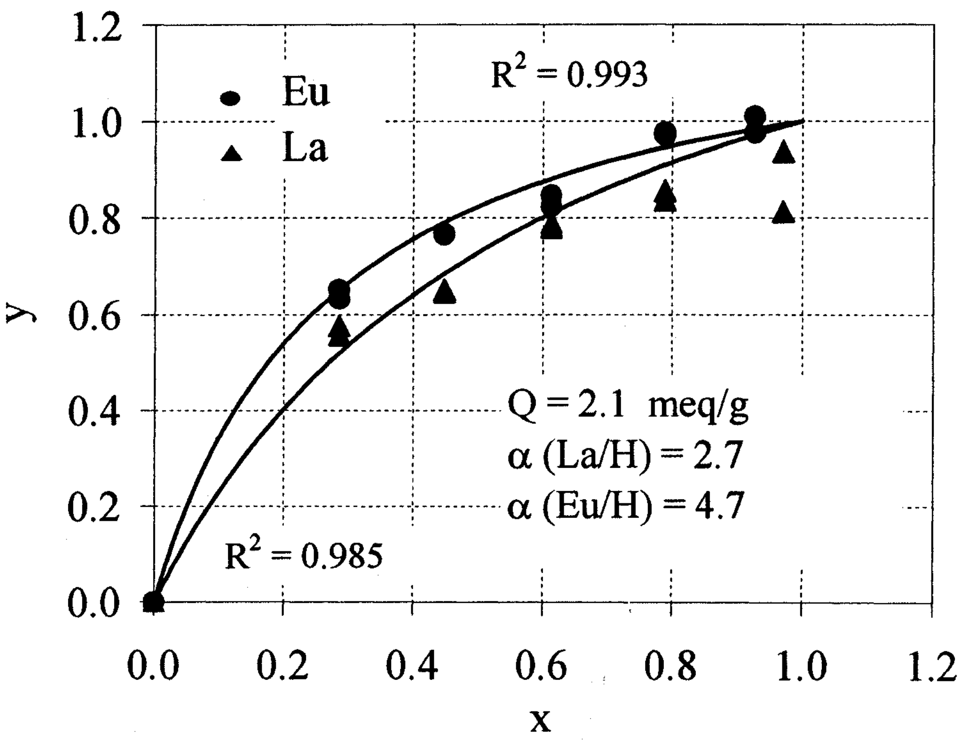

Figure 6.1: Ion exchange equilibrium isotherms for La and Eu at constant total normality of 3 meq L^{-1}.

6.5.2. Void fraction

Figure 6.2 shows that a linear relationship was obtained between bed void fraction and packing density with a R^2 of 0.998. The point of zero packing density and void fraction of 1 was also used for regression. The resulting equation is as follows:

$$\varepsilon_b = -0.0036\rho_b + 1.0032 \qquad (38)$$

The packing density used in the column runs was 123 g L^{-1} and the corresponding void fraction was 0.56.

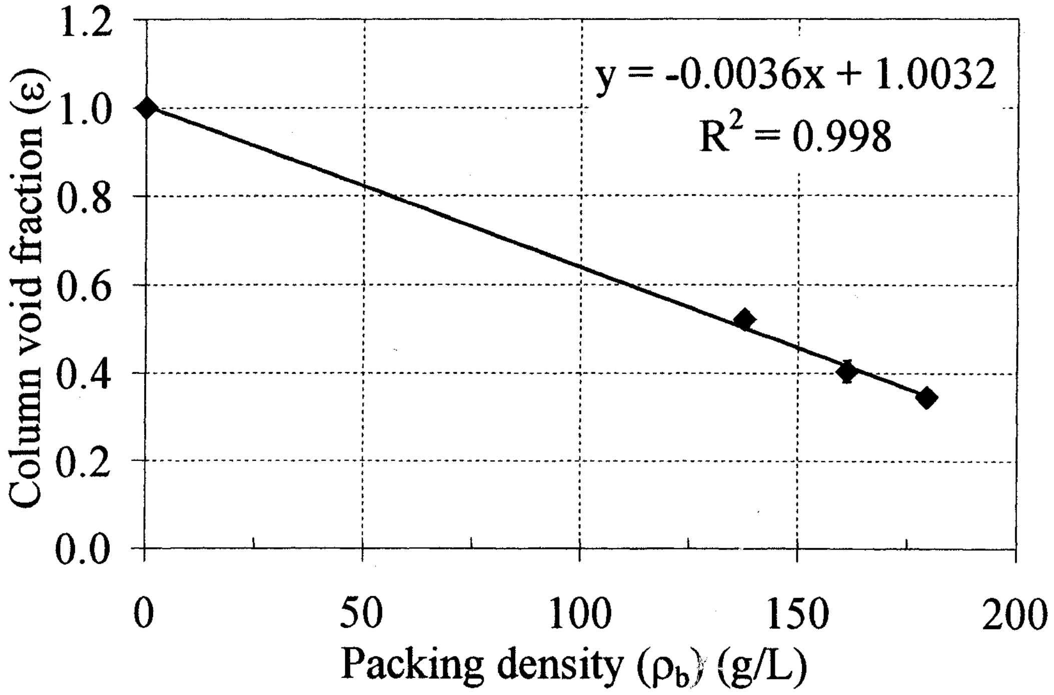

Figure 6.2: Bed void fraction as a function of the bed packing density.

6.5.3. Column binary (metal/proton)

Figures 6.3 and 6.4 show the breakthrough curves obtained for each metal. The binaries studied in this case were the metal/proton system. Protonated biomass was used to pack the column and the metal solution was prepared with no adjustment of pH which was close to the distilled water pH. Therefore, it could be inferred that the concentration of protons was much lower than the metal concentration and could be neglected. The feed solution to the column was considered as pure metal with no protons. Although both curves demonstrated similar breakpoints, the lanthanum uptake was underestimated by the model in the later tailing zone. The axes are expressed in dimensionless forms as the total number of liquid bed volumes and equivalent fractions of the metals in the liquid phase, respectively. The hydrogen equivalent fraction is also shown in the graphs and showed a reasonable agreement between the measured pH values and the ones obtained from the model. The model assumed intra-particle resistance as the rate controlling step and neglected axial dispersion. The mass transfer coefficients obtained were 0.0006 and 0.00037 min^{-1} for lanthanum and europium respectively. The value was higher for lanthanum, MW 138.9, maybe due to a lower molecular weight compared to europium, MW 152.

6.5.4. Column ternary (including validation)

The ternary system was obtained by feeding the column with an equivalent mixture of both lanthanum and europium at natural pH around 6, i.e., without any pH adjustment. As the concentration of hydrogen ions is much lower than the metals concentration, it could be considered as a feed containing only metals neglecting the presence of protons in the solution. The breakthrough curve obtained is depicted in Figure 6.5. It can be observed that europium has a higher affinity than lanthanum, confirming by this way the affinity sequence observed from batch equilibrium experiments.

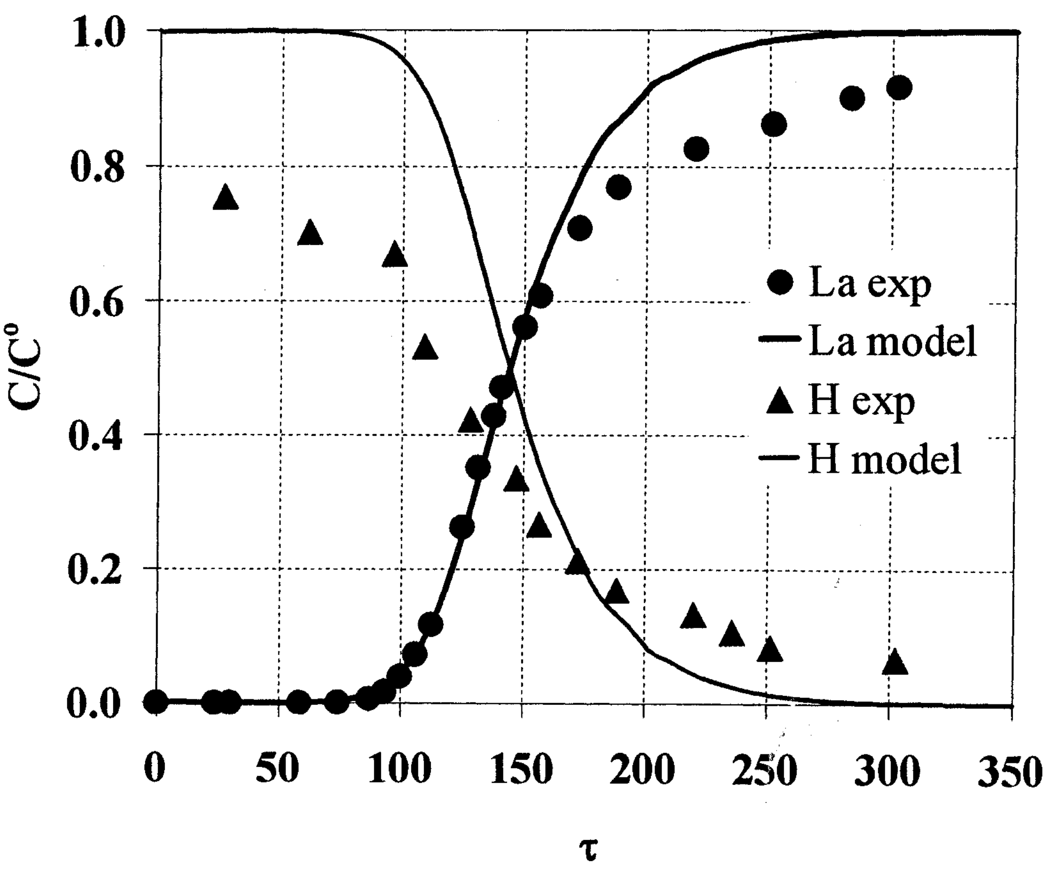

Figure 6.3: Lanthanum and proton column dynamics packed with protonated biomass. Total normality, C°: 3 meq L^{-1}. Feed flow-rate: 15 mL min^{-1}, packing density: 123 g L^{-1}, column length: 25 cm.

