

Research Article

Evaluation of Chelating Resins Efficiency in Recovering Rare Earth Elements from Sulphate-Rich Acid Solutions

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Received: 11 November 2022; **Revised:** 11 January 2023; **Accepted:** 26 January 2023

Abstract: This work investigates the use of chelating resins for recovering rare earth elements (REE) from a laboratory solution with pH and sulphate concentrations similar to those of an acid mine drainage (AMD). The loading experiments were performed in ion exchange columns, fed with a solution at pH 3.5 containing 0.49 g L⁻¹ of REE, 0.06 g L⁻¹ of impurities and 1.11 g L⁻¹ of sulphate ions. The highest loading was obtained for the PUROLITE® MTS 9500 resin activated with Na⁺, and it was 101.8 mg g⁻¹, which corresponds to a sorption efficiency of 73%. The loading results showed that the resins have greater selectivity for REE over impurities. Regarding elution, greater efficiency (i.e., 96%) was obtained with the resin PUROLITE® MTS 9300; however, this resin presented lower loadings. A final liquor with a maximum REE concentration of 1.72 g L⁻¹ and maximum impurities concentration of 0.02 g L⁻¹ was obtained for PUROLITE® MTS 9500 resin activated with H⁺, which presents an elution efficiency of 80%.

Keywords: ion exchange, rare earth elements, elution, chelating resins

1. Introduction

Rare earth elements (REE) are essential raw materials for the growth of modern industry as well as for designing and developing high-technology products used in our daily lives. These metals are essential for the production of magnets, cell phones, televisions, light-emitting diode (LED) light bulbs, wind turbines and electric vehicles [1-3]. They are also used in many medical and healthcare applications, such as antitumor agents, kidney dialysis drugs, surgical equipment, the treatment of cancer and kidney stones, a power source in portable X-ray devices, along with many imaging techniques such as computed tomography and positron emission magnetic resonance [4].

China has the largest REE world reserve (30%) and is also the principal producer [2, 3]. However, REE availability is declining, and its scarcity leads to the development of new alternatives, such as recycling or secondary sources. In this context, acid mine drainage (AMD), commonly considered an environmental issue [5-7], could be interesting, given that the concentration of REE may be significant and worth recovering. In addition, the process looks promising from the economic point of view, as typical mineral processing, such as pre-concentration and leaching, is unnecessary. However, it is important to find technological alternatives that take the specificity of these new sources into account.

There are several techniques for recovering and fractionating REE from aqueous solutions, such as ion exchange, solvent extraction, and precipitation [1]. From these techniques, ion exchange stands out as more environmentally

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DOI: <https://doi.org/10.37256/epr.3120232154>

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friendly and is particularly employed in the treatment of large volumes of effluents containing trace concentrations of metals [1, 8]. Many works used ion exchange resins containing sulfonic, iminodiacetic and aminophosphonic groups to recover and fractionate REE from different solutions, mainly chloride or nitrate solutions [9-11]. However, unlike nitrate and chloride ions, sulphate ions can form multiple complexes with REE, which makes ion exchange more complex [12]. Once the sorption performance of the resins depends on the aqueous medium (chloride, sulphate, nitrate or fluoride), the studies with this type of solution are relevant [12, 13]. In previous work from our group with a sample similar to AMD [14], it was demonstrated that the use of strongly acidic cation resin promoted an overall recovery of REE of around 83%. Moreover, the REEs were partially fractionated. Ion exchange resins containing aminophosphonic and iminodiacetic groups (Figure 1) are also able to form strong coordination bonds with REE groups [9-11] in detriment to other metals, which can contribute to good selectivity over these elements.



Figure 1. Chelating resin structure showing (a) aminophosphonic and (b) iminodiacetic functional groups

Although some studies have considered AMD as a secondary source of REE, a limited number of them investigate the pre-concentration of these elements using ion exchange [5, 8]. Most of them have considered precipitation of REE followed by leaching and concentration or separation by solvent extraction. However, the ion exchange process is an attractive option for this kind of secondary source. Therefore, the present work addressed the potential use of chelating resins containing aminophosphonic and iminodiacetic functional groups in the adsorption of REE present in a diluted acid solution (pH 3.5) with a high sulphate concentration (11.60 mmol L⁻¹). Loading and elution data for the resins were provided. The influence of Na⁺ and H⁺ counter ions in the ion exchange process and the selectivity of resins for impurities were also assessed. The results may help with defining the finest experimental conditions for recovering traces of REE in effluents where sulphate concentration plays an important role.

2. Materials and methods

2.1 Solutions

Individual stock solutions were prepared by: (i) dissolving metal sulphates in MILLI-Q[®] deionized water; or (ii) dissolving metal oxides and carbonates in concentrated H₂SO₄. The reagents were from Sigma-Aldrich with 99.9% purity, except for Eu carbonate, which had approximately 60% purity. Each stock solution contained 3000.0 mg L⁻¹ of a specific REE and a total of 1000.0 mg L⁻¹ of impurities (Al, Ca and Mg). The pH values were in the range of 1.0 to 1.9.

The individual solutions were mixed to prepare a 30 L homogenised laboratory solution that was kept in a gallon plastic jug at room temperature with a pH of 3.5 (adjusted by adding KOH). The characterization of the solution was done in previous work [14] and is shown here in Table 1.

