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Circular economy approach for the development of niobium nano-adsorbents

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Abstract

Niobium (Nb) is a metal of significant commercial importance for Brazil, as it holds approximately 98% of the world's reserves. Niobium can be sourced from primary (ores) and secondary (mining tailings) sources. Columbite is a naturally occurring mineral that may be present in mining tailings. A circular economy process is proposed to recover Nb from columbite as a secondary source and obtain raw material for the synthesis of nano-adsorbents. Initially, columbite was characterized, followed by pre-treatment with NaOH at columbite:NaOH ratios of 5:5, 5:4, and 5:3. The effects of temperature (25–95°C) and time (15–180 min) on the process were evaluated. Subsequently, leaching was performed using mineral acids (H_2SO_4, HCl, HNO_3, and H_3PO_4) and organic acids ($C_2H_2O_4$, $C_4H_6O_5$, $C_4H_6O_6$, and $C_6H_8O_7$) at acid concentrations ranging from 1 to 10 mol/L. Columbite was found to contain 24.5 wt% Nb. The best leaching performances were achieved with HCl (43.1%) and $C_2H_2O_4$ (86.4%). The highest Nb extraction rates were observed at temperatures of 70–80°C over 180 min. The leaching process was effective in extracting Nb, leading to its dissolution in an aqueous solution. This method allowed for the recovery of Nb in a form suitable for controlled precipitation. The extracted niobium can then be used as a raw material for the synthesis of nano-adsorbents, leveraging its chemical properties for applications in photocatalysis, purification, and separation processes.

*Keywords:*Circular economy; secondary sources; columbite; niobium.

1. Introduction

The circular economy is increasingly important in reducing environmental impacts and enhancing resource efficiency, especially in the mining sector, which produces large volumes of waste.[1,2] Mining residues, if properly managed, can be valuable sources of metals like niobium. Columbite, a niobium-rich mineral, can serve as both a primary and secondary source, depending on whether it is mined or recovered from tailings.[3] Adopting a circular approach that recycles mining waste aligns with sustainable practices, enabling the recovery of niobium and its use in the synthesis of nano-adsorbents, supporting green technologies in purification and catalysis.[4]

Hydrometallurgy is a key method for extracting metals like Nb from ores and mining residues using aqueous chemistry, primarily through leaching. It is considered environmentally friendly compared to pyrometallurgy, as it operates at lower temperatures, reducing energy use and emissions.[5] In niobium recovery, hydrometallurgical processes offer an efficient and cleaner alternative, aligning with circular economy principles by minimizing environmental impact while recovering valuable resources.

Niobium precipitated from leaching solution can serve as a valuable raw material for the synthesis of nano-adsorbents, which are widely used in environmental and industrial applications. Nano-adsorbents are typically synthesized using various methods, such as sol-gel processes, hydrothermal synthesis, and co-precipitation, each offering control over particle size, surface area, and morphology.[6]

The objective of this study is to propose a circular economy process to recover Nb from columbite as a secondary source and utilize it as a raw material for the synthesis of nano-adsorbents. By focusing on the recycling of mining residues, the process aims to reduce environmental impact while recovering valuable metals. This approach not only aligns with sustainable resource management but also supports the production of advanced materials, promoting both waste valorization and the development of green technologies.

2. Materials and methods

Columbite was analyzed using X-ray diffraction (XRD, MiniFlex 300, Rigaku) with copper Kα radiation (λ = 1.5418 Å), in step mode operating at 30 kV and 10 mA, over a 2θ range of 20° to 80°, with a step size of 0.02° and a scan speed of 2°/min. The particle size distribution was determined using laser diffraction granulometry, forming the granulometric profile (Malvern Mastersizer 2000 - wet particle size analyzer). For chemical characterization, the columbite was digested using a sample-to-$LiBO_2$ ratio of 1:24. The sample (0.2450 g) was placed in a graphite crucible in a sandwich configuration between two layers of 2.41 g of $LiBO_2$. The crucible was heated in a muffle furnace for 1 h at 1000°C under an argon atmosphere (1.5 L/min). After cooling, the melt was poured into a beaker containing 500 mL of 25% HCl solution. The resulting liquor was analyzed by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, 700 Series, Agilent Technologies) and Energy Dispersive X-ray Fluorescence Spectroscopy (EDXRF-7200 Shimadzu).

2.1 Columbite pretreatment

NaOH was mixed with the ore in three different ratios Columbite:NaOH, 5:5, 5:4 and 5:3. The mixture was calcined in a muffle furnace at 500°C for 2 h. Then, the sample was leached in water at 90°C for 1 h with a solid:liquid ratio of 1:50. After this period, the solution was vacuum filtered, and the solid retained on the filter was dried and weighed.