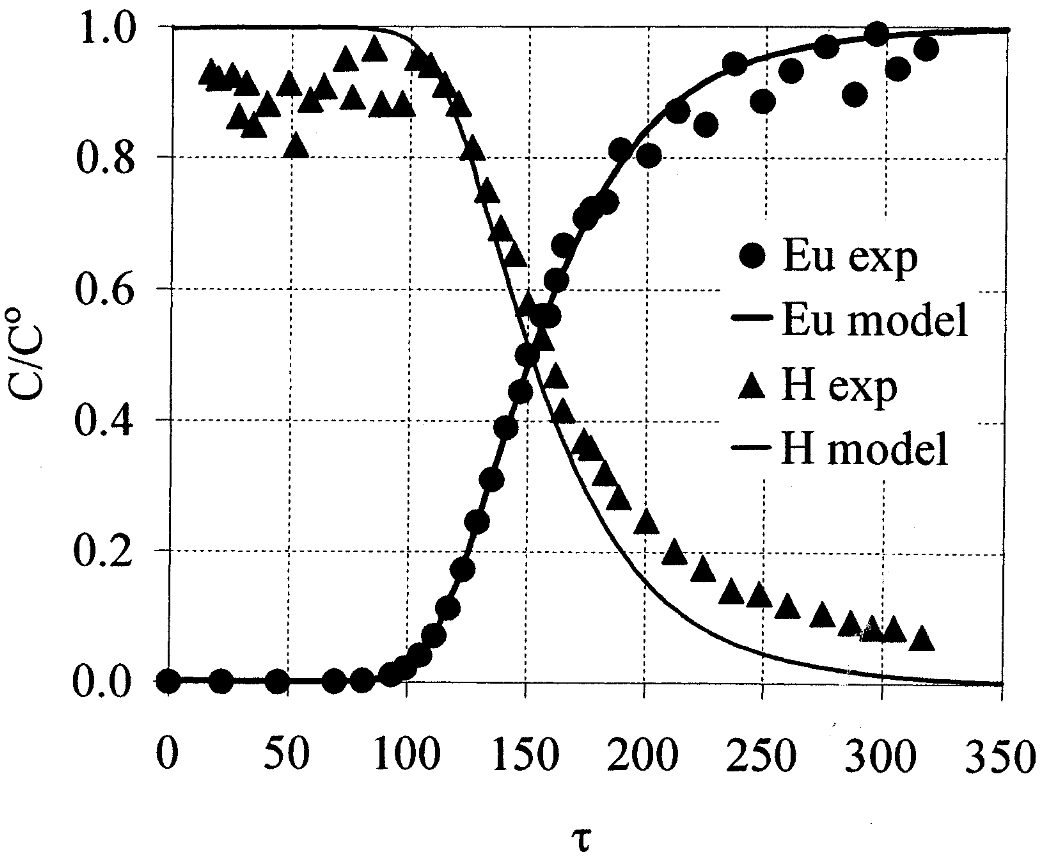

Figure 6.4: Europium and proton column dynamics packed with protonated biomass. Total normality, C°: 3 meq L^{-1}. Feed flow-rate: 15 mL min^{-1}, packing density: 123 g L^{-1}, column length: 25 cm.

It is also observed that lanthanum shows a steeper curve while europium shows a flatter pattern, indicating a lower mass transfer coefficient.

The curves were obtained both experimentally and theoretically for the same column length and operational conditions. The behavior of the ternary system could be predicted reasonably well by solving all four coupled equations with parameters estimated by modeling the binary pair M/H data from both batch equilibrium and column dynamics experiments. It shows that ternary metal-sorption modeling using binary pairs with protons as the common ion is capable of predicting the sorption system behavior. . In this work, protonated biomass was used to pack the column and protons were one of the ion types present in the sorption system confirmed also by measuring the pH of the solution samples taken. The proton equivalent fraction could be calculated by subtracting the experimental metal equivalent fractions from unity, which agreed very well with the proton equivalent fraction calculated from pH measurements. This emphasizes the ion exchange nature of the mechanism involved in the *Sargassum* biosorption process.

The approach used in this work simplifies the way multi-component systems are modeled. A database with batch equilibrium constants for the binary pairs, which include hydrogen ions as the common ion, could be used to predict the behavior of multi-component systems when the hydrogen ion is present. The main advantage of this procedure is that only the binary pair metal/proton should be studied and there would be no need to study the whole multicomponent system again and again every time a new element is introduced.

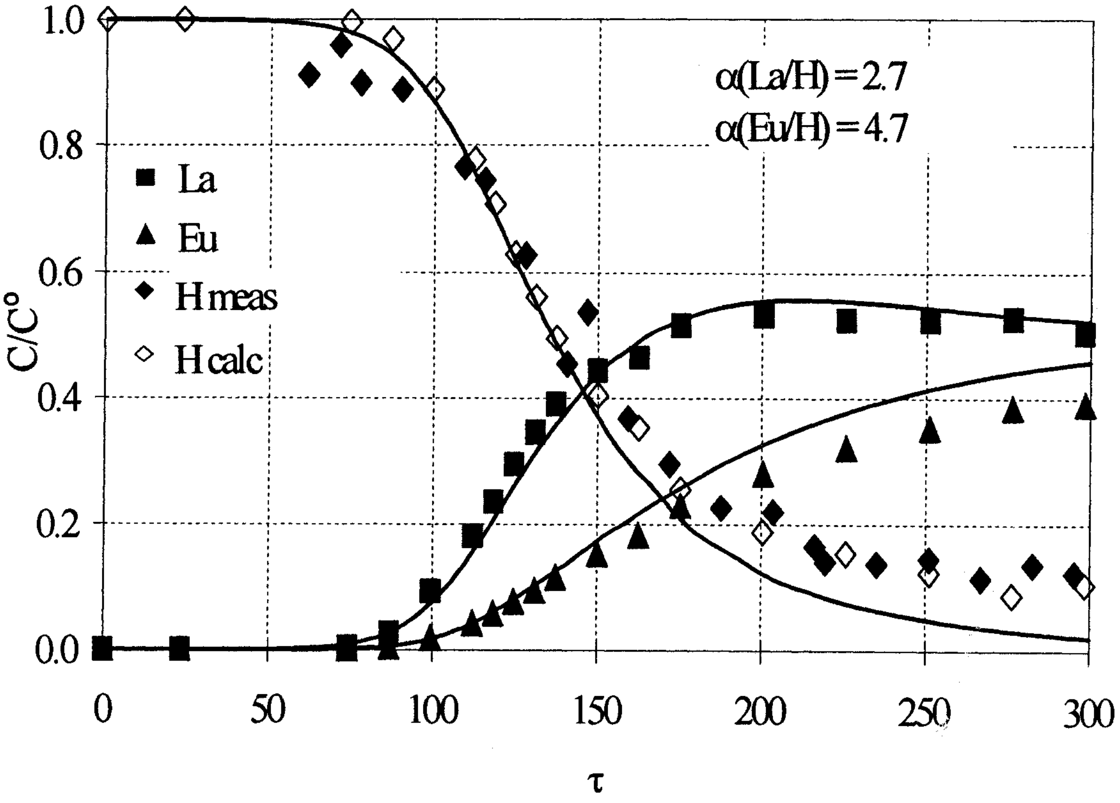

Figure 6.5: Lanthanum, Europium and proton column dynamics packed with protonated biomass. Total normality, C°: 3 meq L^{-1}. Feed flow-rate: 15 mL min^{-1}, packing density: 123 g L^{-1}, column length: 25 cm.

The metal uptakes in the single-metal sorption column systems were 2.1±0.1 meq g^{-1} and 2.0±0.1 meq g^{-1} for La and Eu, respectively. For the two-metal system the uptakes were 0.8±0.1 and 1.4±0.1 meq g^{-1} for La and Eu, respectively. These uptakes agreed well with the estimated total number of binding sites (2.1 meq g^{-1}) obtained from the equilibrium isotherms at the same total normality.

The validation of the model for a longer column length was also performed. A column length of 50 cm was used in the experiment, which is twice as much the size used for calibration which was 25 cm. It can be observed from Figure 6.6 that the model also agreed with the experimental results. The pH measurement also agreed with the model prediction, thus confirming the ion exchange mechanism of the biosorption process.

6.5.5. Consecutive cycles

One important evaluation of the Sargassum biomass is based on the regeneration capacity of the biosorbent after consecutive sorption/desorption operation cycles. In this work, three consecutive sorption/desorption cycles were examined. Each sorption cycle was followed by a desorption cycle. While Figure 6.7 shows the three sorption cycles, Figure 6.8 shows the three desorption cycles. It can be observed that there was no difference among the curves for both sorption and desorption cycles. It can be inferred that no loss of uptake capacity was observed when using protonated biomass for packing the column. The *Sargassum* biomass has been effectively regenerated by 0.1N HCl (Volesky et al., 2003) and in this work it was reutilized in three consecutive cycles of a continuous and recycling biosorption process. Although many more consecutive uptake/desorption cycles would be required to properly assess the reusability of the biomass, this was not feasible in this work due to time and resources limitations.

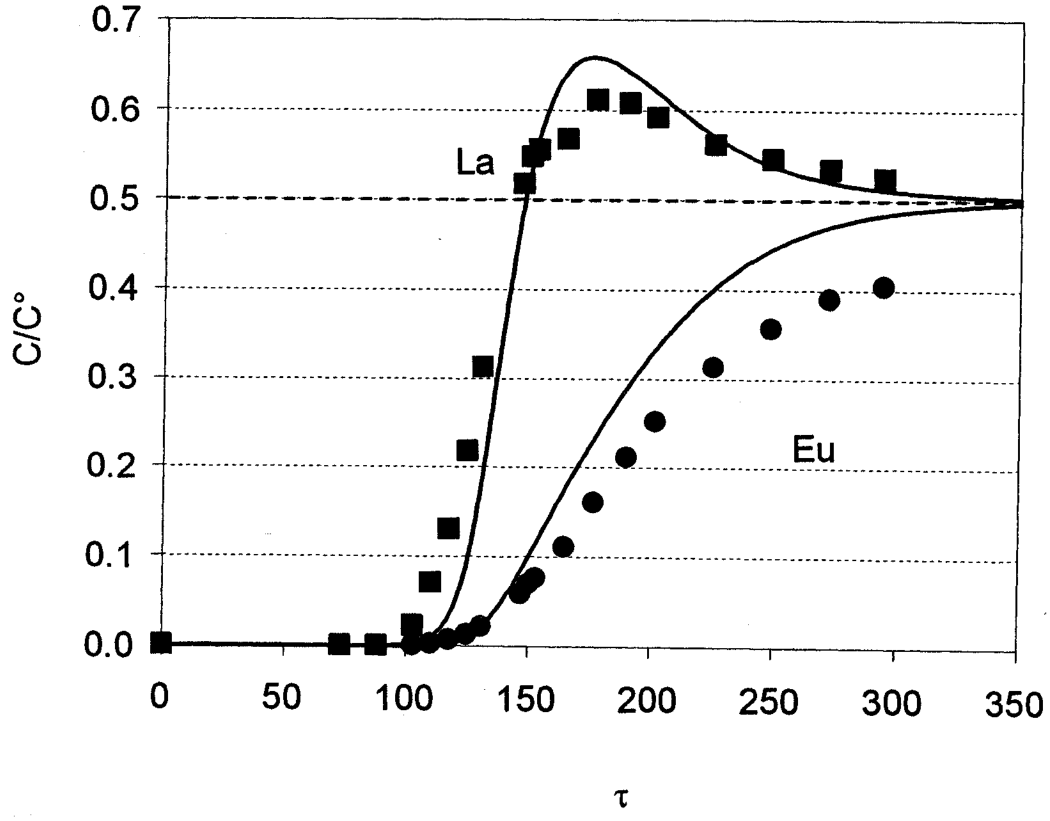

Figure 6.6: Lanthanum and Europium column dynamics packed with protonated biomass. Total normality, C°: 3 meq L^{-1}. Feed flow-rate: 15 mL min^{-1}, packing density: 123 g L^{-1}, column length: 50 cm.