Table 1. Chemical characterisation of the laboratory solution [14]

Elements	mg L ⁻¹	mmol L ⁻¹
Pr	65.7 ± 3.3	0.440 ± 0.022
La	56.6 ± 2.8	0.400 ± 0.020
Sm	61.4 ± 3.1	0.400 ± 0.020
Nd	58.0 ± 2.9	0.390 ± 0.019
Gd	60.2 ± 3.0	0.360 ± 0.018
Eu	61.9 ± 3.1	0.390 ± 0.019
Dy	62.4 ± 3.1	0.370 ± 0.018
Er	67.4 ± 3.3	0.370 ± 0.018
Total REE	493.3 ± 24.68	3.120 ± 0.156
Al	18.0 ± 0.9	0.670 ± 0.034
Ca	20.8 ± 1.0	0.520 ± 0.026
Mg	16.0 ± 0.8	0.660 ± 0.033
Total impurities	54.8 ± 2.74	1.850 ± 0.093
SO ₄ ²⁻ = 11.6 mmol L ⁻¹		
pH = 3.5		

2.2 Chelating resins

Two commercially available ion exchange chelating resins, PUROLITE® MTS 9500 and PUROLITE® MTS 9300, which have a macroporous polystyrene matrix with aminophosphonic (R-CH₂-NH-P(O)(OH)₂) and iminodiacetic (N-CH-COOH) functional groups, were selected. According to the literature [9-11], these chelating resins are able to form strong coordination bonds with REE groups in detriment to other metals, which can contribute to good selectivity over these elements. Their physicochemical properties, as reported in the technical data sheets, are shown in Table 2.

Table 2. General properties of the resin

Resin name	PUROLITE® MTS 9300	PUROLITE® MTS 9500
Type	Chelating	Chelating
Functional group	Iminodiacetic	Aminophosphonic
Ionic form	Na ⁺	Na ⁺
Matrix	Macroporous polystyren	Macroporous polystyren
Size (mm)	0.425 - 1.0	0.3 - 1.2
Capacity (g L ⁻¹)	50 (Cu)	26 (Ca)
Water retention (%)	52 - 60 (Na ⁺ form)	60 - 68 (Na ⁺ form)
Temperature limit (° C)	80	80

2.2.1 Activation of the resins with H^+

Resins were used as supplied in Na^+ form and activated with H^+ to compare both forms during loading and elution. The resin in Na^+ form was washed, vacuum filtered, dried in an oven at 35 °C until constant weight, and then kept in a vacuum desiccator.

For the activation procedure, 300 mL of MILLI-Q[®] deionized water and 100 g of resin were gently shaken mechanically for 30 minutes, using an orbital shaking incubator, model NL-161/03. This procedure was repeated six times until the pH was stable. The resin was placed in the column, and two bed volumes (BV) of 4% HCl solution were passed at a constant flow rate of 3 BV/h for 40 minutes. Soon after, MILLI-Q[®] deionized water was passed through the column until an outlet pH between 5 and 7 was attained.

2.3 Loading experiments

Loading experiments were conducted in columns with a BV of 8.0 mL and a residence time of 9.7 minutes (flow rate: 0.82 mL min⁻¹), according to José and Ladeira [14]. Data were integrated using the Origin 2020 program to determine the REE loading values. The loading efficiency was calculated using Equation 1.

$$Ef_c = \frac{[m_2]}{[m_1]} \times 100 \quad (1)$$

where Ef_c is the loading efficiency (%), m_2 is the mass (g) of the element loaded in the resin, and m_1 is the total mass (g) of the element in the feed solution.

2.4 Elution experiments

The elution was performed with 0.05 mol L⁻¹ NH₄EDTA and a flow rate of 0.64 mL min⁻¹ (residence time: 12.5 minutes), according to José and Ladeira [14]. Equation 2 was used to calculate the elution efficiency.

$$Ef_e = \frac{[m_2]}{[m_1]} \times 100 \quad (2)$$

where Ef_e is the elution efficiency (%), m_2 is the mass (g) of the element in the eluate, and m_1 is the mass (g) of the element previously adsorbed in the resin.

2.5 Chemical analysis

The elemental concentrations in aqueous samples were measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Spectroflame, model FMV 03). The detection limits for magnesium and REE were 0.1 mg L⁻¹, while those for Ca and Al were 0.5 mg L⁻¹. Sulphate ions were determined by an energy dispersive x-ray fluorescence spectroscopy (EDX) (Shimadzu, model 720) with a detection limit of 0.10 g L⁻¹.

3. Results

3.1 REE loading

The effect of the counter ions, Na^+ and H^+ , on the REE loading was investigated. Figure 2 shows the loading curves for REE, where the solid lines correspond to REE feed solution concentrations.

