

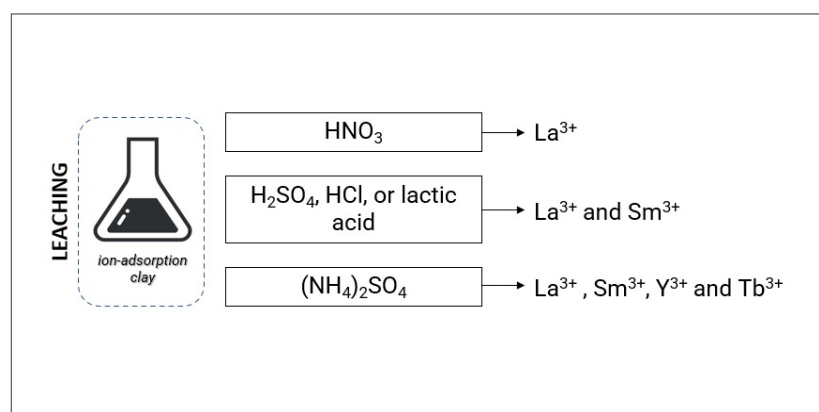
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Recovery of Rare-Earth Elements from Brazilian Ion-Adsorption Clay: A Preliminary Study

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Ion-adsorption clays (IAC) are aluminosilicate ores, considered an essential source of heavy rare-earth elements (REE). With the increasing discovery and exploitation of IAC deposits, the present work sought to evaluate different methods of solubilization of REE through the use of different concentrations of inorganic acids (H_2SO_4 , HCl , and HNO_3), as well as different concentrations of ammonium sulfate and lactic acid. According to the results, the sulfuric acid solution favored the solubilization of both La^{3+} and Sm^{3+} elements. The solubilization of REE in the presence of ammonium sulfate showed no significant differences as a function of the leaching time but favored the solubilization of Y^{3+} and Tb^{3+} . More efficient solubilization of Sm^{3+} was observed with the addition of lactic acid at a concentration of 30 g L^{-1} , leading to 90% (4.5 ppm) of Sm^{3+} extraction. The solubilization of La^{3+} was favored by the contact time, with higher Sm^{3+} extraction yields in 14 days of leaching.

Graphical abstract



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1. Introduction

The Rare Earth Elements (REE) are composed of 17 elements from the periodic table, including lanthanides (atomic number 57 to 71), scandium (atomic number 21), and yttrium (atomic number 39), which have similar chemical behavior due to the occurrence of a phenomenon known as lanthanide contraction. In general, REE can be divided into light rare-earth elements (LREE), comprising atomic numbers lower than those of gadolinium (an atomic number between 57 and 63); and heavy rare-earth elements (HREE), comprising atomic numbers higher than those of europium (an atomic number between 64 and 71). HREE are scarcer and more difficult to process than LREE, which makes them

proportionally more valuable [18, 1].

In terms of mineral resources, 95% of the total REEs are contained in the three minerals bastnaesite-(Ce) [(Ce, La) CO_3F], monazite-(Ce) [(Ce, La) PO_4] and xenotime-(Y) (YPO_4) [14,20]. HREE are found in greater abundance in the mineral known as ion-adsorption clay (IAC), whose levels of rare-earth oxides are relatively low, between 0.05 and 0.30%. The most significant reserves are located in China, followed by Brazil and Vietnam. Nevertheless, it must be considered that most of the world's supply currently originates from China. In 2018, approximately 70% of the world's production was mined in China. In comparison, only 2% of the world's

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mine production originated from Brazil [2]. REEs are found in ions adsorbed in places of permanent negative charge to the outer layers of phyllosilicates. The IAC deposits result from lateritic weathering "in situ" of REE-rich host rocks and consist of aluminosilicate clay minerals, e. g. kaolinite, illite, and smectite [10, 22].

The REE properties make them essential for the high-tech industry due to their diverse uses, influencing an excellent search for REE by the industrial sector. They classified as 'critical' metals as they play an essential role in industrial applications as catalysts, in glass and ceramics, in permanent magnets for CO₂-free energy generation, efficient electrical motors and consumer electronics, catalytic converters in cars and petroleum industry, and special alloys [12,5–6]. Due to their chemical similarity, the separation and purification of individual REEs become expensive and complicated, and the alternative process has been used for the extraction and recovery of REE from primary and secondary sources [21,7–9]. As a result, several studies have been carried out on REE desorption from clays using ion-exchange leaching.

