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Biolixiviação de resíduos eletroeletrônicos e da indústria do petróleo contendo elementos de terras-raras

Relatório de Pós-doutorado realizado na Universidade Estadual Paulista (UNESP), Instituto de Química, Araraquara.

Supervisora: Profa. Dra. Denise Bevilaqua

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Resumo

Os elementos terras-raras (ETRs) possuem uma importância estratégica fundamental para o desenvolvimento tecnológico e a soberania nacional. Eles são essenciais na produção de dispositivos eletrônicos e tecnologias do setor energético. Apesar do Brasil possuir grandes reservas de ETRs, o país praticamente não produz esses elementos e importa quase todos os que consome da China. Portanto, é necessário um forte investimento em pesquisa e desenvolvimento científico e tecnológico para viabilizar processos de extração, isolamento, purificação e recuperação de ETRs. Isso inclui não apenas a exploração de minérios de alto teor, mas também de rejeitos e materiais reciclados. Assim, este projeto propõe explorar o uso da bactéria *Acidithiobacillus thiooxidans* na biolixiviação de rejeitos de dispositivos eletrônicos (lâmpadas fluorescentes) e de rejeitos da indústria do petróleo (cascalhos de perfuração e catalisadores inativados de FCC), ricos em ETRs. A viabilização da recuperação destes elementos estratégicos e materiais descartados como lixo tem o potencial de promover o desenvolvimento econômico sustentável do Brasil.

1 Introdução

1.1 Enunciado do problema

Atualmente, os elementos de terras raras (ETRs) possuem uma importância estratégica extrema para o desenvolvimento tecnológico e a soberania nacional. Essa importância se deve ao fato de que esses elementos são fundamentais para a produção de produtos eletroeletrônicos de alta tecnologia, como lâmpadas, computadores, smartphones, displays, entre outros, além do desenvolvimento de materiais

estratégicos no setor energético, como ímãs permanentes, baterias e catalisadores. Apesar de possuir grandes reservas de ETRs, o Brasil quase não realiza a manufatura desses elementos e depende quase que inteiramente da importação da China, que já utilizou o monopólio do mercado de terras-raras como uma arma de embargo contra outras economias mundiais (BINNEMANS et al., 2018; GAUSTAD; WILLIAMS; LEADER, 2021; JOWITT et al., 2018; QIU; SUH, 2019; SOUSA FILHO; GALAÇO; SERRA, 2019; TEJASWINI; PATHAK; GUPTA, 2022).

Neste contexto, é evidente a necessidade de investimento em pesquisa científica e tecnológica para tornar possível a extração, isolamento, purificação e recuperação de terras-raras. Isso inclui não apenas a exploração de minérios de alto teor, mas também em rejeitos e materiais reciclados. Por exemplo, o descarte de lâmpadas fluorescentes, que são amplamente utilizadas para iluminação pública e doméstica, é pouco explorado para recuperar ETRs. Resíduos de lâmpadas fluorescentes contêm uma quantidade significativa de ETRs em sua composição (cerca de 20-40% dos pós fosfóricos que revestem a superfície interna das lâmpadas), especialmente Eu, Y, Tb, Ce e La (DHAWAN; TANVAR, 2022; GAUSTAD; WILLIAMS; LEADER, 2021; SETHURAJAN et al., 2019; TAN; LI; ZENG, 2015).

Embora muitos países já estejam envolvidos na recuperação de ETRs em resíduos, como as lâmpadas fluorescentes, apenas cerca de 6% do total consumido anualmente no Brasil é reciclado, enquanto a maioria é descartada em aterros sanitários (MOURAO; SATOSHI MIYAMARUEO, 2012). Além disso, somente uma pequena parcela desses resíduos contendo ETRs, que é reciclado, é utilizado para fins de baixo valor, como aditivos na indústria cerâmica em combinação com vidro moído, por exemplo (MOURAO; SATOSHI MIYAMARUEO, 2012). Por sua vez, apesar das indústrias petrolíferas sejam extremamente importantes para a economia global, elas também são responsáveis por uma grande produção de resíduos, incluindo os cascalhos de perfuração e os catalisadores gastos do craqueamento catalítico fluido (FCC), contendo quantidades consideráveis de ETRs (AZEVEDO et al., 2019; FONTANA et al., 2021; SPOSATO et al., 2021).