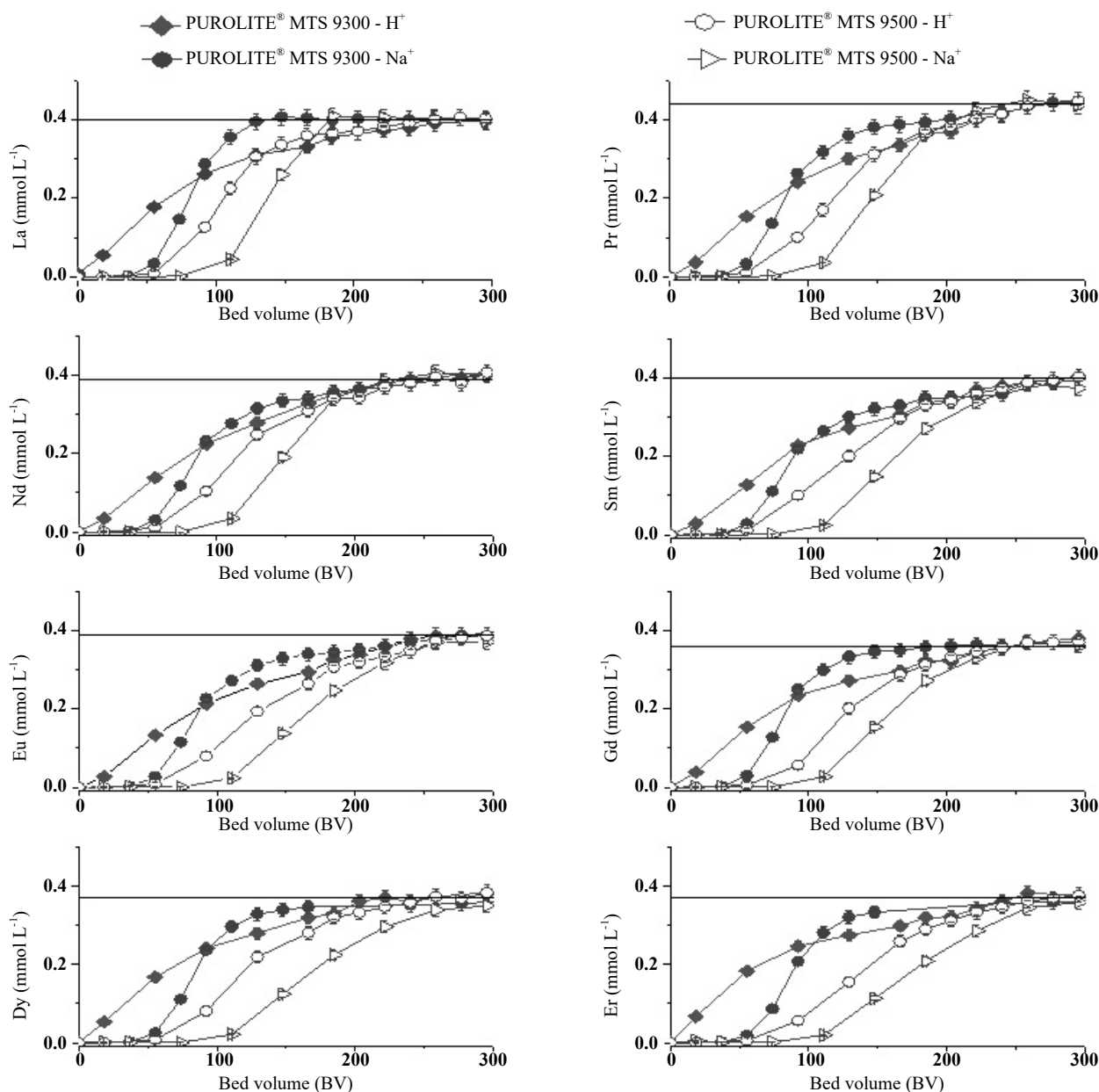


Figure 2. Breakthrough profiles for REE using chelating resins. Note: $\blacklozenge$ = PUROLITE® MTS 9300 H^+ ; $\bullet$ = PUROLITE® MTS 9300 Na^+ ; Δ = PUROLITE® MTS 9500 Na^+ ; $\circ$ = PUROLITE® MTS 9500 H^+ ; pH = 3.5; BV = 8.0 mL; residence time = 9.7 minutes; temperature = $25 \pm 5^\circ\text{C}$; and the horizontal lines represent the REE concentration in the feed solution

3.1.1 Effect of resin activation on loading

The loading curves for the resins in the Na^+ and H^+ forms (Figure 2) show that the breakpoints were reached at different BV values, demonstrating a difference in the sorption efficiency of the REE. Break points for PUROLITE® MTS 9300 resin were obtained at lower BV values (18.45 BV for H^+ and 53.6 BV for Na^+ forms) compared to PUROLITE® MTS 9500 resin (97 BV for H^+ and 111.8 BV for Na^+). The higher the BV at which the breakpoint occurs, the greater the loading capacity of the resin. The loading curves, after the breaking point for the H^+ cycle, rise smoothly, implying a slow ion exchange [15], which reduces the loading efficiency. On the other hand, the profiles for resins in the Na^+ form are less smooth and present a slightly sharper increase after the breakpoint, revealing a higher ion exchange. Table 3 shows the results for the loading of each REE in both resins.

Table 3. Loading (Q) of REE for PUROLITE® MTS 9300 and PUROLITE® MTS 9500 resins

Elements	Loading (mmol g ⁻¹)				Loading efficiency (%)			
	PUROLITE® MTS 9500		PUROLITE® MTS 9300		PUROLITE® MTS 9500		PUROLITE® MTS 9300	
	Na ⁺	H ⁺	Na ⁺	H ⁺	Na ⁺	H ⁺	Na ⁺	H ⁺
Pr	0.09	0.07	0.06	0.06	67	49	38	38
La	0.07	0.06	0.04	0.04	73	46	62	32
Sm	0.09	0.08	0.06	0.05	74	58	39	41
Nd	0.08	0.06	0.05	0.05	79	47	40	39
Gd	0.08	0.06	0.04	0.04	79	53	36	33
Eu	0.09	0.08	0.05	0.05	75	62	39	45
Dy	0.08	0.06	0.04	0.04	66	50	60	32
Er	0.09	0.07	0.05	0.04	69	52	55	48
Total	0.67	0.54	0.39	0.37	73	52	46	38

According to Table 3, the loadings were lower in the H⁺ cycle for both resins. One reason is that for resins in the H⁺ form, there is a reduction in pH during the ion exchange process. The pH was probably reduced to values equal to or less than the pK_{a1} of the iminodiacetic functional group for PUROLITE® MTS 9300 resin, which is 3.3. In solutions with a pH lower than 3.3, the resin does not perform ion exchange because it is fully protonated. In addition, the breakpoints occur at the beginning of the process, indicating that the sorption sites were mostly protonated. For the PUROLITE® MTS 9500, this effect was smaller due to the dissociation of its aminophosphonic group even at an acidic pH, as will be discussed in Section 3.1.2. It is also noticeable in Table 3 that the loading of REE by PUROLITE® MTS 9300 resin was lower in all cycles compared to PUROLITE® MTS 9500 resin, following the literature [9, 10]. However, for both resins, activation with Na⁺ promotes significant recovery of REE. For PUROLITE® MTS 9500 activated with Na⁺, the loading was approximately twice (0.67 mmol g⁻¹) compared to the PUROLITE® MTS 9300 resin (0.39 mmol g⁻¹). The loading efficiencies in the Na⁺ cycle were 73% and 46% for PUROLITE® MTS 9500 and PUROLITE® MTS 9300, respectively, and for the H⁺ cycle, they were 52% and 38%.