The REE cations are adsorbed onto aluminosilicates and are distributed onto Fe- and Mn-oxides or organic fractions, being substituted by K⁺ or Ca²⁺. The leaching of REE from IAC has been used extensively for REE processing. In the IAC, 60-90% of the REE are adsorbed on to the surface of phyllosilicate minerals like kaolinite [Al₂Si₂O₅(OH)₄], halloysite [Al(OH)₆Si₂O₅(OH)₃] or muscovite [KAl₂(AlSi₃O₁₀)(OH)₂]. These adsorbed REEs can be quickly recovered by leaching with monovalent electrolytic salt solutions such as sodium or ammonium-based systems. However, up to now, 10-40 % of the REE are remaining in two phases, a colloid phase as REE-oxides and REE-hydroxides; or a mineral phase. These remaining REE can be liberated by acid leaching [17,23]. Thus, the present work sought to evaluate different leaching agents for REE extraction from a Brazilian ion-adsorption clay sample.

2. Material and Methods

Solubilization of Brazilian ion-adsorption clay by acid leaching

The sample used is an IAC from a central-west Brazilian deposit. The effect of the mixture of three different acids (H₂SO₄, HCl, HNO₃) on the solubilization of REE from IAC was evaluated through a statistical mixture-design totaling 7 experimental runs. The acid solutions were prepared in a concentration equal to 10% (v v⁻¹). For IAC solubilization tests, about 0.5g of IAC was added in 150 mL Becker glass containing 50 mL of different acid mixtures, as shown in Table 1. The experimental runs remained on a shaking table, at room temperature, under constant agitation of 100 rpm over 60 minutes. After the end of the stirring, 20 mL of the leachate was centrifuged at 4000 rpm and 25 °C for 15 minutes, and the supernatant was collected for analysis by the technique of optical emission spectrometry with inductively coupled plasma (ICP-OES).

In a mixture experiment, the sum of the component fractions must be equal to unity, and their proportions must be non-negative. The restrictions on the levels of each factor are expressed as follows:

$$\sum_{i=1}^q x_i = 1 \quad (\text{i.e., 100\%}) \quad (1)$$

x_i represents the proportion of the i^{th} component in the mixture, and q is the number of components. The independent variables in the mixture experiments for optimization of REE extraction (Y , mg L⁻¹) were: x_1 (H₂SO₄, mL), x_2 (HCl, mL), and x_3 (HNO₃, mL) as described in Table 1. Analysis of variance (ANOVA) and multiple regression analyses was performed using Statistica version 13.5 (StatSoft, Inc.).

Table 1. Statistical mixture-design matrix defining conditions for solubilization of Brazilian ion-adsorption clay by acid leaching.

| Run | H ₂ SO ₄ (x_1) | HCl (x_2) | HNO ₃ (x_3) |
|-----|---|------------------|-------------------------------|
| 1 | 0 | 0 | 1 |
| 2 | 1 | 0 | 0 |
| 3 | 0 | 1 | 0 |
| 4 | 0.5 | 0 | 0.5 |
| 5 | 0.5 | 0.5 | 0 |
| 6 | 0 | 0.5 | 0.5 |
| 7 | 0.33 | 0.33 | 0.33 |

Solubilization of Brazilian ion-adsorption clay by (NH₄)₂SO₄ solution and lactic acid

The tests were carried out in a Becker solution containing 200 mL of 0.5 M (NH₄)₂SO₄ for 6 different tests, in duplicate, where 3 tests were performed using concentrations of 1, 2.5, and 5% (v v⁻¹) of IAC; and 3 tests with the addition of lactic acid in concentrations of 10, 20 and 30 g L⁻¹ containing 2.5% (w v⁻¹) of IAC.