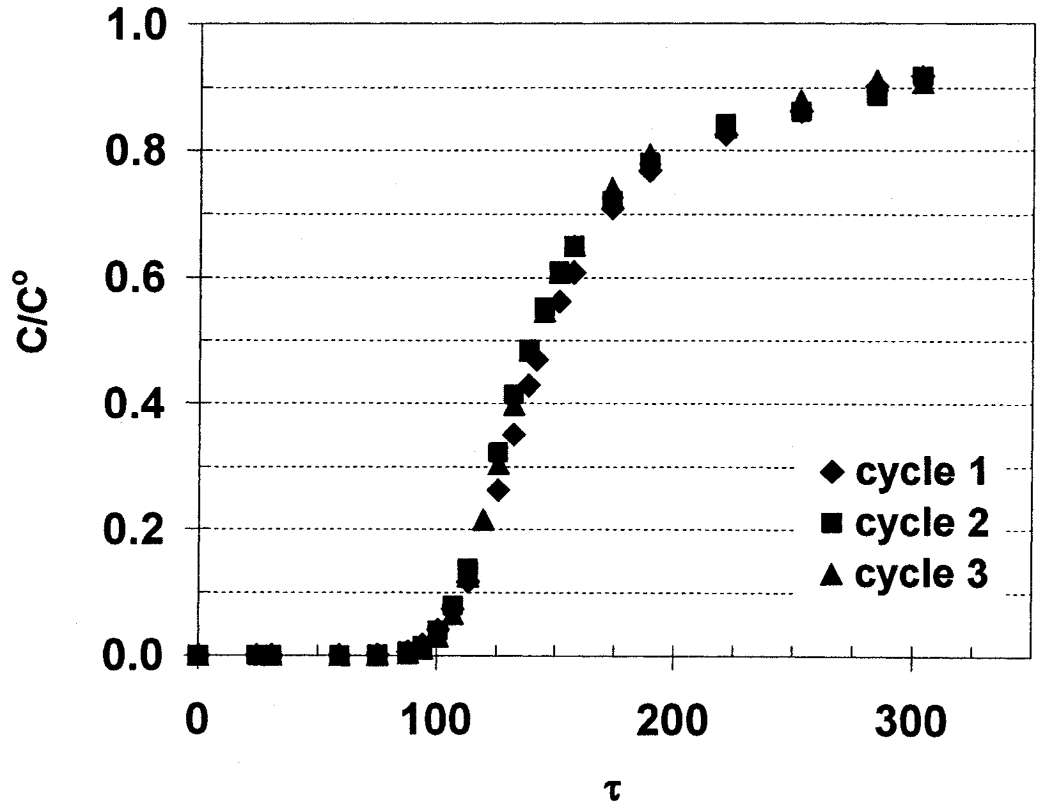

Figure 6.7: Lanthanum consecutive dynamic sorption cycles. Total normality, C°: 3 meq L^{-1}. Feed flow-rate: 15 mL min^{-1}, packing density: 123 g L^{-1}, column length: 25 cm.

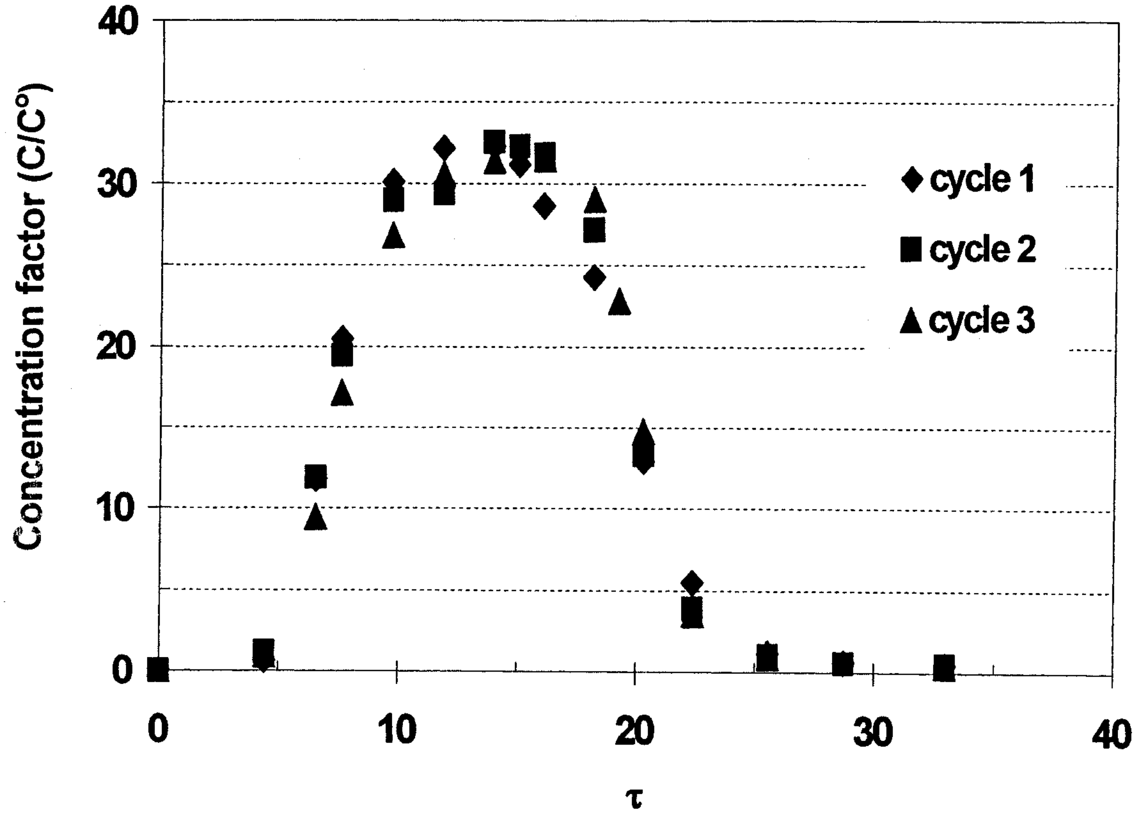

Figure 6.8: Lanthanum consecutive dynamic desorption cycles. HCl 100 meq L^{-1}. Feed flow-rate: 5 mL min^{-1}, packing density: 123 g L^{-1}, column length: 25 cm.

6.6. Conclusions

Prediction of the ternary mixture of La, Eu and H was possible by using estimated parameters based on the binary pairs La/H and Eu/H at the same total constant normality. The equilibrium binary isotherms could be modeled by a relatively constant separation factor. The binary equations could be easily developed for predicting the ternary equilibrium for the metals and proton system. Metals were removed from the feed stream while protons were released during the sorption column run. The breakthrough curves could be well approximated to a model assuming intra-particle resistance as step controlling and no axial dispersion effects. Mass transfer coefficients were estimated for the metals in the binary pair runs and were used to simulate the behavior in a ternary mixture. The separation factors obtained from the binary pairs could be used to simulate the ternary system with protons being the common ion. The model was calibrated for 25cm and could predict the behavior of the ternary mixture for a longer column of 50cm.

The *Sargassum polycystum* could be used in at least three consecutive cycles with no loss of bed metal uptake capacity. The metal was recovered and the biomass could be regenerated by 0.1N HCl.

6.7. Nomenclature

x_M	metal equivalent fraction in the liquid
y_M	metal equivalent fraction in the solid
y_M^*	metal equilibrium equivalent fraction in the solid
α_H^M	separation factor between metal and proton
Q	metal binding capacity [meq g^{-1}]
k_{s_M}	mass transfer coefficient in the solid [min^{-1}]
ξ	dimensionless bed size
z	bed axial variable [cm]
L	total bed length [cm]
C_i	element concentration [meq L^{-1}]
C°	total normality [meq L^{-1}]
x_i	element equivalent fraction in the liquid
y_i	element equivalent fraction in the solid
ε_b	bed void fraction
ρ_b	bed packing density [g L^{-1}]
τ	dimensionless time variable
t	time [min^{-1}]
u	superficial velocity [cm min^{-1}]
v	intersticial velocity [cm min^{-1}]

6.8. Acknowledgement

The international CAPES (Brazil) Scholarship to V. Diniz enabled this work.

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CHAPTER 7

CONCLUSIONS, ORIGINAL CONTRIBUTIONS, AND SUGGESTIONS FOR FUTURE RESEARCH

7.1. Conclusions

The *Sargassum polycystum* biomass tested in this work removed lanthanide ions such as La, Eu and Yb from aqueous solution immobilizing up to 0.8 to 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 to account for valence differences. The single-component isotherms for ytterbium indicated its lower affinity for the biosorbent used compared to the other two lanthanides studied. Moreover, the multi-component system also examined eventually confirmed the metal affinity sequence in the order of Eu>La>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.

The presence of sulphate counterions by using the respective metal salt reduced the lanthanum uptake due to the formation of complexes, while nitrate and chloride anions resulted in similar biosorption behavior. The metal speciation in solution provided a plausible explanation for the differences observed. The addition of sulphuric acid for pH adjustment lowered the metal uptake by increasing the amount of the less-sorbing monovalent lanthanum sulphate complex. Langmnuir model could estimate well the maximum metal uptake capacity and show the differences among the metal-biomass apparent affinities, although it does not represent the sorption mechanism.