3.1.2 Influence of the functional group on loading

Another factor that contributed to the low loading of PUROLITE® MTS 9300 resin in the H⁺ form is the particularly high affinity of its carboxylic functional group for H⁺ ions [15], compared to Na⁺. The weakly acidic nature of its carboxylic functional group makes its dissociation difficult. It has three different pK_as, two from the carboxylic group (3.3 and 8.4) and one from the amino group (between 9.6 and 10.4). Because ion exchange is governed by the dissociation or ionisation of the functional group, which is strongly pH dependent [16], these groups are prone to protonation and lose their ability to ionise under acidic conditions [13]. Consequently, PUROLITE® MTS 9300 resin reaches its maximum loading capacity at basic pH [10]. However, it is unfeasible to work at a basic pH because most metals can precipitate. For the PUROLITE® MTS 9500 resin, the binding strength between H⁺ and the aminophosphonic group is weak, which promotes easy dissociation.

It is possible that the resin incorporates a small fraction of metals in its structure at a pH lower than its pK_{a1} due to the occurrence of two phenomena: (i) pairing or substitution of mobile ions in the resin, and (ii) coordination binding or chelating interaction between the electron donor species of the resin and the target species [17]. According to Zaganianis [17], metals can displace protons from carboxylic or amine groups and form cationic complexes at a relatively acidic pH. This phenomenon was confirmed by Ang et al. [13] when studying the adsorption and separation mechanisms of U(VI), Th(IV) and REE(III) using PUROLITE® MTS 9300 resin. These researchers confirmed that the elements were sorbed by the displacement of protons from carboxylic groups, which was followed by the formation of complexes.

The second deprotonation of PUROLITE® MTS 9300 resin occurs at pKa 8.4 [17], where the second carboxyl group loses one more proton, increasing the loading capacity since the two carboxyl groups are deprotonated. The amino group deprotonates at a pKa between 9.6 and 10.4 [17]. At pH 12, the nitrogen atom and the two carboxylic groups are fully deprotonated, and the ion exchanger performs as a typical weakly acidic cation exchanger. For pH values near neutrality, the iminodiacetic resin behaves as an amphoteric ion exchanger [8].

Regarding the PUROLITE® MTS 9500 resin activated with Na⁺, ion exchange begins at pH 0.5 due to the deprotonation of one of the oxygen atoms in the phosphonic group that occurs at pKa₁ between 0.5 and 1.5 [18], which justifies its higher adsorption compared to the PUROLITE® MTS 9300 resin. Adsorption increases significantly above pH 5 because of the deprotonation of the second oxygen atom in pKa between 5.0 and 6.0. The amino group deprotonates at a pKa between 9.5 and 10.5 [19]. Therefore, for both resins activated with Na⁺, only one oxygen atom participates in the reactions. The amino group plays almost no role in REE loading because deprotonation of this group occurs at basic pH, where the metals precipitate.

The REE loadings for chelating resins were lower when compared with those obtained with the same sample using a strongly acidic cationic resin, LEWATIT® MDS 200H (0.94 mmol L⁻¹) [14]. Several factors may have contributed to this result, such as: (i) at pH below 7, chelating resins are not completely dissociated, implying a lower loading efficiency when compared to strong acidic cationic resins, which are fully dissociated across the entire pH range [8, 17]; (ii) in sulphate media, REE preferentially complexes with sulphate, forming complexes with lower charges (REE(SO₄)⁺), reducing resin attraction [20]; and (iii) the REE-sulphate complexes are more stable (formation constants of 3.59 to 3.82) [21] compared to, for example, the complexes of REE with chloride ions [20]. Moraes et al. [22] studied the complexes of REE that predominated in an AMD with a high content of sulphate ions and several metals. They observed that REE were preferentially complexed with sulphate compared to other ions. However, the behaviour of these complexes in ion exchange is rarely studied.

In conclusion, the adsorption of REE and impurities occurs through the phosphonic group or the carboxylic group. The stability of the bonds between the REE and the phosphonic group is greater compared to the bonds between the REE and the carboxylic group, a fact that determined the difference in the efficiencies in the elution of the two resins.

3.2 Impurities loading

The loading results for the impurities (Figure 3) show that both resins in cycles Na⁺ and H⁺ have lower affinity for magnesium and calcium and exhibit peaks over the head of the feed line when the resin reaches saturation. These peaks represent calcium and magnesium desorption and replacement by REE and Al, which show a higher affinity for the resin. As a result, the elements with lower affinity (Ca and Mg), already adsorbed, are exchanged with REE and Al. This effect is positive, as it favours the parting of REE from impurities (Ca and Mg). The impurities loadings and resin loading efficiencies in both cycles are shown in Table 4.