The tests were carried out in 500mL Erlenmeyer flasks containing 200mL of leaching solution, which were kept under constant agitation at 100 rpm for periods of 3, 10, and 14 days at a temperature of 25 °C. During the collection periods for analysis, 20 mL of solution were removed, centrifuged at 4000 rpm and 25 °C for 15 minutes, and the supernatant was collected for analysis by the technique of optical emission spectrometry with inductively coupled plasma (ICP-OES).

3. Results and Discussion

Solubilization of Brazilian ion-adsorption clay by acid leaching

The evaluation comparing the acid solutions (H₂SO₄, HCl, and HNO₃) indicates higher La³⁺ and Sm³⁺ species recoveries depending on acid-based systems. This can be attributed to the intended liberation of light REE from the exchangeable phase and the colloid phase [16].

In the present work, a statistical mixture-design technique was used to study the effects of different acids and their mixtures on the REE extraction from Brazilian ion-adsorption clay, as described in Table 1. An equation was obtained for the solubilization of La³⁺ (Y_1 , Equation 2) and Sm³⁺ (Y_2 , Equation 3) through the analysis of the multiple regressions of the experimental data.

$$Y_1 = 0.254952x_1 + 0.17895x_2 + 0.118952x_3 \quad (2)$$

$$Y_2 = 0.133143x_1 + 0.133143x_2 \quad (3)$$

According to Figure 1A, the solubilization of La³⁺ was higher in the presence of H₂SO₄ than in the mixture of the different acids (H₂SO₄ > HCl > HNO₃). Already to the solubilization of Sm³⁺ (Figure 1B), both H₂SO₄ and HCl have similar leaching rates, while HNO₃ was not significant.

Preferential solubilization of these two REEs was observed in a single mineral acid presence than when IAC was solubilized

using a mixture of the three different acids tested.

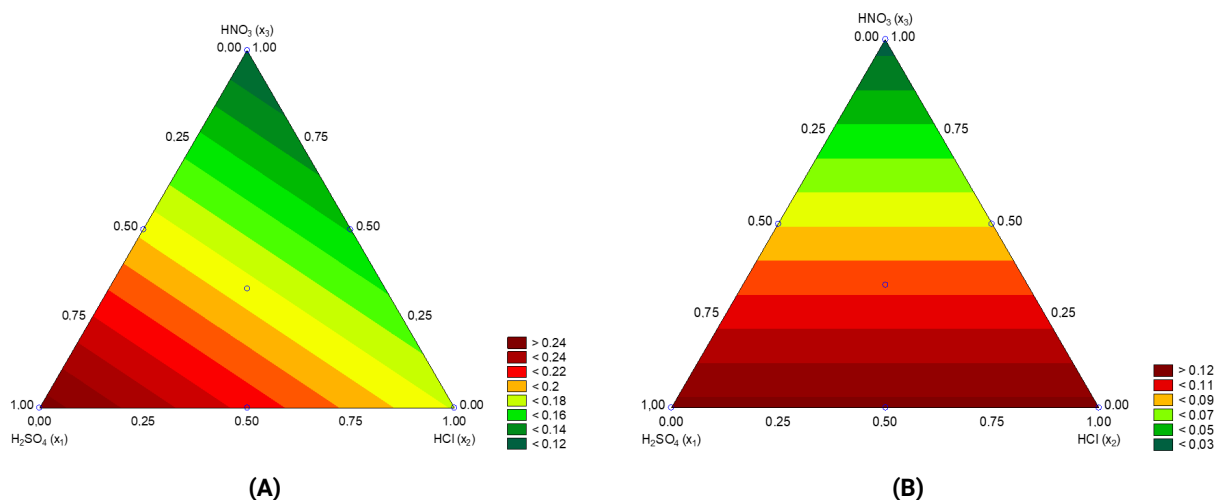


Fig. 1. Response surface contours for solubilization of Brazilian ion-adsorption clay by acid leaching. (A) La³⁺ extraction (mg L⁻¹) and (B) Sm³⁺ extraction (mg L⁻¹).

Pareto charts, depicted in Figure 2A and Figure 2B, show the standardized effects, i.e., the effects divided by their respective standard deviation, enabling the identification of the statistically significant effects and the most relevant factors. The vertical line ($p = 0.05$) indicates the minimum magnitude of statistically significant effects, considering the

statistical significance of 95%. For La³⁺ solubilization, all acids tested presented a statistically significant effect (Figure 2A). On the other hand, for Sm³⁺ solubilization, the variable x₃, HNO₃ concentration, did not statistically significant effect (Figure 2B).