Os cascalhos de perfuração são gerados em larga escala durante as atividades de exploração e perfuração de poços de petróleo, estes resíduos são obtidos a partir de rochas trituradas contaminadas com fluídos de perfuração. A quantidade ETRs presente nos cascalhos de perfuração pode variar de acordo com as características geológicas do local de perfuração, sendo que alguns elementos, La e Ce, podem estar presentes em concentrações da ordem de mg kg^{-1} (FONTANA et al., 2021). Os catalisadores desativados de FCC, que são descartados como resíduos, apresentam concentrações de ETRs que atingem níveis acima de 1% (AZEVEDO et al., 2019; SILVA et al., 2014; SPOSATO et al., 2021). Desta forma, esses resíduos

industriais e urbanos, que são gerados e descartados em grande quantidade, podem ser fontes alternativas importantes de ETRs.

1.2 Biolixiviação

Comparadas aos métodos químicos convencionais, as rotas baseadas em processos biológicos podem ser mais econômicas e ambientalmente sustentáveis para a recuperação de metais de fontes primárias (depósitos minerais) e secundárias (produtos em fim de vida, resíduos industriais) (BROWN et al., 2023; THOMPSON et al., 2018). A extração de metais a partir de fontes sólidas pode ser facilitada por meio da biolixiviação, um processo que envolve diferentes reações biologicamente catalisadas, capaz de liberar vários agentes de lixiviação microbianos, incluindo ácidos (orgânicos e inorgânicos). Diversos microrganismos têm sido utilizados, incluindo arqueas, bactérias e fungos, com o objetivo de biolixiviar ETRs presentes em diferentes materiais sólidos (HOPFE et al., 2018; RASOULNIA; BARTHEN; LAKANIEMI, 2021).

Geralmente, a extração de substâncias valiosas de resíduos exige a dissolução ou destruição parcial de óxidos, hidróxidos, fosfatos, carbonatos ou silicatos que contêm os metais desejados. Esta dissolução ocorre por meio de processos secundários, tais como a produção microbiana de ácidos (dissolução promovida por prótons ou acidólise), agentes complexantes (dissolução promovida por complexação ou complexólise), e redutores ou oxidantes (dissolução promovida por processos redox ou redoxólise) (GLOMBITZA; REICHEL, 2013; RASOULNIA; BARTHEN; LAKANIEMI, 2021).

Dentre a variedades de microrganismos capazes dissolver resíduos contendo ETRs, este projeto propõe utilizar o *Acidithiobacillus thiooxidans*, uma bactéria quimiolitoautotrófica, que tolera meios ácidos com pH entre 0,5 e 6, a presença de concentrações elevadas de metais pesados, e é capaz de utilizar enxofre como fonte de energia, secretando como metabólito ácido sulfúrico (BEVILAQUA et al., 2002; BODEN; HUTT, 2019; BOSECKER, 1997). Apesar de enorme potencial, poucos estudos avaliaram o uso deste microrganismo para recuperação de ETRs de fontes secundárias, foram encontrados apenas doze publicações (AUERBACH; BOKELMANN; et al., 2019; AUERBACH; RATERING; et al., 2019; FUNARI et al., 2017; HOPFE et al., 2018; HOSSEINI et al., 2022; MARRA et al., 2018; MIKODA; POTYSZ; KMIECIK, 2019; MURAVYOV et al., 2015; SU; TAN; LIN, 2020; TAYAR; PALMIERI; BEVILAQUA, 2022; TSAPLINA et al., 2015; ZHANG et al., 2021), e nenhum sobre os resíduos propostos neste projeto, que possuem relevância para o contexto brasileiro.

A biolixiviação com o uso da *A. thiooxidans* pode promover a dissolução de ETRs tanto pela acidólise quanto por complexação, pois, além do ácido forte liberado, há também a produção de sulfato, que é capaz de complexar com ETRs, aumentando sua solubilidade, portanto, evitando sua precipitação (GIMENO SERRANO; AUQUÉ SANZ; NORDSTROM, 2000; JOHANNESSON; LYONS, 1995; VERPLANCK et al., 2004).

Assim sendo, considerando que métodos de extração de ETRs baseados em processos biológicos são mais ambientalmente sustentáveis do que os métodos convencionais empregados na indústria de mineração, tais como a lixiviação ácida e a extração por solvente, e as vantagens da biolixiviação com uso da *A. thiooxidans* na promoção da dissolução de ETRs por acidólise e complexação. Este projeto propõe explorar o uso da *A. thiooxidans* na biolixiviação de rejeitos de dispositivos eletrônicos (lâmpadas fluorescentes) e de rejeitos da indústria do petróleo (cascalhos de perfuração e catalisadores inativados de FCC) visando solubilizar ETRs, que podem ser aplicados em produtos de maior valor agregado, promovendo a economia brasileira e sua independência perante fornecedores estrangeiros.