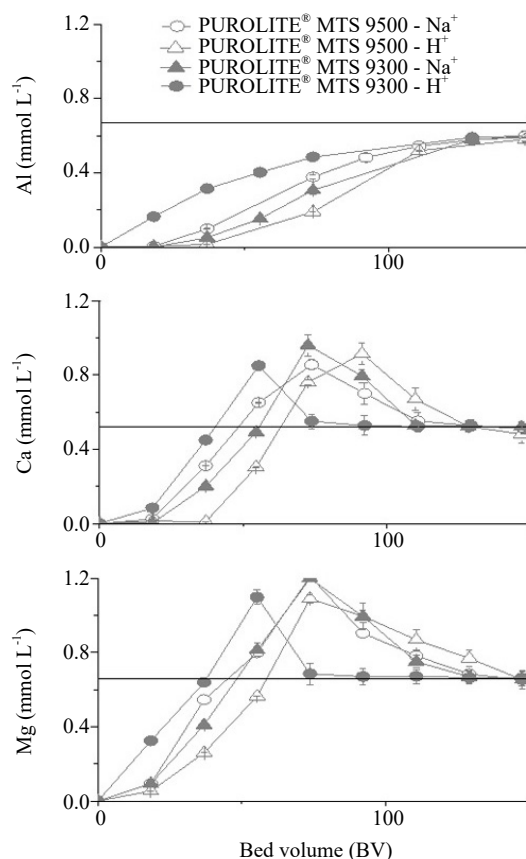


Figure 3. Breakthrough profiles for impurities in Purolite MTS resins. Note: $\blacktriangle$ = PUROLITE® MTS 9300 H^+ ; $\bullet$ = PUROLITE® MTS 9300 Na^+ ; Δ = PUROLITE® MTS 9500 Na^+ ; $\circ$ = PUROLITE® MTS 9500 H^+ ; horizontal lines represent the concentration of each impurity in feed solution; pH = 3.5; BV = 8.0 mL; residence time = 9.7 minutes; and temperature = 25 ± 5 °C

Table 4. Loadings and loading efficiencies of the impurities (Al, Ca and Mg)

Elements	Loading ($mmol\ g^{-1}$)				Loading efficiency (%)			
	PUROLITE® MTS 9500		PUROLITE® MTS 9300		PUROLITE® MTS 9500		PUROLITE® MTS 9300	
	Na^+	H^+	Na^+	H^+	Na^+	H^+	Na^+	H^+
Al	0.085	0.076	0.06	0.050	28	27	26	24
Ca	0.016	0.010	0.009	0.008	23	20	17	15
Mg	0.010	0.003	0.006	0.002	19	13	9	6
Total	0.111	0.088	0.075	0.060	23	20	17	15

Aluminium loadings were the highest for all resins, followed by Ca. On the other hand, Mg had the lowest loadings, not exceeding $0.01\ mmol\ g^{-1}$. As aluminium presents a higher ionic charge than Ca and Mg, its hydration radius is greater, and consequently the complexes formed with the functional groups are more stable. Moreover, the incorporation of impurities in the resins may also occur by complexation with the iminodiacetic and aminophosphonic functional groups of the resins, in addition to ion exchange [16-18]. The presence of Al^{3+} ions along with REE in sulphate solutions constitutes a major challenge in the recovery of REE since they have similar complexation constants with sulphate, as follows: $\log k_1\ Al(SO_4)^+ = 3.50$; $\log k_1\ REE(SO_4)^+$ between 3.59 and 3.89 [21, 23], which justifies greater competition with REE.

Regarding Ca and Mg, it is observed in Table 4 that Ca shows a higher loading. Although both have the same number of protons, Ca is more electropositive and has a larger size, which promotes its greater sorption. Therefore, the following series of affinities of the resins for impurities is proposed: $\text{Al} > \text{Ca} > \text{Mg}$. The increased binding strength of the functional groups with the impurities in the same direction is responsible for these affinities sequence. This finding corroborates the affinity series presented in the literature for the PUROLITE® MTS 9300 Na^+ form ($\text{Fe}^{3+} > \text{Cu}^{2+} > \text{H}^+ > \text{Hg}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+$).

The results of the loading experiments show that the selection of a resin for the recovery of REE must consider the pH of the solution. The most suitable resins are the ones whose functional groups dissociate at a pKa lower than the pH of the solution. Regarding the counter ion, activating the resin with ions that form fewer stable bonds with the functional groups and dissociate more easily is recommended. The PUROLITE® MTS 9500 activated with Na^+ showed greater efficiency in loading REE and impurities compared to the PUROLITE® MTS 9300 resin in both cycles studied, making it more indicated for this purpose.

3.3 Elution

Elution was performed with $0.05 \text{ mol L}^{-1} \text{ NH}_4\text{EDTA}$, which is considered a very suitable reagent for elution as it forms stable complexes with REE [15]. The main factor for the high stability of the complexes is that the EDTA molecule can complex metals using six potential sites for binding metal ions: four carboxylic groups and two amino groups, with each of the latter having an unpaired electron [24]. Another advantage of EDTA is its greater selectivity for REE over impurities compared to inorganic acids and salts. The elution curves of PUROLITE® MTS 9300 and PUROLITE® MTS 9500 chelating resins activated with H^+ and Na^+ are shown in Figure 4. The most important difference is observed for PUROLITE® MTS 9500 activated with Na^+ (Figure 4c), as all elements were eluted together and the curves are quite flat, especially for La. In addition, all elution peaks are superimposed. The reason for this phenomenon is the greater affinity that PUROLITE® MTS 9500 resin has for REE, as discussed in Section 3.1.2. For PUROLITE® MTS 9500 resin, it is believed that a higher concentration of NH_4EDTA could break the bond strength barrier between REE and the resin, promoting greater elution. On the other hand, from a thermodynamic point of view, the weak stability of the bonds can be used to fractionate REE using a diluted eluent, which is economically more advantageous. The profiles of all the elution curves (Figure 4) show that the fractionation of the REE was not expressive.

