An exploratory study of recovery of rare-earth elements from monazite in mild conditions using statistical-mixture design

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Abstract: Monazite is a phosphate mineral, considered an essential source of light rare-earth elements (REE). 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) and organic acids (citric, oxalic, and lactic) in mild conditions at room temperature. According to the results, the inorganic acid solutions favored the solubilization in order of Ce^{3+}, La^{3+}, Nd^{3+}, Pr^{3+}, and Sm^{3+} elements, while organic acid solutions only favored the solubilization of Ce^{3+} and La^{3+}. Nitric acid was the more efficient leaching agent for the first group. In the case of organic acids, lactic acid solubilized Ce^{3+}, while mixtures of lactic and citric acids appeared to solubilize La^{3+}.

Keywords: Monazite, Rare-Earth elements, Chemical leaching, Design of Experiments.

1. Introduction

Monazite is an orthophosphate with a predominance of light rare-earth elements (REE). Monazite has a chemical formula (Ce, La, Nd, Th)O_4, containing approximately 70% of rare-earth oxides (REO). Radioactive elements, about 0.1-30% thorium (Th) and up to 1.5% uranium (U), can be found in its composition, responsible for imparting electrical, magnetic, and catalytic properties to some REO. In addition to these elements, moderate amounts of iron (Fe), aluminum (Al), calcium (Ca), magnesium (Mg), silica (Si), titanium (Ti), and zirconium (Zr) can be found in monazite also [1].

Lanthanides or REE can be classified into (i) light (57-60): lanthanum (La), cerium (Ce), praseodymium (Pr) and neodymium (Nd); (ii) medium (61-64): promethium (Pm), samarium (Sm), europium (Eu) and gadolinium (Gd); (iii) heavy (65-71): terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb) and lutetium (Lu). Currently, REE is increasingly used in industries related to green energy, as for hybrid cars, electric motors, and wind turbines [2].

The first mineral containing REE to be explored industrially was the monazite. Its name is derived from the Greek monazein, which means "to be alone," observed for its characteristics of crystals granted and

for being quite rare during its discovery, giving an allusion to the rarity of the mineral [3]. In physical processing, heavy minerals concentration comes from various methods, involving density, electrostatic and magnetic separations, depending on the mineralogical assembly of the minerals to be used [4]. Monazite is predominantly a by-product of sand mining with heavy minerals, from where Ti and Zr minerals are also commonly explored.

The acid leaching process is a technique that aims at solubilizing metals using an acid, which can be under constant agitation and controlled temperature. During the process, a substance that is sought to be obtained is extracted from a solid matrix through its dissolution by a leaching agent, selectively chosen according to its ability to dissolve the metal [5]. According to Kim & Osseo-Asare [6], monazite undergoes physical processing first, followed by chemical processing, which can occur through acid treatment using sulfuric acid. The sulfate (SO_4^{2-}) ion of sulfuric acid can act as a ligand which reacts with REE as follows [7]:

$$2REEPO_4(s) + 3H_2SO_4 = (REE)_2(SO_4)_3(s) + 6H^+ + 2PO_4^{-3}$$

In the last decade, several studies have been published addressing the interactions between microorganisms and minerals carrying REE, including the solubilization of REE from definite matrices through

reactions with microbial metabolites [8] and immobilization of REE of liquid matrices, mainly by sorption by biomass [9-13].

The microbially mediated REE solubilization occurs mainly via acidolysis, oxidoreduction, and complexation reactions. Acidolysis, that is, the proton-induced metal ion solubilization implies the exchange and replacement of metallic elements from mineral surfaces by protons. The REE mobilization through reducing or oxidative reactions or through the action of metabolically produced complexing agents has also been described in the literature [14].

Biohydrometallurgy can be considered an emerging green technology for the recovery of metals due to its environmentally friendly, simple, and economical processing. Bioleaching consists of a hydrometallurgical process of dissolving minerals through a group of microorganisms capable of producing acids and or oxidizing agents from the constituents of the ore itself in the leaching process [15]. However, few studies seek to elucidate the biological advantage of the interaction between microorganisms and minerals with REE [16, 17].

Few researchers have studied the assistance of microbial organic acid producers in the monazite bioleaching process. Thus, the present work sought to evaluate different leaching agents for REE extraction from a Brazilian monazite sample using a mixture-design experiment.

