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Effect of counterions on lanthanum biosorption by *Sargassum polycystum*

Vivian Diniz, Bohumil Volesky*

Department of Chemical Engineering, McGill University, 3610 University Street, Montreal, Que., Canada H3A 2B2

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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 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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*Corresponding author. Tel.: +1 514 3984276; fax: +1 514 3986678.
E-mail address: boya.volesky@mcgill.ca (B. Volesky).

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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: $NO_3^- \cong Cl^- > SO_4^{2-}$.

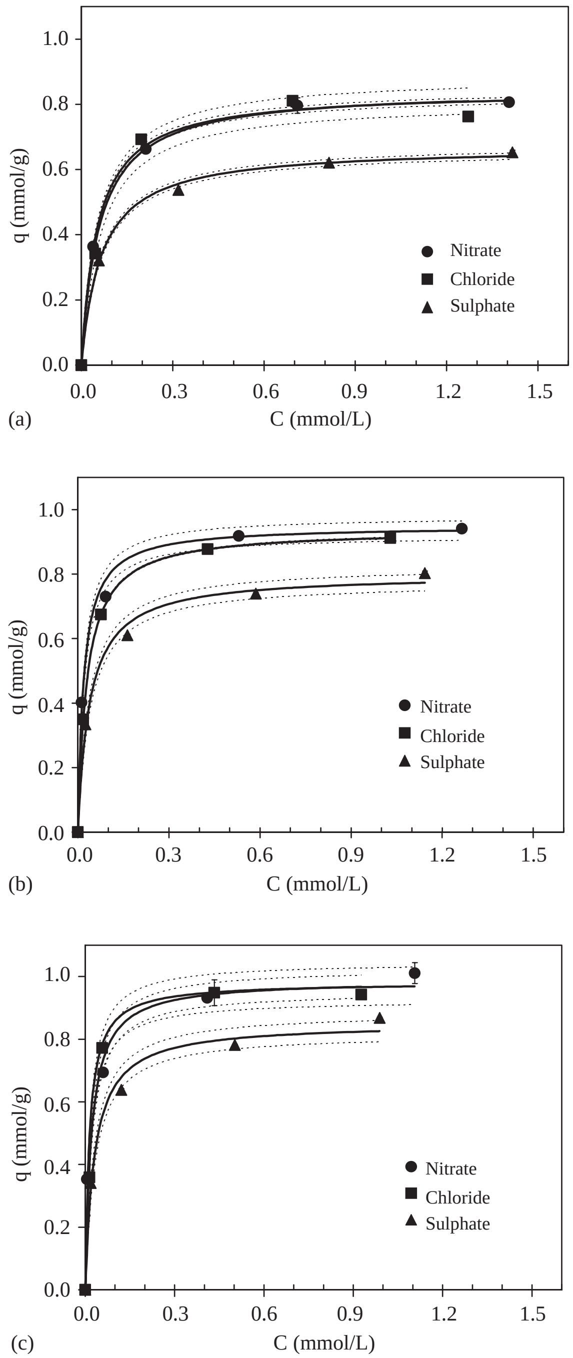

Fig. 1. Effect of La for nitrate, sulphate and chloride solutions at different values of pH: (a) pH 3, (b) pH 4, (c) pH 5.

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	$R^2 = 99.87$	$R^2 = 99.80$	$R^2 = 99.63$	$R^2 = 98.80$	$R^2 = 99.71$
	$q = q \pm 0.02$	$q = q \pm 0.02$	$q = q \pm 0.04$	$q = q \pm 0.07$	$q = q \pm 0.03$
pH 4	$R^2 = 99.31$	$R^2 = 99.40$	—	$R^2 = 100.0$	—
	$q = q \pm 0.06$	$q = q \pm 0.05$		$q = q \pm 0.005$	—
pH 5	$R^2 = 97.77$	$R^2 = 99.10$	$R^2 = 99.49$	$R^2 = 99.20$	$R^2 = 99.51$
	$q = q \pm 0.11$	$q = q \pm 0.06$	$q = q \pm 0.03$	$q = q \pm 0.07$	$q = q \pm 0.05$