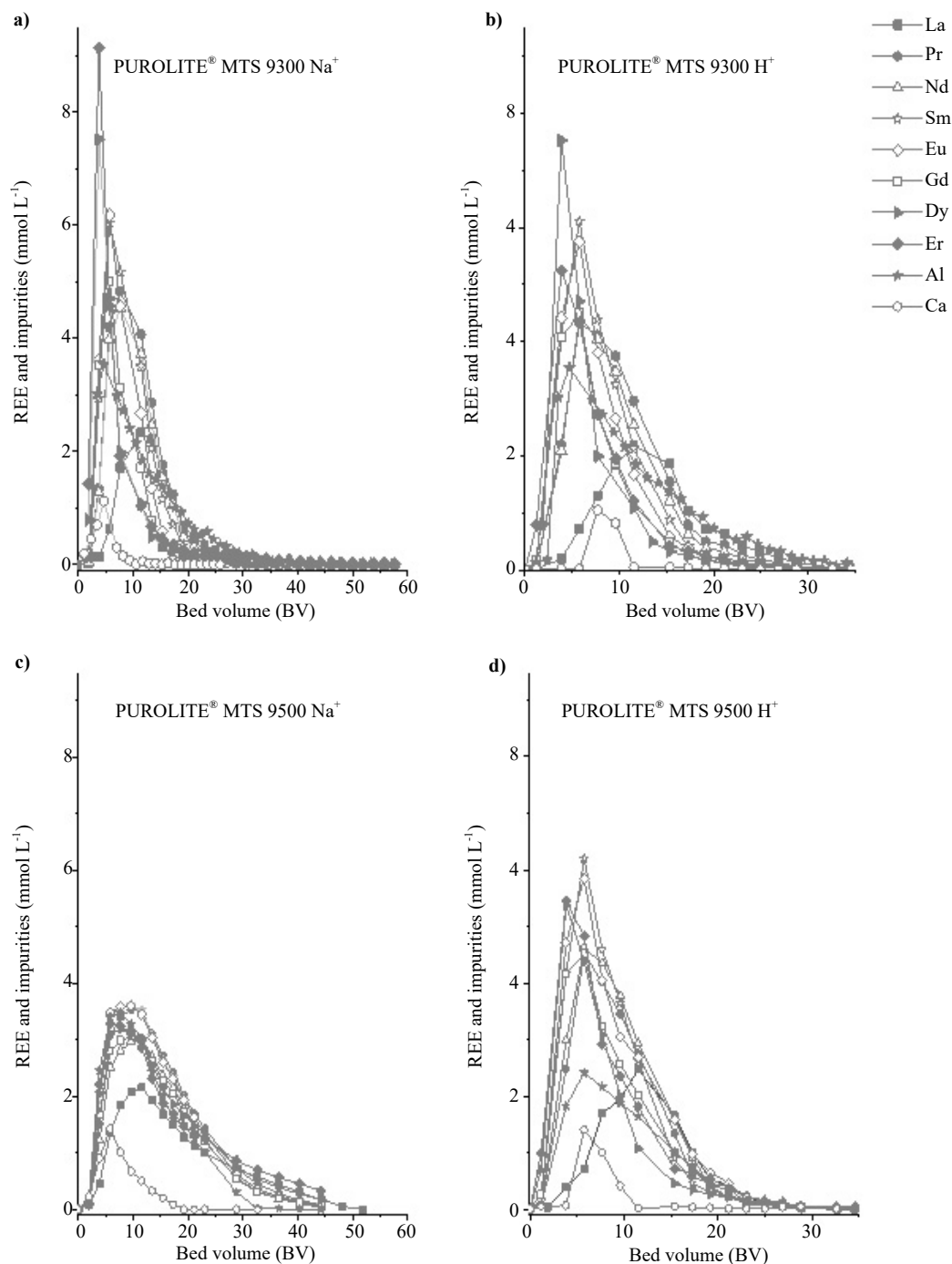


Figure 4. Elution curves for REE adsorbed in chelating resins of a) PUROLITE® MTS 9300 Na⁺, b) PUROLITE® MTS 9300 H⁺, c) PUROLITE® MTS 9500 Na⁺, and d) PUROLITE® MTS 9500 H⁺. Note: NH₄EDTA = 0.05 mol L⁻¹; residence time = 12.5 minutes; bed height = 8.0 cm; and temperature = 25 ± 5 °C

The PUROLITE® MTS 9500 H⁺ resin (Figure 4d) presents curves that are less flattened since the H⁺ form leads to lower loading of REE than activation with Na⁺, similar to those obtained by the PUROLITE® MTS 9300 resin (Figures 4a and 4b); however, the intensity of the peaks is lower, leading to a lower concentration of the elements in the eluate. For this resin, all elements were eluted at a lower BV compared to PUROLITE® MTS 9500 Na⁺ resin. For PUROLITE® MTS 9300 resin in both cycles (Na⁺ and H⁺), the elution curves are less flattened, sharper, and more intense, leading to a high content of the elements in the eluate, except for La. For both resins, the concentration of La in the eluate is lower

compared to the other REE, which demonstrates less affinity with EDTA as it prefers the REE with smaller ionic radii and larger hydrated radii which is not the case with La. A higher intensity peak for Er is observed in the elution of the PUROLITE® MTS 9300 activated with Na⁺ (Figure 4a) compared to the same resin activated with H⁺ (Figure 4b).

The Ca sorbed on the PUROLITE® MTS 9300 activated with Na⁺ was eluted from 2 BV to 8 BV, while for the same resin activated with H⁺, the Ca was eluted from 7 BV to 12 BV. That is because the hydrogen delays the complexation of elements with lower affinity for the eluent [25]. The same effect was observed for PUROLITE® MTS 9500 resin, although less intense. The concentrations of REE and metallic impurities as well as the respective elution efficiencies are shown in Table 5.