2. Experimental

Analytical grade reagents were used in preparing acid concentrations of 100 g L^{-1}. These acids were used in chemical leaching tests that mimicked metal dissolution achieved by microorganisms under mild temperature conditions. For monazite leaching tests, about 0.5 g of monazite sample was added in 150 mL Becker glass containing 50 mL of different acid mixtures.

The effect of the mixture of two sets containing three different inorganics (H_2SO_4, HCl, HNO_3) (Table 1) or organics (citric, oxalic, lactic) (Table 2) acids on the solubilization of REE from Brazilian monazite was evaluated through a statistical mixture-design.

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. Determination of the final concentration of metal ions in solution was performed by inductively-coupled plasma atomic emission spectrometry (ICP-OES Perkin Elmer, OPTIMA3000, USA).

Table 1. Statistical mixture-design matrix defining conditions for inorganic leaching of Brazilian monazite.

Run	H_2SO_4	HCl	HNO_3	Ce	La	Nd	Pr	Sm
	(x_1)	(x_2)	(x_3)	(Y_1)	(Y_2)	(Y_3)	(Y_4)	(Y_5)
1	0	0	1	1.03	0.52	0.39	0.11	0.09
2	1	0	0	2.58	1.21	0.96	0.26	0.19
3	0	1	0	3.63	2.00	1.37	0.37	0.26
4	0.5	0	0.5	1.00	0.48	0.39	0.10	0.08
5	0.5	0.5	0	3.13	1.61	1.17	0.31	0.22
6	0	0.5	0.5	1.07	0.67	0.42	0.11	0.09
7	0.33	0.33	0.33	1.22	0.69	0.46	0.12	0.11

Table 2. Statistical mixture-design matrix defining conditions for organic leaching of Brazilian monazite.

Run	Citric	Oxalic	Lactic	Ce	La	Nd	Pr	Sm
	(x_4)	(x_5)	(x_6)	(Y_6)	(Y_7)	(Y_8)	(Y_9)	(Y_{10})
1	0	0	1	0.15	0.09	N.D.	N.D.	N.D.
2	1	0	0	0.06	0.06	N.D.	N.D.	N.D.
3	0	1	0	0.19	0.10	N.D.	N.D.	N.D.
4	0.5	0	0.5	0.04	0.04	N.D.	N.D.	N.D.
5	0.5	0.5	0	0.03	0.04	N.D.	N.D.	N.D.
6	0	0.5	0.5	0.16	0.09	N.D.	N.D.	N.D.
7	0.33	0.33	0.33	0.02	0.03	N.D.	N.D.	N.D.

N.D., not detected.

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:

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

x_i represents the proportion of the ith 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: inorganic acid leaching set: x_1 (H_2SO_4, mL), x_2 (HCl, mL), and x_3 (HNO_3, mL); and organic acid leaching set: x_1 (citric, mL), x_2 (oxalic, mL), and x_3 (lactic, mL).

Analysis of variance (ANOVA) and multiple regression analyses was performed using Statistica version 13.5 (StatSoft, Inc.).

3. Results and Discussion

The use of statistical methodologies such as response surface methodology (RSM) and Box-Behnken to optimize monazite ore leaching has been reported in the literature [18]. In the present work, a statistical mixture-design technique was used to study the effects of different inorganic and organic acids and their mixtures on the REE extraction from Brazilian monazite, as described in Table 1 and Table 2. An equation was obtained for the inorganic acid leaching (H_2SO_4, HCl, HNO_3) of Ce^{3+} (Y_1, Equation 2), La^{3+} (Y_2, Equation 3), Nd^{3+} (Y_3, Equation 4), Pr^{3+} (Y_4, Equation 5) and Sm^{3+} (Y_5, Equation 6) through the analysis of the multiple regressions of the experimental data:

$$Y_1 = 3.218095x_3 \qquad (2)$$

$$Y_2 = 1.807048x_3 \qquad (3)$$

$$Y_3 = 1.215810x_3 \qquad (4)$$

$$Y_4 = 0.325143x_3 \qquad (5)$$

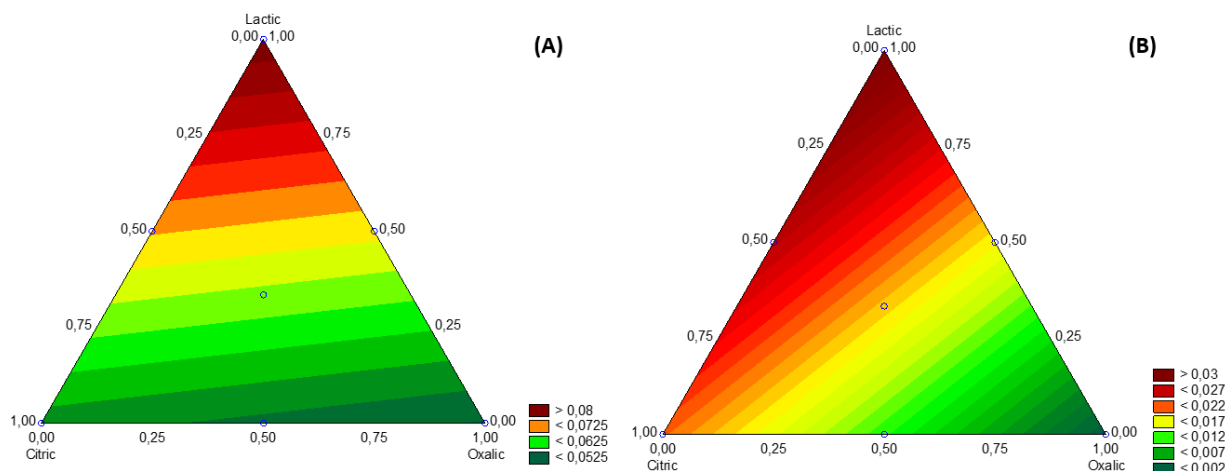$$Y_5 = 0.232571x_3 \qquad (6)$$

Effect terms of the variable x_1 (sulfuric acid) and x_2 (chloridric acid) were discarded as non-significant, as shown in the variance analysis (ANOVA). According to Figure 1, the solubilization of REE had increased following the REE molecular weight, and the order of REE extractions was $Ce^{3+} > La^{3+} > Nd^{3+} > Pr^{3+} > Sm^{3+}$.

To date, sulfuric acid is the primary acid that has been used industrially for extracting REE from monazite. However, different researchers used nitric acid to dissolve monazite and other associated metals from apatites (phosphorites) containing monazite [19]. Apparently, nitric acid is more effective for leaching REE from phosphorites than sulfuric acid [20]. Monazite from East Siberia, e.g., containing 3-7% REO, was leached in HNO_3 [21].

Organic acids have been studied as alternative leaching reagents for REE extraction from REE-bearing ores to address those issues and provide environmentally acceptable techniques. The organic acid is an alternative chemical to replace the strong acid in the leaching process. This is because the organic acid has a low level of a hazard than the strong acid [22]. The dissolution of minerals by organic acid weathering is usually explained based on surface reaction models in which the dissolution rate is positively correlated with the concentration of protonated, deprotonated, and organic complexes on the surface of the solid phase [23]. Metabolic products from the growth of *Aspergillus terreus* and *Paecilomyces* spp. Fungal strains have leached REE from monazite to concentrations 1.7-3.8 times those of HCl solutions. Organic acids released by these microorganisms included acetic, citric, gluconic, itaconic, oxalic, and succinic acids [16].
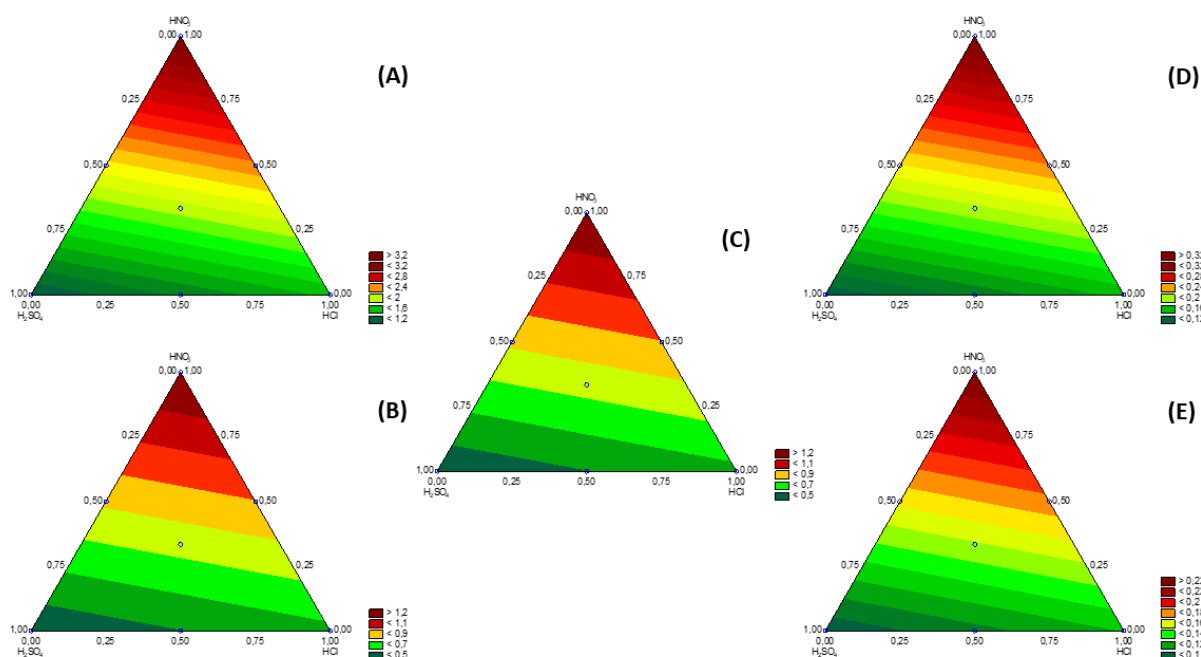
Figure 1. Response surface contours for chemical leaching of Brazilian monazite by inorganic acid leaching. (A) Ce^{3+} extraction (mg L^{-1}); (B) La^{3+} extraction (mg L^{-1}); (C) Nd^{3+} extraction (mg L^{-1}); (D) Pr^{3+} extraction (mg L^{-1}) and (E) Sm^{3+} extraction (mg L^{-1}).