1.3 Objetivos

Este projeto objetiva estudar o uso da bactéria *Acidithiobacillus thiooxidans* na biolixiviação de rejeitos de dispositivos eletrônicos (lâmpadas fluorescentes) e de rejeitos da indústria do petróleo (cascalhos de perfuração e catalisadores inativados de FCC) para extrair ETRs.

2 Materiais, Métodos, Resultados e Discussões

As próximas seções (3 e 4) descrevem os Materiais e Métodos, bem como os Resultados e Discussões, apresentados na forma de dois Manuscritos, sendo o primeiro já submetido e na etapa de revisão por pares.

3 Manuscrito I

Urban Mining of Rare Earth Elements from Fluorescent Lamp Recycling Waste via *Acidithiobacillus thiooxidans*: A Sustainable and High-Performance Bioleaching Approach

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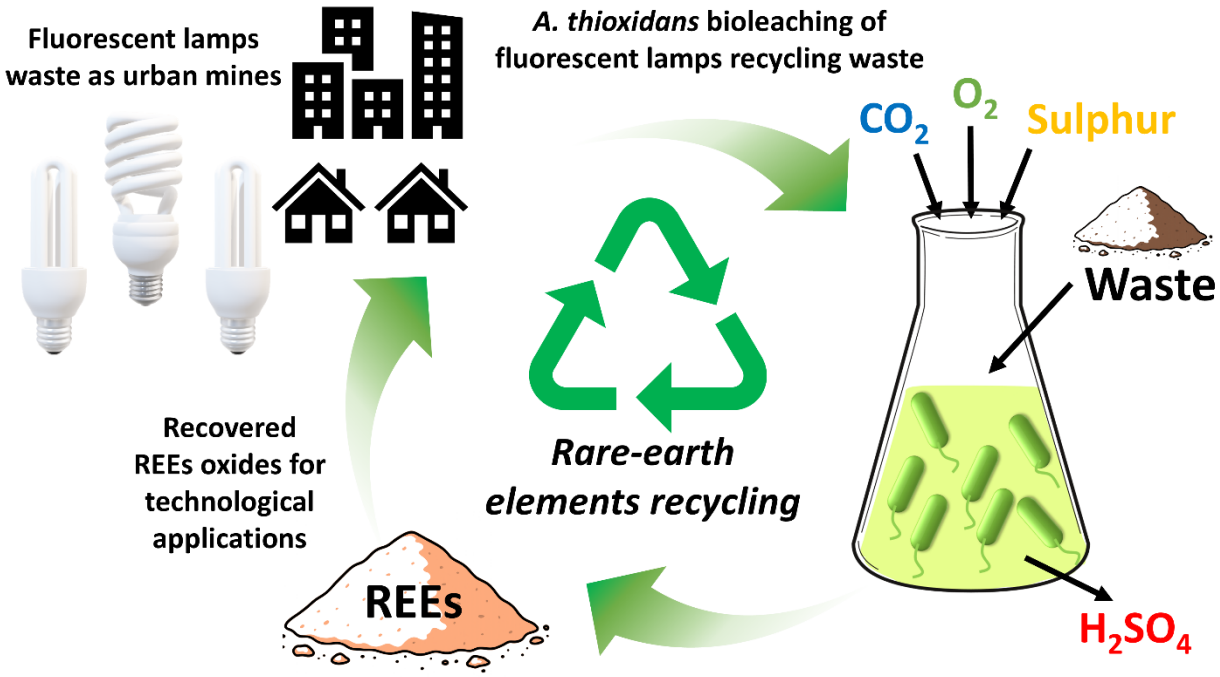
Abstract

Rare earth elements (REEs) are critical for modern technologies, yet their sustainable recycling from electronic waste, remains a significant challenge. While bioleaching presents a green alternative to conventional hydrometallurgy, its efficiency for complex real wastes is often limited. This study pioneers the application of the acidophilic bacterium *Acidithiobacillus thiooxidans* for the bioleaching of industrial fluorescent lamp waste (FLW). Results demonstrate that both one and two-step bioleaching approaches successfully achieved complete solubilization of Yttrium and Europium, which constitute over 95% of the REE content in this residue. The two-step process, particularly in baffled flasks, showed superior performance, achieving near-complete extraction (>98%) of Y and Eu in approximately three days. This represents the most efficient bioleaching strategy reported to date for FLW. Inhibition assays revealed that the bacterial growth is specifically suppressed by Y^{3+} and La^{3+} ions. Furthermore, the study successfully closed the recycling loop by upcycling the leached REEs into a high-value functional product. Through selective oxalate precipitation and subsequent thermal decomposition, we synthesized Y_2O_3:Eu^{3+} phosphors with excellent luminescent properties and 96% purity. These findings offer crucial insights for process optimization and establish a promising, environmentally sustainable biotechnology for REE recovery within a circular economy framework.