2.2 Columbite leaching without pretreatment

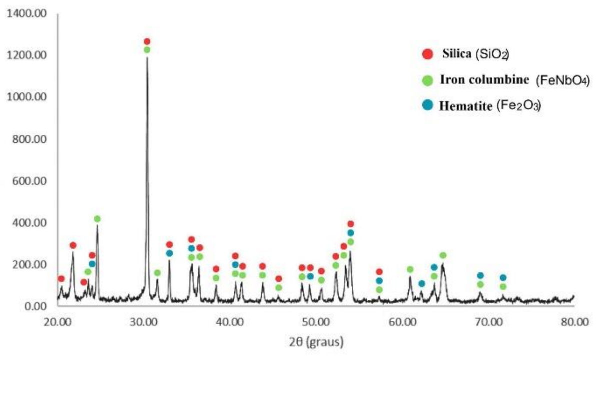
The established base parameters were a temperature of 80°C, a solid-to-liquid ratio (S:L) of 1:100, and a duration of 3 h. Leaching was carried out under constant magnetic stirring (200 rpm) and heating in 200 mL reactors connected to condensers, which were attached to a thermostatic bath. The leaching process was performed using sulfuric acid (H_2SO_4), hydrochloric acid (HCl), and nitric acid (HNO_3). The acid concentrations used were 1, 5, and 10 mol/L.

2.3 Columbite leaching with pretreatment

Leaching experiments were conducted using the same parameters and mineral acids described in Section 2.2, with the addition of organic acids: oxalic acid ($C_2H_2O_4$), malic acid ($C_4H_6O_5$), tartaric acid ($C_4H_6O_6$), and citric acid ($C_6H_8O_7$), at concentrations of 1, 1.5, and 2 mol/L.

3. Results and discussion

The X-ray diffraction pattern of columbite and the particle size distribution analysis are shown in Figure 1. The columbite studied exhibits three predominant phases: silica (SiO_2), ferrocolumbite ($FeNbO_4$), and hematite (Fe_2O_3). Particle size analysis revealed that 10% of the material has a size of 60 µm, 50% corresponds to 65 µm, and 90% is equivalent to 70 µm, indicating that the majority of the particles range between 60 and 70 µm in diameter. At 74 µm, the cumulative volume reaches 99.99%. In terms of chemical composition, the niobium content in the columbite is 24.5%.



(a)

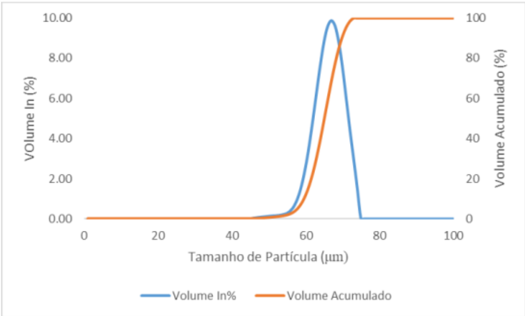


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Fig. 1. (a) Diffractogram of columbite. (b) Particle size analysis of columbite.

The initial leaching results using mineral acids directly on columbite, along with the extraction percentages for H_2SO_4, HCl, HNO_3, and H_3PO_4, are shown in Figure 2. It can be observed that the extraction percentage of Nb did not exceed 50%. Based on these findings, a pre-treatment method was investigated prior to leaching. The proposed thermal-alkaline pre-treatment is expected to influence the crystalline structure of columbite, particularly by weakening the strong bond between the metal and silica, thereby enhancing the solubilization of Nb. This modification aims to facilitate the extraction of niobium in subsequent leaching tests, making it more easily recoverable.

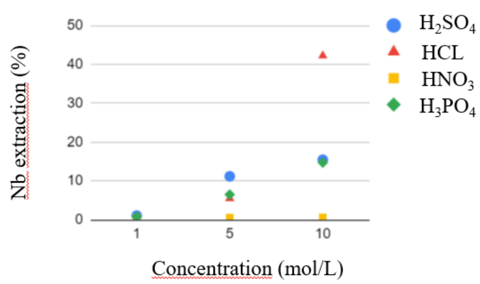


Fig. 2. Graph of percentage extraction of Nb from columbite at different concentrations of inorganic acids.

Three samples that underwent alkaline treatment were subjected to leaching with H_2SO_4 at a concentration of 5 mol/L. These conditions were chosen because the extraction percentage was higher than with other acids in the leaching process without pre-treatment. A concentration of 10 mol/L was not used due to technical challenges associated with handling highly concentrated acids. After leaching, the results obtained are presented in Table 1.

Table 1. Nb extraction in leaching with H2SO4, 5 mol/L, under different thermal-alkaline pre-treatment ratios.

Solid:liquid ratio	Nb extraction (%)
without pretreatment	11.1
5:3	17.3
5:4	19.4
5:5	21.8

Based on the results obtained, it is evident that the pre-treatment was effective in increasing Nb extraction, as the percentage improved when compared to the same conditions without pre-treatment (from 11.1% to 21.8%). Given these values, the 5:5 ratio was selected for the subsequent stages, as it demonstrated the highest extraction percentage.