Figure 2. Response surface contours for chemical leaching of Brazilian monazite by organic acid leaching. (A) Ce^{3+} extraction (mg L^{-1}) and (B) La^{3+} extraction (mg L^{-1})

An equation was obtained for the organic acid leaching (citric, oxalic, lactic) of Ce^{3+} (Y_6, Equation 7) and La^{3+} (Y_7, Equation 8) through the analysis of the multiple regressions of the experimental data:

$$Y_6 = 0.084286x_3 \qquad (7)$$

$$Y_7 = 0.033238x_3 \qquad (8)$$

Effect terms of the variables x_1 (citric acid) and x_2 (oxalic acid) were discarded as non-significant, as shown in the variance analysis (ANOVA). According to Figure 2, REE's solubilization has increased following the REE molecular weight, and the order of REE extractions was $Ce^{3+} > La^{3+}$.

No contents of Nd^{3+}, Pr^{3+}, and Sm^{3+} were detected in the leachates. Greater than 40% solubilization of Ce^{3+} and La^{3+} was obtained by Lazo et al. [24] from an oxalic acid leaching following EDTA precipitation. Analysis of the solids determined that the REE were re-precipitating as oxalate salts [25]. Also, according to Figure 2, lactic acid was able to solubilize Ce^{3+} (Figure 2A) while mixtures of lactic and citric acid seemed to be able to solubilize La^{3+} (Figure 2B). The order of strength of studied acids is oxalic ($pK_a = 1.25$) > citric ($pK_a = 3.13$) > lactic ($pKa = 3.83$).

Lactic acid is an α-hydroxy acid and contains a carboxyl group adjacent to a hydroxyl group. The presence of an α-hydroxyl group increases the acidity compared with that of an average monobasic acid. Lactic acid leaching systems have been employed successfully in sustainable REE recovery from monazite [26]. In addition to reducing pH, which somewhat increases phosphate minerals' solubility, some organic acids can form complexes with the cations released from phosphate minerals and thus improve overall solubilization.

4. Conclusion

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 monazite depends on the acid used, possibly the solubilization of Ce^{3+} and La^{3+} under organic acid leaching conditions. These studies are essential to developing bioleaching process methods for a sustainable REE extraction.

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Author's contribution
Ana Carolina S. P. de Souza carried out the experiments. Ellen C. Giese conceived the original idea, supervised the project and wrote the manuscript.

Conflict of interest
The authors have no conflicts of interest to declare that they are relevant to the content of this article.

Cite this Article

A.C.S.P. Souza, E.C. Giese, An exploratory study of recovery of rare-earth elements from monazite in mild conditions using statistical-mixture design, International Research Journal of Multidisciplinary Technovation, Vol 3, Iss 2 (2021) 20-25. DOI: https://doi.org/10.34256/irjmt2124