Desorption of the metals from the biomass and consequently, the regeneration of the biosorbent was possible with mineral acids, especially HCl, among other elutants tested from batch equilibrium experiments. The desorption of La, Eu and Yb was best achieved using mineral acids such as hydrochloric and nitric acids, resulting in 95 to 100% desorption with 0.3 mol L^{-1} HCl and 77 to 90% with 0.1 mol L^{-1}. The desorption levels decreased with increasing metal sorption affinity. The metal recovery 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} HNO_3, which had resulted in 80 to 90% at a L/S ratio of 0.5 $L.g^{-1}$, and complete metal desorption from single metal batch systems was achieved with 0.2 mol L^{-1} HCl. Washing the biomass after sorption either once or twice or not at all resulted in no difference in the amount of metal recovered from the biomass.

Behavior prediction for the ternary mixture of La, Eu and H was possible by using estimated parameters based on the binary pairs La/H and Eu/H at the same total constant normality. The binary equilibrium isotherms could be modeled by a relatively constant separation factor. The binary equations could be easily developed for predicting the ternary equilibrium for the metals and proton system. Metals were removed from the feed stream while protons were released during the sorption column run where protonated *Sargassum* biomass was used. The breakthrough curves could be well approximated by the model assuming intra-particle resistance as rate controlling and no axial dispersion effect. Mass transfer coefficients were estimated for the metals in the binary pair runs and were used to simulate the behavior of a ternary mixture. The separation factors obtained from the binary pairs could be used to simulate the ternary system with protons being the common ion. The model was calibrated for 25cm of column length and could predict the behavior of the ternary mixture for a longer column of 50cm.

The *Sargassum polycystum* could be used in at least three consecutive cycles with no apparent loss of metal uptake capacity. Lanthanum was recovered and concentrated and the biomass could be regenerated by 0.1N HCl. Lanthanum desorption levels were increased in continuous flow through columns compared to batch equilibrium experiments. This is because the column is always fed with fresh elutant solution resulting thus in no metal equilibrium restriction that may occur in batch equilibrium experiments because of limited volume and high metal concentration in the solution.

The FEMLAB software presented itself as a fast and powerful user friendly software that could conveniently be used for solving the set of coupled partial differential equations for multi-component ion exchange systems.

7.2. Original contributions

The present work demonstrates the applicability of the biosorption process in the removal of lanthanides by using a natural brown seaweed type of biomass such as *Sargassum polycystum,* showing excellent metal uptake levels and selectivity.

The effect of counterions was also studied and metal speciation was considered to explain the phenomenon. In addition, it was also established that different acids used for adjusting the pH can have different effects and should be considered in biosorption systems. Speciation in the solution when using different counterions was not explained in the literature before.

Modeling the ion exchange system through constant total normality isotherms with protons as the common ion was able to reflect the behavior of the binary pairs and predict that of ternary systems as well as the behavior of longer sorption columns. This demonstration confirms that it is not necessary to study a whole multiple-component mixture system all over again if there is a database for separation factors for a certain metal and the hydrogen ion. This approach has not been applied before for a biosorption process involving heterovalent ions, especially trivalent ones. It shows that normalizing concentrations in terms of equivalents per mass unit or volume and using the liquid-vapor equilibrium approach for relative volatility can be used to describe any multi-component heterovalent system, and at the same time represent the ion exchange mechanism well while preserving the electroneutrality of the solution.

The software FEMLAB was never used before for solving the sorption column mathematical model equations and its potential and applicability to the sorption process was demonstrated in this work. This software represents a new breakthrough in computational engineering. Such a type of software allows more time to be spent on experimental work that, in turn, could be meaningfully directed by the computer process simulation results.

7.3. Suggestions for future research

- To model the equilibrium ion exchange for binary pairs with metal and protons at different total normalities which could generate an equation to predict the separation factors for other sorption column feed solution total normality concentrations.
- To increase the database for binary metal/proton separation factors to validate the methodology for a wider selection of metals for simulation of other multi-component systems.
- To verify the applicability of the equilibrium and column model for predicting quaternary mixtures and even for larger number of elements, i.e., a minimum of three metals in the sorption column feed mixture.
- To attempt separation of the respective elements through chromatographic techniques directed by effective modeling and computer simulations. This

would give a separation process a productive process application perspective rather than only considering it for an environmental application in wastewater clean-up problems. In addition, this would increase the feasibility of optimizing the sorption column for separation of the metal components through sorption and desorption processes.

- To study behavior and manipulation of component separation in columns using non-constant elution mixtures ("ramping" the eluant characteristic parameters and/or composition concentrations).
- To study biosorption behavior in non-aqueous systems or in solution systems containing varying amounts of water-miscible organic phase as there is residual heavy metal content in some organic industrial effluents.
- To attempt using biosorbents for applications other than removing and recovering heavy metal ions. New and highly selective biosorbents could be devised for immobilization, recovery and purification of economically important organic substances such as, for instance, high-value pharmaceuticals that are difficult and prohibitively expensive to recover by conventional processing sequences.

APPENDIX

APPENDIX 1: FEMLAB

This appendix has the purpose to show how the partial differential equations were expressed in the femlab program and and the system is solved. Femlab solves the system of partial differential equations using the finite elements method. The mesh refinement can be peformed by doubling the number of elements and verifying the impact on solution. A mesh of 360 elements was selected above which no difference in solution was observed. Time increments were chosen of 1 dimensionless time.

Partial differential equations in a general form can be expressed as the following:

$$d_{11}\frac{\partial u_1}{\partial t}+d_{12}\frac{\partial u_2}{\partial t}+\nabla\cdot\Gamma_1=F_1 \tag{39}$$

$$d_{21}\frac{\partial u_1}{\partial t}+d_{22}\frac{\partial u_2}{\partial t}+\nabla\cdot\Gamma_2=F_2 \tag{40}$$

Considering, for example, the following set of equations:

$$\frac{\partial C}{\partial t}+\frac{\partial C}{\partial x}-\frac{1}{Pe}+\frac{\partial^2 C}{\partial x^2}=\frac{\rho_b}{\varepsilon}\frac{\partial q}{\partial t} \tag{41}$$

$$\frac{\partial q}{\partial t}=k_m(q^*-q) \tag{42}$$

Rearranging equations (41) and (42) to match the format of equations (39) and (40) results in the following equations:

$$1.\frac{\partial C}{\partial t}+0.\frac{\partial x}{\partial t}.+\frac{\partial C}{\partial x}\left(-\frac{1}{Pe}\frac{\partial\ C}{\partial x}\right)=\frac{\rho_b}{\varepsilon}\frac{\partial q}{\partial t}-\frac{\partial C}{\partial x} \tag{43}$$

$$0.\frac{\partial C}{\partial t}+1.\frac{\partial q}{\partial t}+\nabla.0=k_m(q^*-q) \tag{44}$$

Comparing both system of equations (1) and (2) to (5) and (6), the following coefficients are obtained:

$$d_{11}=1 \tag{45}$$

$$d_{12}=0 \tag{46}$$

$$d_{21}=0 \tag{47}$$

$$d_{22}=1 \tag{48}$$

$$\frac{\partial u_1}{\partial t}=\frac{\partial C}{\partial t} \tag{49}$$

$$\frac{\partial u_2}{\partial t}=\frac{\partial q}{\partial t} \tag{50}$$

$$\Gamma_1=-\frac{1}{Pe}\frac{\partial\ C}{\partial x} \tag{51}$$

$$\Gamma_2=0 \tag{52}$$

$$F_1=\frac{\rho_b}{\varepsilon}\frac{\partial q}{\partial t}-\frac{\partial C}{\partial x} \tag{53}$$

$$F_2=k_m(q^*-q) \tag{54}$$

APPENDIX 2: Manuscript 1

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Water Research 39 (2005) 239–247

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

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Received 21 April 2004; received in revised form 1 September 2004; accepted 15 September 2004

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 (0.8–0.9) mmol g^{-1} for La (0.8–0.9) mmol g^{-1} for Eu, and (0.7–0.9) 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 Eu > La > Yb, and the maximum metal uptake obtained was 0.29, 0.41, 0.28 mmol g^{-1} for La, Eu and Yb, respectively.

Keywords: Biosorption; Ion exchange; Lanthanum; Europium; Ytterbium; *Sargassum*

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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 smal 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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doi:10.1016/j.watres.2004.09.009

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., 1995). 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} $CaNO_3$ (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 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: $LaNO_3 \cdot 6H_2O$, $EuNO_3 \cdot 6H_2O$, $YbNO_3 \cdot 6H_2O$ (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 (25–200 mmol L^{-1} 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

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

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

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

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

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

The total number of binding sites was determined by protonating the biomass with 100 mmol L^{-1} 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

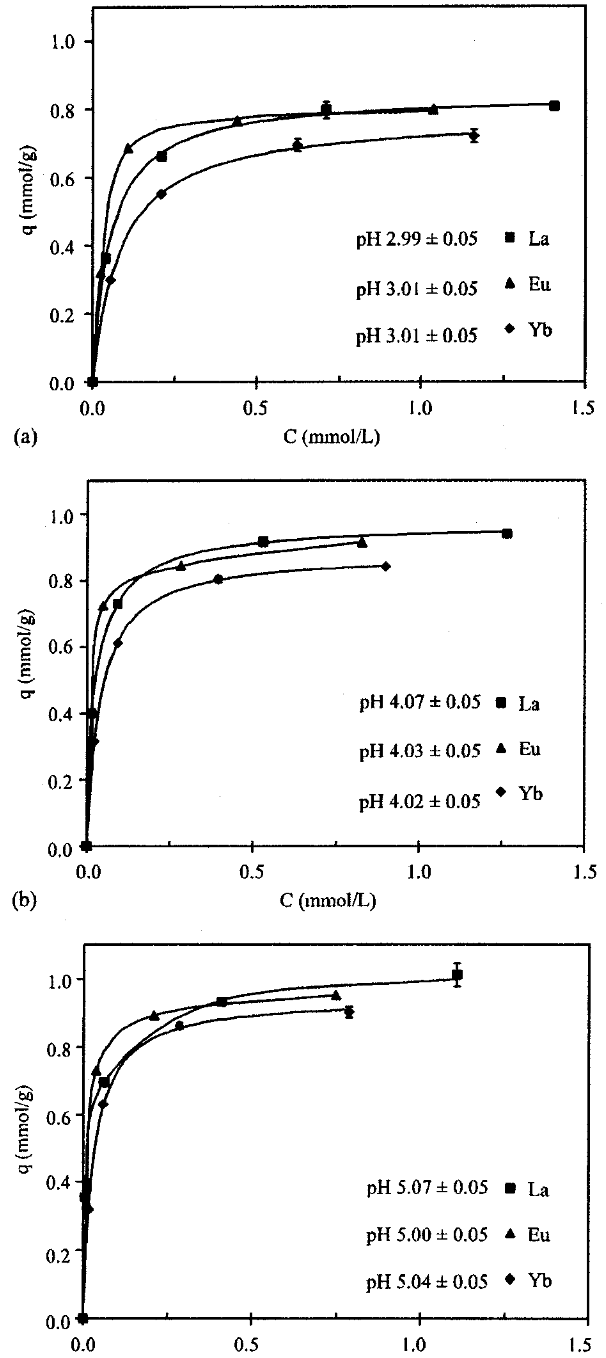

Fig. 1. Effect of La, Eu, Yb for nitrate solutions at different values of pH: (a) pH 3, (b) pH 4, (c) pH 5.