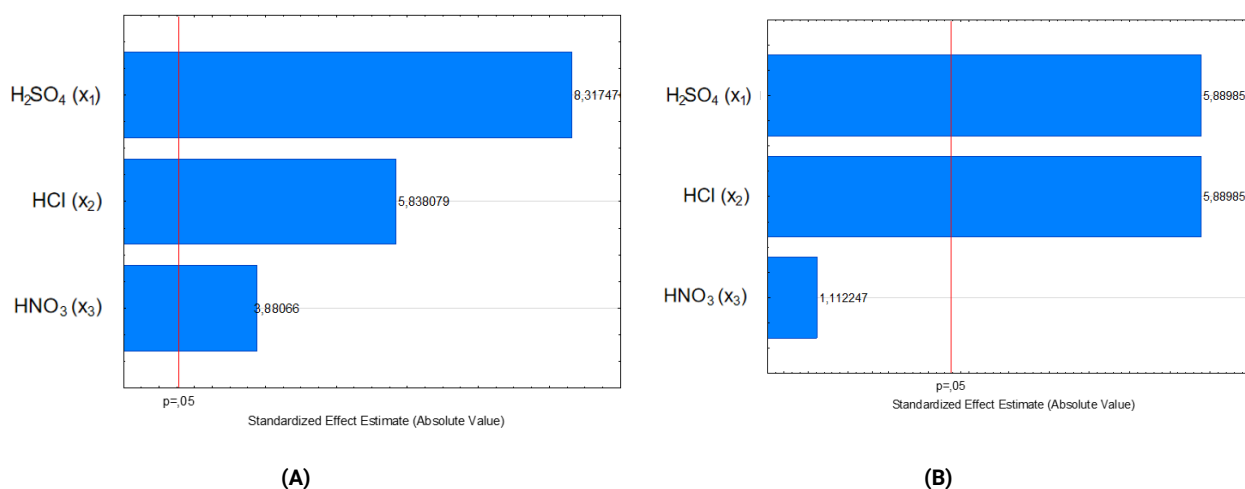


Fig. 2. Pareto charts of standardized effects for solubilization of Brazilian ion-adsorption clay by acid leaching. (A) La³⁺ extraction (mg L⁻¹) and (B) Sm³⁺ extraction (mg L⁻¹).

Solubilization of Brazilian ion-adsorption clay by (NH₄)₂SO₄ solution and lactic acid

Table 2 shows the solubilization of REE from IAC in different concentrations of (NH₄)₂SO₄. According to the data presented, the solubilization of La³⁺, Sm³⁺, Y³⁺, and Tb³⁺ did not show significant differences in the leaching time. The increase in the concentration of IAC favored the solubilization of La³⁺. Rare-earth elements are incorporated in accessory minerals in various rocks as bastnäsite, monazite, xenotime, and ion-adsorption ores [18]. Ion-adsorption ores are substantially lower grades than other types of lanthanide sources, and a simple leach using monovalent sulfate or chloride solutions at ambient temperature can recovery REE

[11].

Table 3 shows the solubilization of REE from IAC under different concentrations of lactic acid conditions. The most efficient Sm³⁺ solubilization was observed than in the test conditions used previously, obtaining better results at lactic acid concentrations equal to 30 g L⁻¹, leading to 90% (4.5 ppm) of extraction. In 14 days, the solubilization of La³⁺ proved to be more efficient than in the presence of only (NH₄)₂SO₄, not being different for shorter times, also with a higher rate of solubilization with the addition of lactic acid, as shown in Table 3. Fuguo et al. [4] had shown that about 86.2% REE colloid sediment phase was dissolved into the leaching liquor when MgSO₄ (0.15 mol L⁻¹) and ascorbic acid (1.0 g L⁻¹) was

used.