Keywords: Bioleaching, urban mining, *Acidithiobacillus thiooxidans*, fluorescent lamp, rare earth elements, circular economy.

Graphical abstract



3.1 Introduction

Currently, rare earth elements (REEs) hold extremely strategic importance for technological development and national sovereignty. This importance stems from the fact that these elements are essential for the production of high-tech electronic products such as light bulbs, computers, smartphones, and displays, among others, as well as the development of strategic materials in the energy sector, such as permanent magnets, batteries, and catalysts [1–8].

In this context, the need for investment in scientific and technological research to enable the extraction, isolation, purification, and recovery of REEs is evident. This includes not only their exploitation from natural reserves, primarily located in China, Vietnam, Russia, and Brazil, but also from waste and recycled materials [9]. The demand for alternatives to conventional mining is also driven by increasingly frequent environmental issues associated with this sector. Notable examples include the catastrophic dam failures in Minas Gerais, specifically in Mariana, Brumadinho, and Itabirito. The collapse of the Fundão dam at the Samarco mine in Mariana stands as the most severe disaster of its kind, both in terms of the volume of tailings released and the distance over which they spread, impacting vast areas across the states of Minas Gerais and Espírito Santo [10–12].

Thus, there is an increasing demand to develop technological strategies to enable the extraction and recovery of REEs through urban mining, promoting a circular economy. Fluorescent lamp waste (FLW) generated from the recycling of spent lighting devices is one of the most promising secondary sources of REEs for urban mining. The phosphor coating containing these elements accounts for up to 2% of the total weight of the fluorescent lamp, with up to 26% mass content of REEs, especially Eu, Y, Tb, Ce, and La [2,13–15]. In fact, such waste has a significantly higher proportion of REEs compared to rare earth ore deposits, making it an important alternative source of these economically strategic elements [16]. Despite this considerable potential, according to 2024 data from the UN's Global e-Waste Monitor, approximately 1.9 million tons of lamps are discarded annually worldwide, yet the recycling rate remains at only 5%, the lowest among all categories of e-waste [17].

Compared to conventional chemical methods, routes based on biological processes may offer greater economic and environmental sustainability for the recovery of metals from both primary sources (mineral deposits) and secondary sources (end-of-life products, industrial waste) [7,18,19]. Metal extraction from solid sources can be facilitated through bioleaching, a process involving various biologically catalyzed reactions capable of releasing several microbial leaching agents, including acids (organic and inorganic). Various microorganisms, including archaea, bacteria, and fungi, have been employed to bioleach REEs present in different solid materials [20,21]. To contextualize the bioleaching performance observed in this work, a systematic literature review was conducted on the extraction REEs from fluorescent lamp waste. All relevant studies identified are compiled in Table 1, providing a comparative overview of existing approaches for this specific waste stream.

Table 1. Overview of bioleaching studies from fluorescent powder.

Waste type	Microorganism used for leaching	Experiment type*	Identified Leaching agents	REE leaching efficiency	Time*	Reference
Cathode Ray Tube (CRT) powders	Mixed culture of (*Acidithiobacillus ferrooxidans*, *At.*	One-step, 250 mL Pyrex flasks, 175 rpm, 10% (w/v)	Fe^{3+}	Y (70%)	16d	Beolchini et al. [22]