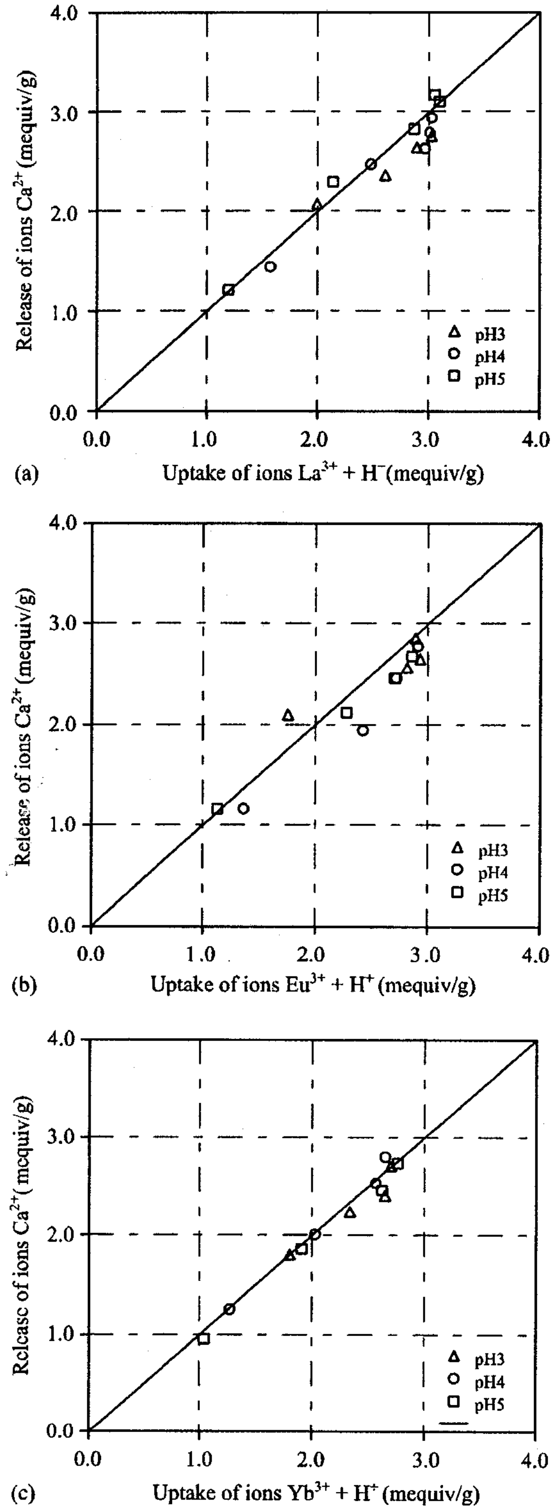

Fig. 2. Ion exchange for (a) La, (b) Eu, (c) Yb.

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.

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

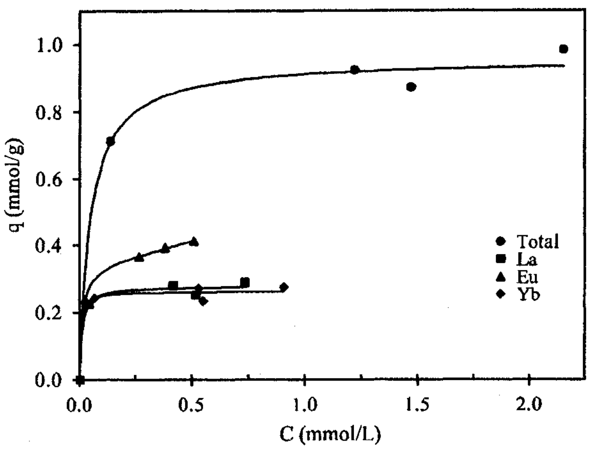

Fig. 3. Multi-component isotherms at pH 4.

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. hemiphyllum* (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 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, 6 s 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 $Ln(H_2O)_6^{3+}$ (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 $Ln(OH)^{2+}$, $Ln(OH)_3(aq)$, and $Ln(OH)^{4-}$ 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, $Ln(OH)^{2+}$ and $Ln(OH)_3$ (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 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 ± 0.11 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 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.

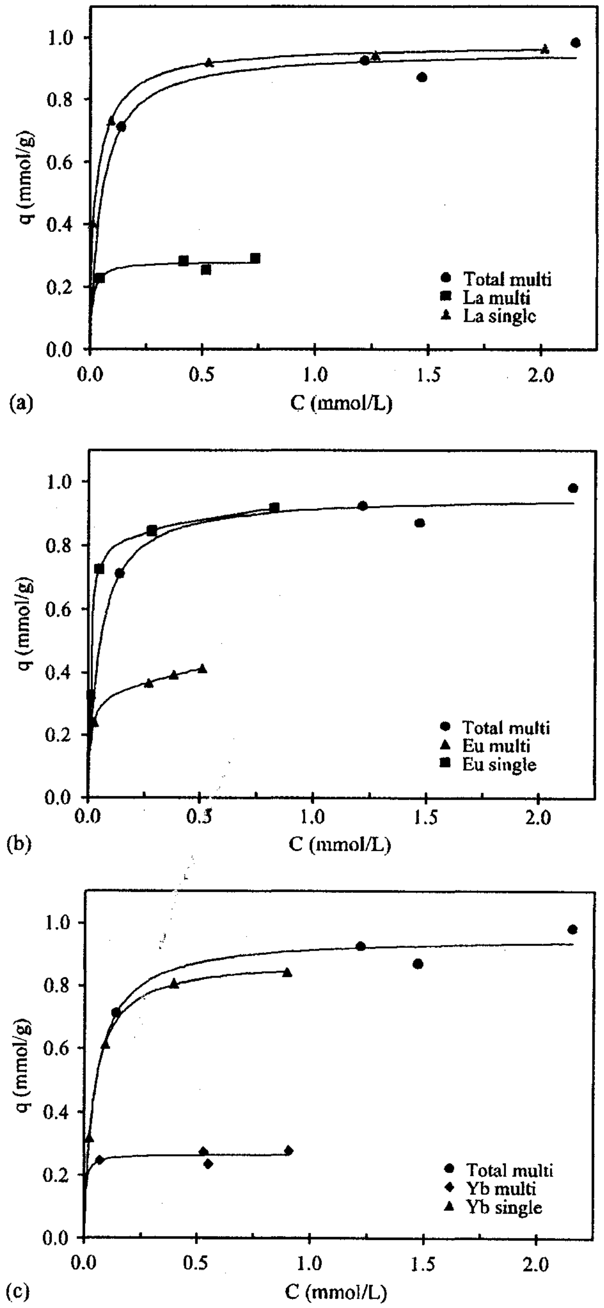

Fig. 4. Single- and multi-component individual isotherms compared to the total uptake of the different metals in the multi-component system for (a) lanthanum, (b) europium, and (c) ytterbium at pH 4.

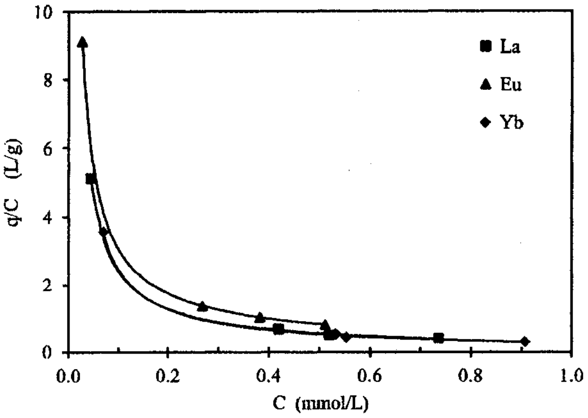

Fig. 5. q/C coefficient distribution for lanthanum, europium and ytterbium in multi-component systems.

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 $\mathrm{Eu} \geqslant \mathrm{Yb} > \mathrm{La}$ (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 $\mathrm{Eu} > \mathrm{La} > \mathrm{Yb}$. In addition, the water structure parameter could be used to explain the affinity sequence observed in the multi-component system tested in this work.

Acknowledgements

The international CAPES (Brazil) Scholarship to V. Diniz enabled this work.

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APPENDIX 3: Manuscript 2

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Effect of counterions on lanthanum biosorption by *Sargassum polycystum*

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Received 17 September 2004; received in revised form 7 March 2005
Available online 17 May 2005

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 $\mathrm{mmol\,g^{-1}}$. 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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0043-1354/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.watres.2005.04.004

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 prepared with three different types of lanthanum salts, $La(NO_3)_3$, $La_2(SO_4)_3$ and $LaCl_3$ under pH 3–5. It can be observed that there is an effect of the type of anion present on the lanthanum uptake. The presence of sulphate notably decreased the metal uptake for all three different levels of pH tested. On the other hand, the presence of chloride does not seem to have a significant effect. The metal removal decreased according to the following sequence: $NO_3^- \cong Cl^- > SO_4^{2-}$.