Table 2. Solubilization of Brazilian ion-adsorption clay in the presence of ammonium sulfate [(NH₄)₂SO₄].

| IAC (%) | Time (days) | La (ppm) | Sm (ppm) | Y (ppm) | Tb (ppm) |
|---------|-------------|----------|----------|---------|----------|
| 1.0 | 3 | 0.07 | 0.24 | 0.09 | 0.09 |
| | 10 | 0.07 | 0.00 | 0.08 | 0.09 |
| | 14 | 0.11 | 0.13 | 0.06 | 0.06 |
| 2.5 | 3 | 0.09 | 0.05 | 0.08 | 0.09 |
| | 10 | 0.10 | 0.14 | 0.07 | 0.06 |
| | 14 | 0.18 | 0.13 | 0.06 | 0.06 |
| 5.0 | 3 | 0.10 | 0.15 | 0.08 | 0.09 |
| | 10 | 0.10 | 0.14 | 0.06 | 0.06 |
| | 14 | 0.15 | 0.13 | 0.06 | 0.06 |

Table 3. Solubilization of Brazilian ion-adsorption clay in the presence of ammonium sulfate [(NH₄)₂SO₄] and lactic acid.

| Lactic acid (g/L) | Time (days) | La (ppm) | Sm (ppm) | Y (ppm) | Tb (ppm) |
|-------------------|-------------|----------|----------|---------|----------|
| 10 | 3 | 0.08 | 0.94 | N.D. | N.D. |
| | 10 | 0.10 | 0.94 | N.D. | N.D. |
| | 14 | 0.35 | 1.65 | N.D. | N.D. |
| 20 | 3 | 0.09 | 1.45 | N.D. | N.D. |
| | 10 | 0.08 | 1.65 | N.D. | N.D. |
| | 14 | 0.20 | 3.1 | N.D. | N.D. |
| 30 | 3 | 0.09 | 1.80 | N.D. | N.D. |
| | 10 | 0.11 | 2.30 | N.D. | N.D. |
| | 14 | 0.19 | 4.5 | N.D. | N.D. |

N.D. = not detected.

The ion-adsorption ores contain clays with permanent negative surface charge, responsible for REE adsorption via electrostatic bonds [15]. REE can be deposited in (a) colloidal phase, as insoluble oxides or hydroxides or as part of colloidal polymeric organometallic compounds, which can be extracted only by acid leaching; (b) exchangeable phase, as soluble hydrated cations or part of positively-charged complexes which can be recovered by ion-exchange leaching with monovalent salts or (c) mineral phase, as part of fine solid particles with the same mineral matrix as the host rocks [3]. The processes of REE adsorption to the clays are involved and affected by many factors [13]. The results from Brazilian ion-adsorption clay acid leaching showed that light REE La³⁺ and Sm³⁺ were recovered in sulfate and nitrate systems, respectively. In acid electrolyte systems, light REE La³⁺ and Sm³⁺ and heavy REE Y³⁺ and Tb³⁺ could be recovered using ammonium sulfate and lactic acid as leaching agents.

4. Conclusions

The ongoing development of new advanced technologies created increasing demands for REE in the international markets, emphasizing new resources to ensure adequate supply and access. This preliminary study indicated that the mechanism of acid leaching of Brazilian ion-adsorption clay depending on the acid used, being possible the solubilization of La³⁺ in HNO₃, HCl, and H₂SO₄, and the best results were obtained in the presence of H₂SO₄. Sm³⁺ solubilization did not occur in the presence of HNO₃, being more efficient in the presence of H₂SO₄. The IAC solubilization with (NH₄)₂SO₄ solutions resulted in the extraction of Y³⁺ and Tb³⁺. The extraction yields of La³⁺ and Sm³⁺ occurred with levels of 90% in 14 days. The addition of lactic acid favored only the solubilization of LREE La³⁺ and Sm³⁺ to the detriment of HREE,

Y³⁺, and Tb³⁺. These studies are essential due to REE are quickly released from ion-adsorption clays by low-cost processes, either by *in-situ* leaching or heap leaching with acid and electrolyte solutions.

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Author Contributions

Ana Carolina S. P. de Souza: Data curation, Investigation, Writing – original draft. Ellen C. Giese: Conceptualization, Formal analysis, Methodology, Resources, Supervision, Writing – review & editing.

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