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

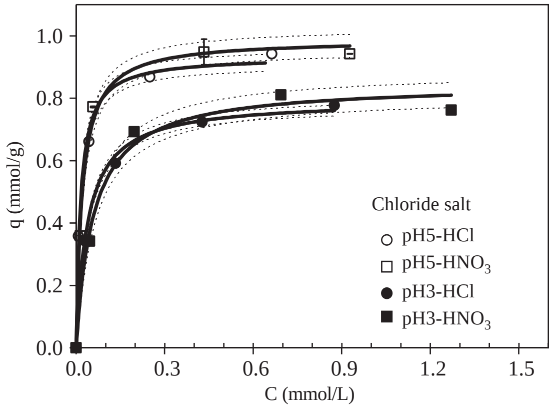

Fig. 2. Effect of adjusting pH with HCl and HNO_3 for chloride systems at pH 3 and 5.

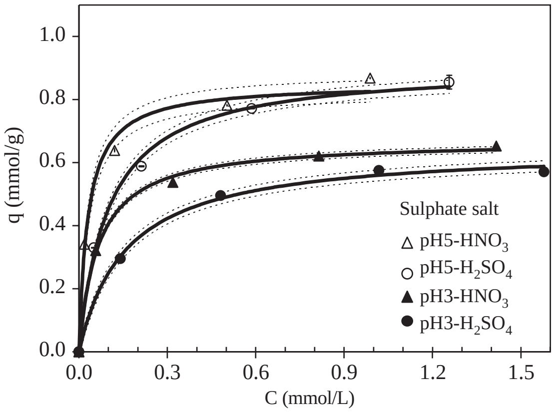

Fig. 3. Effect of adjusting pH with H_2SO_4 and HNO_3 for sulphate systems at pH 3 and 5.

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 $\text{mol}\,L^{-1}$ 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

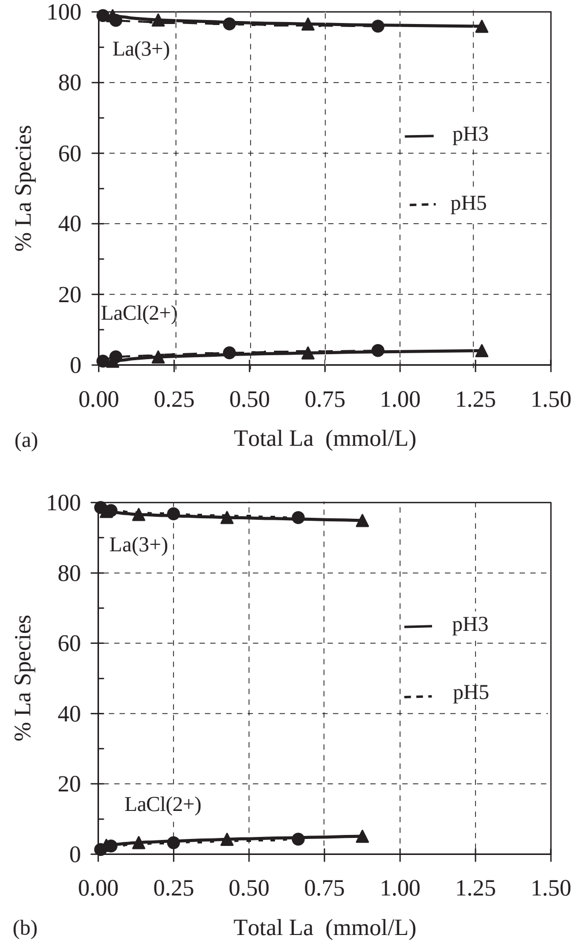

Fig. 4. Speciation of La in chloride systems representing the conditions obtained from the isotherms under pH 3, 4 and 5. The pH was adjusted with (a) HNO_3 and (b) HCl, respectively.