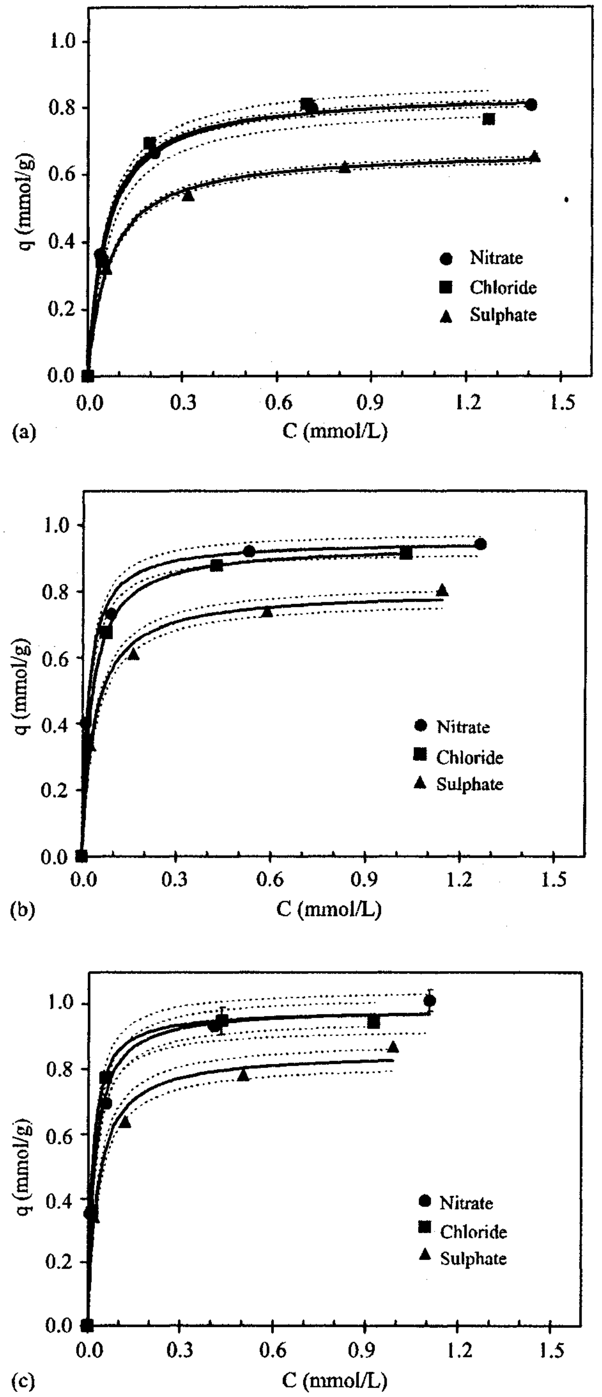

Fig. 1. Effect of La for nitrate, sulphate and chloride solutions at different values of pH: (a) pH 3, (b) pH 4, (c) pH 5.

The concentration of anions in the system comes from two different sources. The first source is the metal salt used for solution preparation. Consequently, the concentration of anions is equivalent to the concentration of metal in the initial solution. Therefore, the concentration of anions in the system is higher at higher metal concentration levels, i.e., in the plateau region, and smaller at low metal concentrations, i.e., in the linear region of the sorption isotherm. The second source of anions is the mineral acid used to adjust the pH of the solution to the desired levels. The amount of anions that came from the acid added to adjust the pH to 4 and 5 was negligible compared to the concentration of metal in solution, which approximately ranged from 0.1 to 1 mmol L^{-1}. The hydrogen ions concentration in the system was 0.1 mmol L^{-1} at pH4 and 0.01 mmol L^{-1} at pH5, which was much lower than the metal content in the solution.

In a previous work (Diniz and Volesky, 2005), ion exchange was indicated to be the main mechanism involved during the lanthanum sorption process using a nitrate salt. The active groups involved were the carboxylic groups present in the biomass and the exchangeable ions were calcium, lanthanum and protons. However, the Langmuir model, which represents the adsorption phenomenon, was shown to describe the process well and quantitatively (Zouboulis et al., 1997) and for this reason was used for comparative purposes, although it is necessary to realize that it does not represent the mechanism involved in the biosorption process. The calculated R^2 values and standard errors are summarized in Table 1 while the respective adjustable parameters are reported in Tables 2 and 3. Experimental errors were low and always below 0.02 while larger errors were caused by model inadequacy. All R^2 values obtained were above 97.8% and demonstrated significant regression. From the results it can be inferred that the maximum metal uptake was identical for both nitrate and chloride systems. It was slightly lower for sulphate systems for all levels of pH tested. The sorption constant K obtained must be considered as reflecting an "apparent affinity" due to the non-Langmuirian nature of the sorption system. These apparent sorption affinities showed large variation in some cases, reflecting part of the inadequacy of the Langmuir model for the present sorption process. Despite the variation it can be concluded that the sorption constant increased with pH, although it was quite similar for pH 4 and 5. In addition, it was obviously lower for the sulphate systems. Therefore, the following sequence of affinity could be drawn for the systems studied: $NO_3^- = Cl^- > SO_4^{2-}$.

Table 1
Estimated values of R^2 and standard error

	NO_3^-	SO_4^{2-} (HNO_3)	SO_4^{2-} (H_2SO_4)	Cl^- (HNO_3)	Cl^- (HCl)
pH 3	$R^2 = 99.87$ $q = q \pm 0.02$	$R^2 = 99.80$ $q = q \pm 0.02$	$R^2 = 99.63$ $q = q \pm 0.04$	$R^2 = 98.80$ $q = q \pm 0.07$	$R^2 = 99.71$ $q = q \pm 0.03$
pH 4	$R^2 = 99.31$ $q = q \pm 0.06$	$R^2 = 99.40$ $q = q \pm 0.05$	—	$R^2 = 100.0$ $q = q \pm 0.005$	— —
pH 5	$R^2 = 97.77$ $q = q \pm 0.11$	$R^2 = 99.10$ $q = q \pm 0.06$	$R^2 = 99.49$ $q = q \pm 0.03$	$R^2 = 99.20$ $q = q \pm 0.07$	$R^2 = 99.51$ $q = q \pm 0.05$

Table 2
Maximum metal uptake capacity by Langmuir model: $q = QKC/(1 + KC)$

	Q (mmol g^{-1})				
	NO_3^-	SO_4^{2-}(HNO_3)	SO_4^{2-} (H_2SO_4)	Cl^- (HNO_3)	Cl^- (HCl)
pH 3	0.84±0.01	0.67±0.02	0.65±0.02	0.85±0.06	0.79±0.03
pH 4	0.95±0.06	0.80±0.04	—	0.94±0.00	—
pH 5	0.98±0.16	0.85±0.06	0.91±0.05	0.99±0.10	0.93±0.06

Table 3
Apparent affinity constant by Langmuir model: $q = QKC/(1 + KC)$

	K (L mmol^{-1})				
	NO_3^-	SO_4^{2-} (HNO_3)	SO_4^{2-} (H_2SO_4)	Cl^- (HNO_3)	Cl^- (HCl)
pH 3	19.0±3.7	15.3±5.6	6.3±1.3	17.0±10.7	25.9±3.2
pH 4	51.3±12.1	25.5±4.7	—	33.5±0.2	—
pH 5	69.4±31.6	32.5±7.9	9.9±1.8	48.0±11.2	67.0±13.0

Kuyucak and Volesky studied the effect of counter-ions on cobalt biosorption using the brown seaweed *Ascophyllum nodosum* at pH 2 and 4.5. Nitrate (NO_3^-) ions seemed to strongly inhibit cobalt removal reducing the metal uptake capacity by 35% at pH 4.5. The presence of carbonate (CO_3^{2-}) also suppressed the cobalt removal by 4%, while the presence of phosphate and sulphate did not have an impact on the metal removal. The effect of all the anions tested was less pronounced under pH 2 (Kuyucak and Volesky, 1989). The presence of nitrate or sulphate ions also reduced cobalt biosorption by biomass of *Oscillatoria anguistissima* (Ahuja et al., 1999a, b). However, other studies on the removal of zinc using *O. anguistissima* (Ahuja et al., 1999a, b) demonstrated that nitrate ions did not affect zinc uptake, while especially sulphate and also chloride ions contributed to reducing the metal uptake. Similar results were observed for lanthanum biosorption using another seaweed biomass (Palmieri et al., 2003). The maximum lanthanum uptake for *Pseudomonas auruginosa* reached 1 mmol g^{-1} at pH5 from a chloride salt solution (Philip et al., 2000).

Another work (Pulsawat et al., 2003) studied the effect of chloride, nitrate and sulphate ions on manganese removal using extracellular polymeric substance from *Rhizobium etli*. It was observed that the metal removal decreased in the following order SO_4^{2-} (2.26 meq g^{-1}) > NO_3^- (1.93 meq g^{-1}) > Cl^- (0.76 meq g^{-1}). While sulphate and nitrate produced similar results, chloride strongly inhibited the metal uptake. However, there was no discussion concerning the metal speciation in solution and how it could affect the metal removal. The values of pH tested ranged from 5.2 to 5.8, which could promote the formation of monovalent chloride complexes and even anionic chloride complexes contributing thus to the reduction of metal uptake. A more thorough study of metal speciation in these systems is necessary to explain the differences in metal uptake.

Another work involved sorption studies of europium salts including nitrate, chloride and sulphate using *P. aeruginosa* (Texier et al., 2000). The presence of these anions did not inhibit quantitatively the metal binding. However, there was evidence that chemical moieties of these anions were present in the chemical structure surrounding europium in the bacterial cell wall. It was also verified that the carboxyl and phosphate groups were responsible for the europium uptake (Texier et al., 2000).

One possible explanation of the differences and similarities obtained as the results of the present work when compared to those in the literature seems to rest in the speciation of metals in solution. A closer examination, considering the possibility of metal complex formation with counterions in solution, revealed a significant effect on the overall metal uptake by the biomass. The speciation of cobalt in solution is different from that of lanthanum and, on the other hand, zinc may behave more similarly to lanthanum. It should be pointed out that the type of biosorbent material could also affect the behaviour observed. The formation of complexes with valences lower than the free metal ion reduce the total metal affinity as multivalent ions usually show higher selectivity than the monovalent ones.

3.2. Effect of NO_3^- and Cl^- from pH adjustment on La sorption

The adjustment of the pH can be done in different ways. In this study, results depicted in Fig. 1(a,b and c) were based on adjusting pH with nitric acid. This was done in order to keep the total concentration of sulphate and chloride constant for each point of the isotherm. The addition of sulphate or chloride would contribute even more to the formation of complexes and precipitate. Other isotherms were derived at pH 3 and 5 for chloride systems with the pH being adjusted with hydrochloric acid. Fig. 2 shows both isotherms at pH 3 and 5 where pH was adjusted with either nitric or hydrochloric acids. The figure shows that the isotherms were similar for both levels of pH.

Tables 2 and 3 show the Langmuir model parameters obtained from the chloride isotherms. Overall, nitrate and chloride solutions produced similar isotherms with practically no difference in both the metal uptake and the sorption affinity constant.