With the pre-treatment ratio defined, leaching tests were performed using this sample, maintaining the initial parameters. Additionally, experiments were conducted with organic acids. The results, in mg/L of Nb for each leaching test, are presented in Table 2, and the extraction percentage of Nb with different acids at various concentrations is shown in Figure 3.

Table 2. Values extracted in mg/L of Nb with different acids and different concentrations.

Acid	Acid concentration (mol/L)	Nb concentration (mol/L)
H_2SO_4	1	38
	5	524
	10	832
HCl	1	24
	5	553
	10	1094
HNO_3	1	29
	5	43
	10	29
H_3PO_4	1	93
	5	932
	10	900
$C_2H_2O_4$	1	1290
	1.5	1960
	2	1830
$C_4H_6O_5$	1	802

	1.5	1210
	2	1172
$C_4H_6O_6$	1	720
	1.5	1304
	2	1046
$C_6H_8O_7$	1	880
	1.5	1314
	2	1550

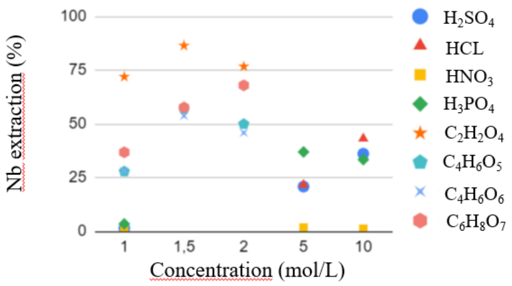
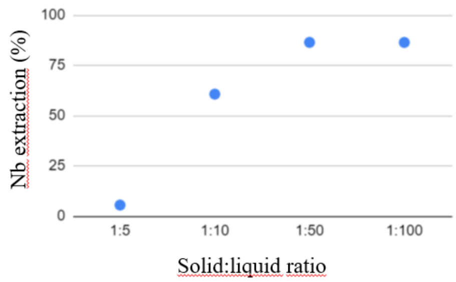


Fig. 3. Graph of the percentage of Nb extraction from columbite using different concentrations of inorganic and organic acids.

There was an increase in Nb extraction with inorganic acids, except for HNO_3, which remained the least effective. The increase in acid concentration led to higher extraction yields with H_2SO_4, $C_6H_8O_7$, and HCl, with the latter showing the highest performance among the inorganic acids at 10 mol/L (43.1%). For H_3PO_4, $C_2H_2O_4$, $C_4H_6O_5$, and $C_4H_6O_6$, the peak extraction occurred at intermediate concentrations (5 mol/L for the inorganic acid and 1.5 mol/L for the organic acids), following a parabolic trend. Among all the experiments, oxalic acid ($C_2H_2O_4$) at 1.5 mol/L achieved the highest Nb extraction percentage, reaching 86.4%.

Based on the acid study, the best-performing acid for Nb extraction ($C_2H_2O_4$ at 1.5 mol/L) was selected to vary the solid:liquid (S:L) ratio in order to further increase the extraction percentage. In this phase, five different S:L ratios were tested: 1:5, 1:10, 1:50, and 1:100. The results, shown in Figure 4(a). Based on the study of the S:L ratio, the 1:50 ratio was adopted for the subsequent stage, focusing on temperature variation. The extraction of Nb was investigated at different temperatures, ranging from room temperature to the boiling point of water (25, 50, 70, 80, 90, and 97°C), as illustrated in Figure 4(b). As the temperature increased, the extraction efficiency also increased, reaching a maximum value of 86.4% at 80°C. However, beyond this temperature, the percentage of Nb recovered decreased to 61%, and remained constant up to the maximum temperature tested.



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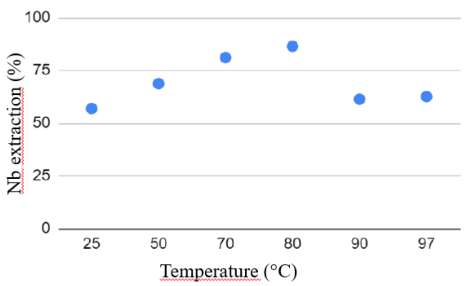

(b)

Fig. 4. Extraction of Nb in different solid-liquid ratios using acid $C_2H_2O_4$ at 1.5 mol/L.

4. Conclusion

The pre-treatment method proved to be effective in most cases, significantly enhancing the percentage of Nb extraction and underscoring its importance in the overall metal recovery process. Additionally, the acid study demonstrated that organic acids outperformed inorganic acids, with oxalic acid ($C_2H_2O_4$) at 1.5 mol/L showing the best results among the eight acids tested, achieving an extraction efficiency of 86.4%. These findings highlight the potential of combining thermal-alkaline pre-treatment with targeted organic acid leaching to optimize niobium recovery from columbite. Furthermore, the results support the proposed circular economy approach, as they provide a viable pathway for transforming mining residues into valuable raw materials for the synthesis of advanced nanomaterials, such as nano-adsorbents, contributing to sustainable resource management and green technologies.

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