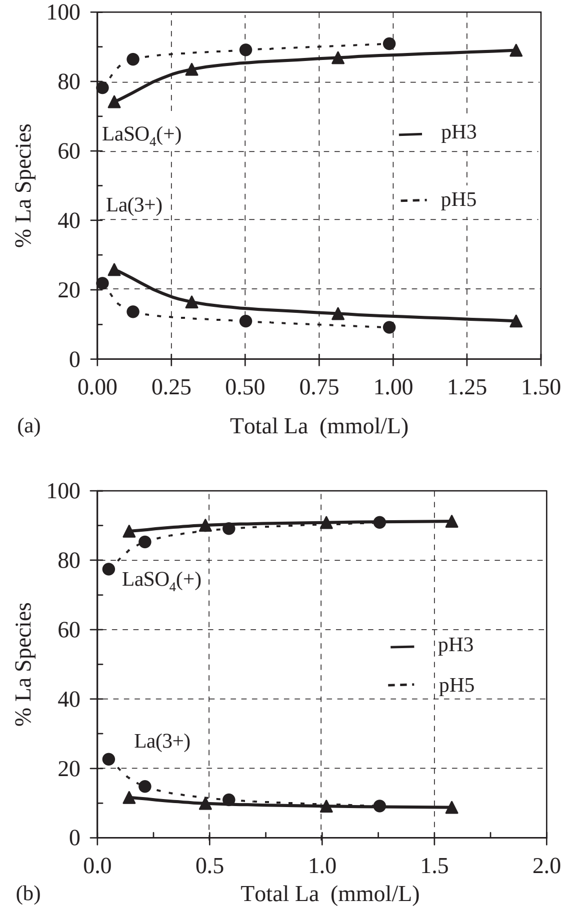

Fig. 5. Speciation of La in sulphate systems representing the conditions obtained from the isotherms under pH 3, 4 and 5. The pH was adjusted with (a) HNO_3 and (b) H_2SO_4, respectively.

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.

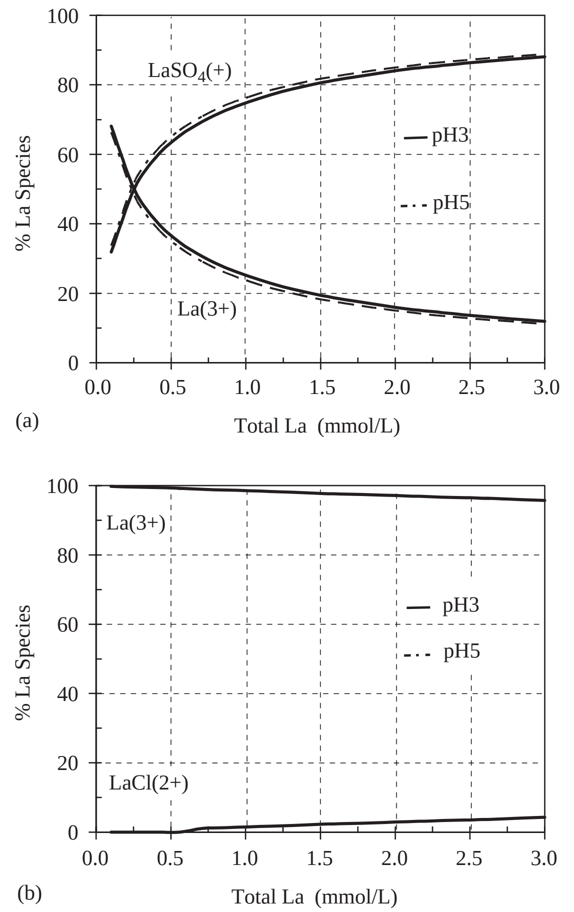

Fig. 6. Speciation of La at pH 3 and 5 in the presence of equivalent concentrations of either (a) sulphate or (b) chloride ions.

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