3.3. Effect of SO_4^{2-} and NO_3^- for pH adjustment on La sorption

The effect of adjusting the pH of lanthanum sulphate solutions with either nitric or sulphuric acid on the La uptake was verified in this study. The addition of sulphuric acid increases the total concentration of sulphate ions in the solution. That, in turn, affects the speciation of the metal in the liquid phase. It is important to point out that when adding nitric acid to adjust the pH, the only source of sulphate ions is the lanthanum sulphate salt. On the other hand, adjusting the pH using sulphuric acid increases the total sulphate concentration in the liquid, contributing even more to the formation of complexes. Fig. 3 shows the isotherms for lanthanum sulphate solutions at pH 3 and 5. It can be clearly seen that the apparent affinities reflected by the slope of the curves at low metal concentrations were lower when using sulphuric acid rather than nitric acid. However, the maximum uptake capacity was similar with both acids, especially at pH 5. The difference is more pronounced for lower metal concentrations in the solution, especially at pH 3 when the amount of sulphuric acid added to adjust the pH is much higher than the amount added at pH 5. The parameters obtained by fitting the isotherms with the Langmuir

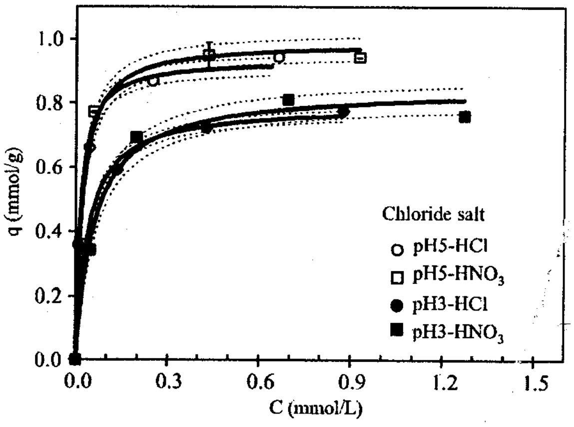

Fig. 2. Effect of adjusting pH with HCl and HNO_3 for chloride systems at pH 3 and 5.

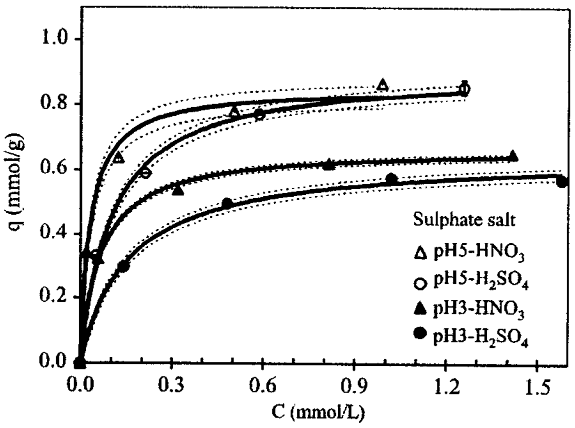

Fig. 3. Effect of adjusting pH with H_2SO_4 and HNO_3 for sulphate systems at pH 3 and 5.

model are summarized in Table 1. The values of the apparent affinity constant K are much lower for the sulphuric acid addition compared to the nitric acid addition, indicating a much less steep isortherm curve and, consequently, lower selectivity. The maximum La uptake capacity was similar at pH 5 and lower for the sulphuric acid addition at pH 3. From the results it can be inferred that the addition of sulphuric acid inhibits the lanthanum removal from the solution as it increases the total concentration of sulphate ions in the system. Studying the speciation of the ions in solution provided a reasonable explanation for the differences observed from the isotherms obtained for lanthanum sulphate salts.

3.4. Speciation of La in the presence of NO_3^-, Cl^- and SO_4^{2-}

A closer look into the solution chemistry of the La sorption system could assist in explaining the results obtained, especially those involving complexation and/or precipitation, and to verify the metal uptake mechanisms occurring during the biosorption process. A good knowledge of the real metal deposition mechanism(s) serves as a basis for composing mathematical process models that eventually could reliably predict the biosorption process performance. Metal speciation in solution can explain the differences observed in the lanthanum uptake due to the presence of a specific anion. The speciation was calculated using the software Mineql+ (Schecher, 1998). The usefulness of this program has already been demonstrated in other biosorption works (Diniz and Volesky, 2005; Yang and Volesky, 1999a, b). Table 4 describes the main possible reactions that can occur in the systems under study, and their respective overall stability constants. Some complexes and precipitates have a high potential to occur, including sulphate and chloride complexes.

The total final concentrations of all species present in solution were used as input to the MINEQL program. The species included lanthanum, nitrate, sulphate, chloride, protons, hydroxyls, and calcium. As the ionic strength is known to suppress metal removal (Zouboulis et al., 1997), it was also computed and ranged from 0.004 to 0.024 mol L^{-1} along the curves and the values obtained increased with the metal concentration and were similar for all different salt systems at the same final metal concentration. Therefore, the curves obtained at the same pH levels could be compared. The data obtained from the isotherms in Figs. 1–3, were used for the calculations, considering the pH and the total concentration of both anions and cations present in the system, including the calcium released from the biomass during the ion exchange process. According to previous work (Diniz and Volesky, 2005), Lanthanum was always present as a trivalent ion in nitrate systems.

Table 4
Overall metal stability constant values

Reaction	Log β
$La^{3+} + OH^- \leftrightarrow [LaOH]^{2+}$	−9.000
$La^{3+} + 3OH^- \leftrightarrow La(OH)_3$	−21.291
$La^{3+} + Cl^- \leftrightarrow [LaCl]^{2+}$	0.700
$La^{3+} + SO_4{}^{2-} \leftrightarrow [LaSO_4]^+$	3.300
$Ca^{2+} + SO_4{}^{2-} \leftrightarrow [CaSO_4]_{aq}$	2.360
$Ca^{2+} + OH^- \leftrightarrow [CaOH]^+$	−12.697
$Ca^{2+} + NO_3{}^- \leftrightarrow [CaNO_3]^+$	0.500

Source: Schecher (1998).

Figs. 4 and 5 show the speciation for each specific anion—sulphate and chloride, respectively—in the presence of lanthanum. Every curve shows the speciation at a certain pH varying the total concentration of metal and the anion type present in the experiments.

The La speciation in the chloride system can be seen from Fig. 4(a,b). Most of the lanthanum present in the liquid is in the free trivalent form. Some of the La was complexed with chloride producing a divalent cation whose percentage in solution varied from 1% to 4%. The formation of this complex could explain the slight decrease in the metal uptake observed in chloride systems when compared to the nitrate ones, being even more pronounced when hydrochloric acid was added.

Fig. 5(a,b) shows that a monovalent cation complex is formed with lanthanum and sulphate. The percentage of this complex increases with metal concentration. Needless to say, with increasing metal concentration, the concentration of the corresponding anion also increases. The behaviour was similar for all pH values tested. From the results it can be inferred that the monovalent lanthanum sulphate complex formed has a lower apparent affinity towards the biomass. This was responsible for the decreased metal uptake from solution as seen in the isotherms. The same trend was observed for all levels of pH tested. When sulphuric acid was added to adjust the pH, the percentage of the monovalent lanthanum sulphate complex increased due to the addition of sulphate ions into the solution, confirming thus that this complex has a lower apparent affinity to the biomass than the free trivalent lanthanum cation. The total metal uptake from solution was thus correspondingly reduced. Fig. 6 shows the metal

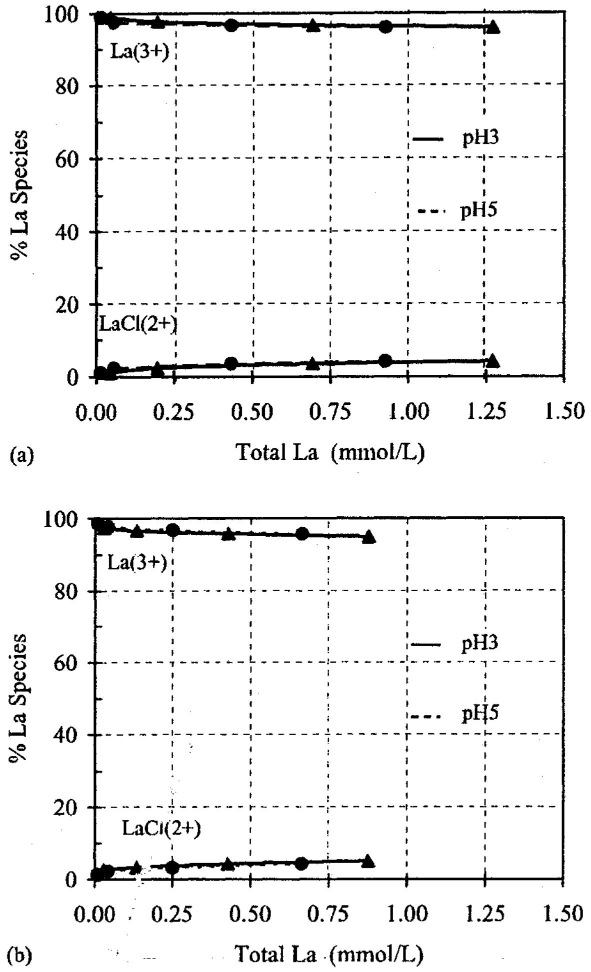

Fig. 4. Speciation of La in chloride systems representing the conditions, obtained from the isotherms under pH 3, 4 and 5. The pH was adjusted with (a) HNO_3 and (b) HCl, respectively.

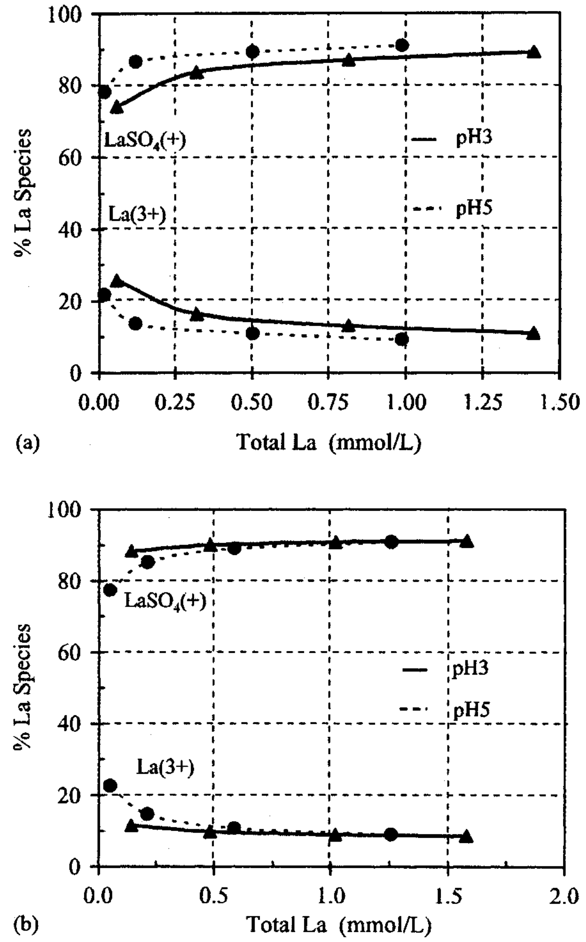

Fig. 5. Speciation of La in sulphate systems representing the conditions obtained from the isotherms under pH 3, 4 and 5. The pH was adjusted with (a) HNO_3 and (b) H_2SO_4, respectively.

speciation in the presence of equivalent concentrations of either sulphate or chloride ions. They simulated the presence of species under initial experimental conditions.