Table 5. Eluted quantity (mmol L⁻¹), elution efficiency (%) and REE concentration in the final eluate (mmol L⁻¹). The estimated error is ± 5%

		PUROLITE® MTS 9500		PUROLITE® MTS 9300	
		Na ⁺	H ⁺	Na ⁺	H ⁺
Eluted quantity (mmol g ⁻¹)	Pr	0.08	0.06	0.06	0.05
	La	0.05	0.03	0.04	0.03
	Sm	0.08	0.06	0.06	0.05
	Nd	0.07	0.06	0.05	0.05
	Gd	0.07	0.05	0.04	0.04
	Eu	0.08	0.07	0.05	0.05
	Dy	0.08	0.05	0.04	0.04
	Er	0.08	0.06	0.05	0.05
	Total	0.58	0.43	0.37	0.36
	Al	0.070	0.030	0.049	0.026
	Ca	0.010	0.002	0.004	0.004
	Total	0.080	0.032	0.054	0.030
Elution efficiency (%)	Pr	89	77	102	101
	La	77	56	87	80
	Sm	89	77	102	93
	Nd	85	100	97	100
	Gd	85	88	100	99
	Eu	89	83	87	98
	Dy	96	80	93	98
	Er	84	82	98	100
	Total	87	80	96	96
	Al	82	39	80	52
	Ca	63	22	82	82
	Total	73	31	81	67

REE concentration in the final eluate (mmol L ⁻¹)	Pr	1.30	1.46	1.51	1.50
	La	0.88	0.83	0.95	0.88
	Sm	1.30	1.61	1.54	1.30
	Nd	1.10	1.59	1.31	1.32
	Gd	1.11	1.39	1.04	1.01
	Eu	1.30	1.74	1.22	1.38
	Dy	1.25	1.25	1.02	1.02
	Er	1.23	1.46	1.17	1.04
	Total	9.48	11.33	9.76	9.45
	Al	1.14	0.78	1.30	0.68
	Ca	0.16	0.05	0.13	0.12
	Total	1.30	0.80	1.42	0.79

Elution results shown in Table 5 confirm the lower removal of La, and the best elution efficiency result was obtained by the PUROLITE® MTS 9300 resin activated with Na⁺. Although the loading was higher for PUROLITE® MTS 9500 resin in both cycles, the elution efficiency of REE was lower (87% and 80%) compared to PUROLITE® MTS 9300 resin in both cycles (96%). It can be explained by the higher electrostatic force exerted between the PUROLITE® MTS 9500 resin and the REE, as discussed before. In the Na⁺ and H⁺ cycles, about 13% and 20% of the REE previously adsorbed on PUROLITE® MTS 9500 resin were not eluted.

About impurities, Al was more eluted compared to Ca. Magnesium was not complexed by EDTA, remaining in the resin. This is due to the lower affinity of EDTA for Mg, which is advantageous for its separation from REE. This result is promising since one of the goals is to separate REE from impurities.

The final liquor contained 1.44 g L⁻¹ and 1.72 g L⁻¹ of REE for the PUROLITE® MTS 9500 resin in the Na⁺ and H⁺ cycles, respectively, and 1.47 g L⁻¹ and 1.42 g L⁻¹ of REE for the PUROLITE® MTS 9300 resin in the Na⁺ and H⁺ cycles, respectively. For the impurities, the liquor contained 0.04 g L⁻¹ and 0.02 g L⁻¹ of REE for the resins in the Na⁺ and H⁺ cycles, respectively. The concentrations for the impurities correspond to Al and Ca since the Mg was not eluted.

4. Conclusion

PUROLITE® MTS 9300 and PUROLITE® MTS 9500 resins are highly selective in adsorbing REE, to the detriment of some impurities generally found in AMD, such as Ca, Al and Mg. The efficiency of the resins in loading the REE varied from 38% to 73%, and the highest loading was obtained for PUROLITE® MTS 9500 activated with Na⁺, which was almost twice (0.67 mmol g⁻¹) the one obtained by the PUROLITE® MTS 9300 resin (0.39 mmol g⁻¹). Activation with H⁺, which forms stronger bonds with the resins, inhibited the ion exchange process due to ineffective dissociation or ionisation of the resins.

Although it presented the lowest loading for the REE, the PUROLITE® MTS 9300 showed an elution efficiency of 96%, and for the other resins, it varied from 80% to 87%. The strength of the bonds between the REE and the carboxylic group is lower compared to the bonds between the REE and the phosphonic group, which implies high elution efficiency. To summarise, the resin that loads the most REE is also the most difficult resin to elute.

Though the concentrations of the impurities in the feed solution were significantly higher than the ones for REE, Mg could be separated from the REE, and the Ca and Al content in the final liquor was significantly low, i.e., 0.02 g L⁻¹ for both resins. The maximum content of REE in the liquor after elution was 1.72 g L⁻¹. Effective fractionation or separation of the individual REE during elution with NH₄EDTA was not achieved under the experimental conditions of this work. Therefore, the use of chelating resins can be recommended mainly for the pre-concentration of REE.

Acknowledgements

The authors would like to thank CNPq, FAPEMIG, FINEP, INCT-Agua, INCT-Patria, RenovaMin, REGINA, the World Bank, Unipung, and MCTESTP-Mozambique for financial support.

Conflict of interest

There is no conflict of interest in this study.