Palmieri's study (Palmieri et al., 2003) suggested that fewer disturbances on the inner coordination sphere caused by chloride anions would improve the interaction with carboxylate groups present in the biomass. However, the metal speciation in solution was not even discussed in this work. Results of the present work are indicative of its importance.

4. Conclusions

Lanthanum could be removed from aqueous solutions by *S. polycystum* biomass. Different metal removal capacities and relative biosorption affinities were observed when different La salts were applied. While nitrate and chloride salts resulted in similar biosorption behaviour, sulphate salts inhibited the metal uptake. The metal speciation in solution provided a plausible explanation for the differences observed. Complexation of the metal and sulphate ions, resulting in a less-sorbing monovalent complex, reduced the total lanthanum removal. The addition of sulphuric acid for pH adjustment lowered the metal uptake as it increased the amount of the less-sorbing monovalent lanthanum sulphate complex. This effect was more pronounced at lower pH values when more acid was added to maintain constant pH. Although the R^2 values calculated for fitting the data with the Langmuir model were good, the model could not be considered adequate for describing some sorption behaviour observed. However, it estimated well the maximum metal uptake capacity and showed the differences among the metal-biomass apparent affinities.

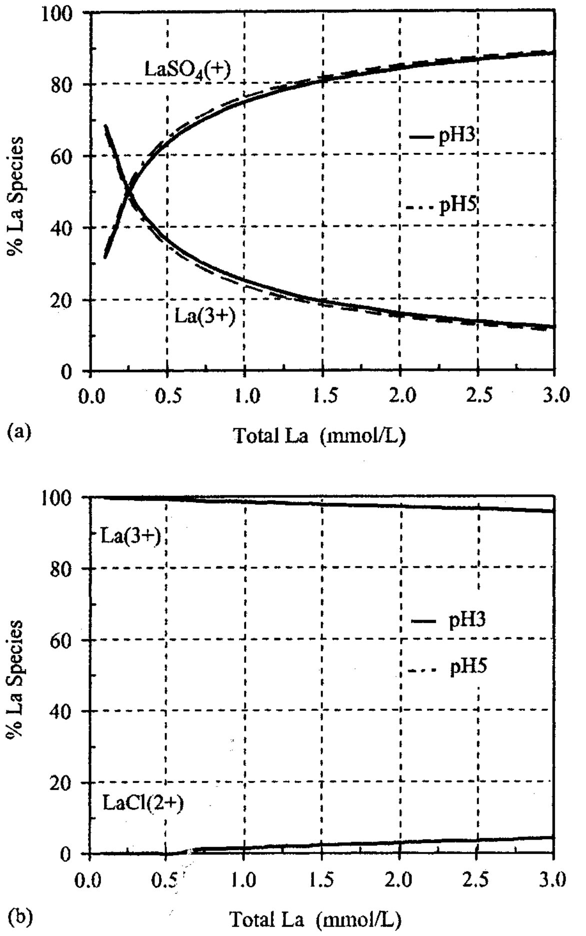

Fig. 6. Speciation of La at pH 3 and 5 in the presence of equivalent concentrations of either (a) sulphate or (b) chloride ions.

Acknowledgements

The international CAPES (Brazil) Scholarship to V. Diniz enabled this work. Valuable suggestions by Dr. G. Demopoulos, Dr. M.E. Weber and Dr. J.H. Vera were greatly appreciated.

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APPENDIX 3: Manuscript 3

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Desorption of lanthanum, europium and ytterbium from *Sargassum*

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Received 15 April 2005; received in revised form 10 November 2005; accepted 14 November 2005

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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1383-5866/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.seppur.2005.11.010

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}:

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

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.

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

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.

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

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

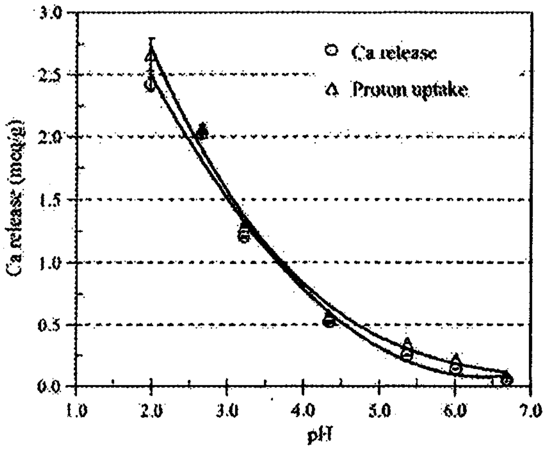

Fig. 1. Release of calcium from biomass and removal of protons at different levels of pH.

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

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

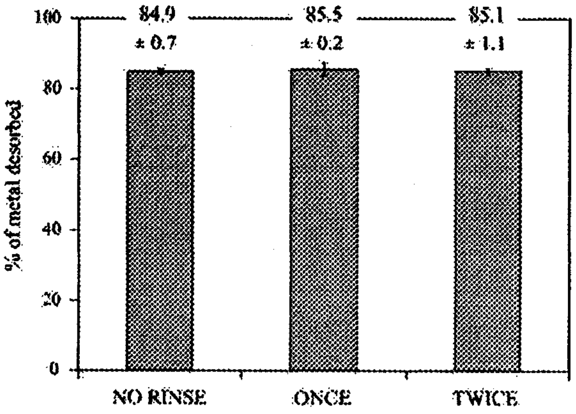

Fig. 2. Effect of washing the biomass after La sorption and before its desorption.

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

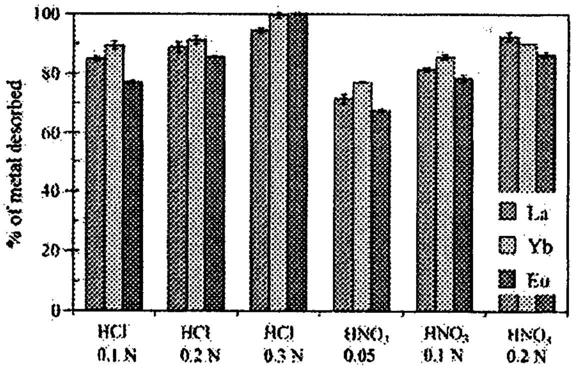

Fig. 3. Desorption of individual elements with different concentrations of mineral acids. Single-element systems containing respectively La, Eu and Yb.

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 Eu > La > 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" Yb > La > 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 ± 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].

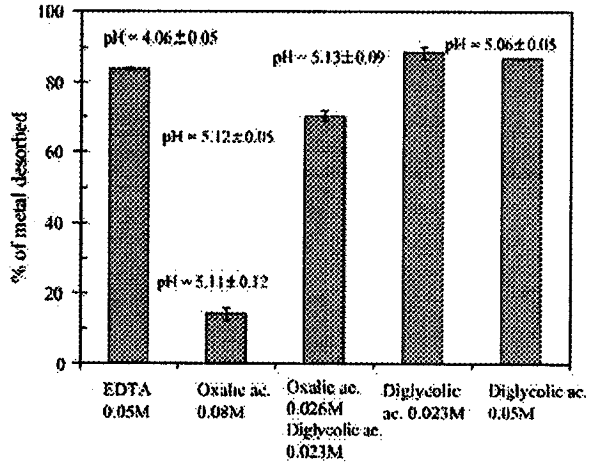

Fig. 4. Single-element system desorption of La using different organic acids.

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

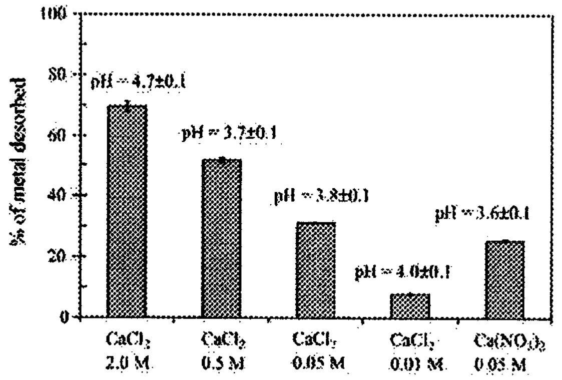

Fig. 5. Single-element system desorption of La using different concentrations of calcium nitrate and chloride solutions.

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, $CaCl_3$ 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 anguistissima*. 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 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.

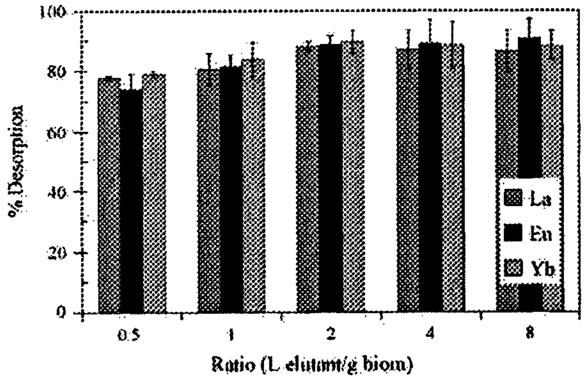

Fig. 6. Effect of liquid to solid ratio on the percentage of desorption for La, Eu and Yb in each respective single-element system.

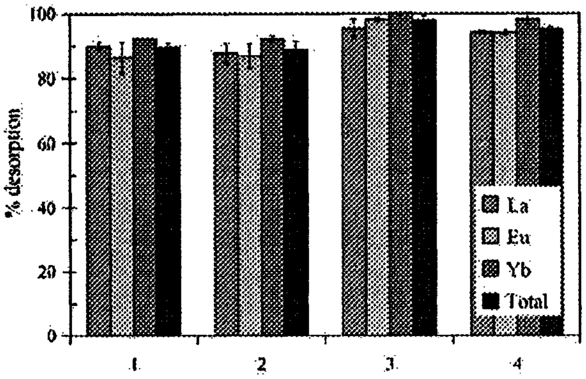

Fig. 7. Desorption of La, Eu and Yb from biomass loaded with all three elements.

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} HNO_3.

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} HNO_3, 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.

Acknowledgement

The international CAPES (Brazil) Scholarship to V. Diniz enabled this work.

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