References

- [1] Balaram V. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. *Geoscience Frontiers*. 2019; 10(4): 1285-1303. <https://doi.org/10.1016/j.gsf.2018.12.005>
- [2] Ortiz CEA, Viana Júnior EM. Rare earth elements in the international economic scenario. *Rem: Revista Escola de Minas*. 2014; 67(4): 361-366. <https://doi.org/10.1590/0370-44672014670162>
- [3] Charalampides G, Vatalis KI, Apostoplos B, Ploutarch-Nikolas B. Rare earth elements: Industrial applications and economic dependency of Europe. *Procedia Economics and Finance*. 2015; 24: 126-135. [https://doi.org/10.1016/S2212-5671\(15\)00630-9](https://doi.org/10.1016/S2212-5671(15)00630-9)
- [4] Giese EC. Rare earth elements: Therapeutic and diagnostic applications in modern medicine. *Clinical and Medical Reports*. 2018; 2(1): 1-2. <https://doi.org/10.15761/CMR.1000139>
- [5] Royen H, Fortkamp U. *Rare earth elements - Purification, separation and recycling*. IVL Swedish Environmental Research Institute. Report number: C211, 2016. <https://www.ivl.se/english/ivl/publications/publications/rare-earth-elements---purification-separation-and-recycling.html>
- [6] Bwapwa JK. A review of acid mine drainage in a water-scarce country: Case of South Africa. *Environmental Management and Sustainable Development*. 2018; 7(1): 1-20. <https://doi.org/10.5296/emsd.v7i1.12125>
- [7] Akcil A, Koldas S. Acid Mine Drainage (AMD): Causes, treatment and case studies. *Journal of Cleaner Production*. 2006; 14(12-13): 1139-1145. <https://doi.org/10.1016/j.jclepro.2004.09.006>
- [8] Hubicki Z, Kołodyńska D. Selective removal of heavy metal ions from waters and waste waters using ion exchange methods. In: Kilislioglu A. (ed.) *Ion exchange technology*. London, UK: IntechOpen; 2012. p.193-240. <https://doi.org/10.5772/51040>
- [9] Ruan W. *Recovery of rare earth elements through chelating resin*. BEng thesis. Higher Technical School of Industrial Engineering from Barcelona; 2016. https://upcommons.upc.edu/bitstream/handle/2117/98411/REE_recovery.pdf
- [10] Page MJ, Soldenhoff K, Ogden MD. Comparative study of the application of chelating resins for rare earth recovery. *Hydrometallurgy*. 2017; 169: 275-281. <https://doi.org/10.1016/j.hydromet.2017.02.006>
- [11] Hérès X, Blet V, Di Natale P, Ouattou A, Mazouz H, Dhiba D, et al. Selective extraction of rare earth elements from phosphoric acid by ion exchange resins. *Metals*. 2018; 8(9): 682. <https://doi.org/10.3390/met8090682>
- [12] Silva GC, Bertoli AC, Duarte HA, Ladeira ACQ. Recovery of rare earth elements from sulfate-rich acid mine water: Looking through the keyhole the exchange reaction for cationic resin. *Journal of Environmental Chemical Engineering*. 2022; 10(6): 108715. <https://doi.org/10.1016/j.jece.2022.108715>
- [13] Ang KL, Li D, Nikoloski AN. The effectiveness of ion exchange resins in separating uranium and thorium from rare earth elements in acidic aqueous sulfate media. Part 1. Anionic and cationic resins. *Hydrometallurgy*. 2017; 174: 147-155. <https://doi.org/10.1016/j.hydromet.2017.10.011>
- [14] José LB, Ladeira ACQ. Recovery and separation of rare earth elements from an acid mine drainage-like solution using a strong acid resin. *Journal of Water Process Engineering*. 2021; 41: 102052. <https://doi.org/10.1016/j.jwpe.2021.102052>
- [15] George WW. Comprehensive inorganic chemistry. *Journal of the American Chemical Society*. 1959; 81(1): 253-254. <https://doi.org/10.1021/ja01510a070>
- [16] Silva RA, Hawboldt K, Zhang Y. Application of resins with functional groups in the separation of metal ions/species - A review. *Mineral Processing and Extractive Metallurgy Review*. 2018; 39(6): 395-413. <https://doi.org/10.1080/08827508.2018.1459619>
- [17] Zaganianis EJ. *Ion exchange resins and adsorbents in chemical processing*. 2nd ed. Paris, France: Books on

Demand; 2016.

- [18] Smichowski P, Polla G, Gómez D, Espinosa AJF, López AC. A three-step metal fractionation scheme for fly ashes collected in an Argentine thermal power plant. *Fuel*. 2008; 87(7): 1249-1258. <https://doi.org/10.1016/j.fuel.2007.07.011>
- [19] Villemin D, Didi MA. Aminomethylenephosphonic acids syntheses and applications (A Review). *Oriental Journal of Chemistry*. 2015; 31(Special Issue1): 01-12. <https://doi.org/10.13005/ojc/31.Special-Issue1.01>
- [20] Page MJ, Quinn JE, Soldenhoff KH. The impact of sulfate ions on the ion exchange of rare earth elements. *Hydrometallurgy*. 2019; 186: 12-20. <https://doi.org/10.1016/j.hydromet.2019.03.003>
- [21] Wood SA. The aqueous geochemistry of the rare-earth elements and yttrium: 1. Review of available low-temperature data for inorganic complexes and the inorganic REE speciation of natural waters. *Chemical Geology*. 1990; 82: 159-186. [https://doi.org/10.1016/0009-2541\(90\)90080-Q](https://doi.org/10.1016/0009-2541(90)90080-Q)
- [22] Moraes MLB, Murcieto A, Álvarez-Ayuso E, Ladeira ACQ. The role of Al₁₃-polymers in the recovery of rare earth elements from acid mine drainage through pH neutralization. *Applied Geochemistry*. 2020; 113: 104466. <https://doi.org/10.1016/j.apgeochem.2019.104466>
- [23] Serrano MJG, Sanz LFA, Nordstrom DK. REE speciation in low-temperature acidic waters and the competitive effects of aluminum. *Chemical Geology*. 2000; 165(3-4): 167-180. [https://doi.org/10.1016/S0009-2541\(99\)00166-7](https://doi.org/10.1016/S0009-2541(99)00166-7)
- [24] Skoog DA, West DM, Holler FJ, Crouch SR. *Fundamentals of analytical chemistry*. [Fundamentos da química analítica]. 8th ed. Massachusetts, United States: Cengage Learning; 2006.
- [25] Spedding FH, Wheelwright EJ, Powell JE. *Method of separating rare earths*. US2798789A (Patent) 1954.