	thiooxidans and *Leptospirillum ferrooxidans*)					
Retorted phosphor powder	*Acinetobacter calcoaceticus*	Two-step (4d of cultivation), 50 mL tubes, 150 rpm, 1.5% (w/v)	Mainly gluconic acid	≈1.2% (total)	24h	Reed et al. [23]
Retorted phosphor powder	*Pseudomonas frederiksbergensis*	Two-step (4d of cultivation), 50 mL tubes, 150 rpm, 1.5% (w/v)	Mainly gluconic acid	≈0.5% (total)	24h	
Retorted phosphor powder	*Gluconobacter oxydans*	Two-step (4d of cultivation), 50 mL tubes, 150 rpm, 1.5% (w/v)	Mainly gluconic acid	≈2.2% (total)	24h	
Retorted phosphor powder	*Talaromyces purpureogenus*	Two-step (4d of cultivation), 50 mL tubes, 150 rpm, 1.5% (w/v)	Mainly gluconic acid	≈0.9% (total)	24h	
Retorted phosphor powder	*Acinetobacter calcoaceticus*	Spent medium** (4d of cultivation), 50 mL tubes, 150 rpm, 1.5% (w/v)	Mainly gluconic acid	≈1.7% (total)	24h	
Retorted phosphor powder	*Pseudomonas frederiksbergensis*	Spent medium** (4d of cultivation), 50 mL tubes, 150 rpm, 1.5% (w/v)	Mainly gluconic acid	≈0.6% (total)	24h	
Retorted phosphor powder	*Gluconobacter oxydans*	Spent medium** (4d of cultivation), 50 mL tubes, 150 rpm, 1.5% (w/v)	Mainly gluconic acid	≈2.3% (total)	24h	
Retorted phosphor powder	*Talaromyces purpureogenus*	Spent medium** (4d of cultivation), 50 mL tubes, 150 rpm, 1.5% (w/v)	Mainly gluconic acid	≈1.0% (total)	24h	
Pure red fluorescent phosphor (Y_2O_3:Eu)	*Acidithiobacillus ferrooxidans*	Two-step, 100 ml flasks, 85 rpm, 1.0% (w/v)	Fe^{3+}	Y (100%) Eu (25%)	4d	Auerbach et al. [24]
Fluorescent lamp powder	Mixed culture Kombucha	One-step, 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly acetic and gluconic acids	Y (9,5%) Eu (11.1%) Gd (1.6%) La (0.8%) Ce (0.0%) Tb (0.1%)	14d	Hopfe et al. [25]
Fluorescent lamp powder	Mixed culture Kombucha	One-step, 100 ml Erlenmeyer flask, stationary, 2.8% (w/v)	Mainly acetic and gluconic acids	Y (7.8%) Eu (9.1%) Gd (1.2%) La (0.6%) Ce (0.0%) Tb (0.1%)	14d	

Fluorescent lamp powder	Mixed culture Kombucha	Spent medium** (2w of cultivation), 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly acetic and gluconic acids	Y (12.6%) Eu (12.1%) Gd (2.8%) La (1.0%) Ce (0.1%) Tb (0.1%)	14d	
Fluorescent lamp powder	Mixed culture Kombucha	Spent medium** (2w of cultivation), 100 ml Erlenmeyer flask, stationary, 2.8% (w/v)	Mainly acetic and gluconic acids	Y (8.3%) Eu (7.3%) Gd (1.1%) La (0.3%) Ce (0.0%) Tb (0.1%)	14d	
Fluorescent lamp powder	*Zygosaccharomyces lentus*	One-step, 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly acetic and gluconic acids	Y (0.1%) Eu (0.0%) Gd (0.0%) La (0.0%) Ce (0.0%) Tb (0.0%)	14d	
Fluorescent lamp powder	*Komagataeibacter hansenii*	One-step, 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly acetic and gluconic acids	Y (6.7%) Eu (5.5%) Gd (0.5%) La (0.2%) Ce (0.0%) Tb (0.0%)	14d	
Fluorescent lamp powder	*Komatogateibacter xylinus*	One-step, 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly (iso)citric and gluconic acids	12.6% (total)	14d	Hopfe et al. [20]
Fluorescent lamp powder	*Lactobacillus casei*	One-step, 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly lactic acid	6.1% (total)	14d	
Fluorescent lamp powder	*Yarrowia lipolytica*	One-step, 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly (iso)citric acid	10.6% (total)	14d	
Fluorescent lamp powder	*Komatogateibacter xylinus*	Spent medium** (2w of cultivation), 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly (iso)citric and gluconic acids	2,9% (total)	14d	
Fluorescent lamp powder	*Lactobacillus casei*	Spent medium** (2w of cultivation), 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly lactic acid	5.8% (total)	14d	
Fluorescent lamp powder	*Yarrowia lipolytica*	Spent medium** (2w of cultivation), 100 ml Erlenmeyer flask, 300 rpm, 2.8% (w/v)	Mainly (iso)citric acid	7.3% (total)	14d	
Fluorescent lamp powder	*Aspergillus niger*	One-step, 250 ml Erlenmeyer flasks, 150 rpm, 1% (w/v)	Mainly gluconic, citric and oxalic acids	Y (13.4%) Eu (12.0%) La (0.9%) Ce (0.7%) Tb (0.7%)	7d	Castro et al. [26]

Fluorescent lamp powder	*Aspergillus niger*	Spent medium** (4d of cultivation), 250 ml Erlenmeyer flasks, 150 rpm, 1% (w/v)	Mainly gluconic and citric acids	Y (≈12%) Eu (≈11%)	2d	
Fluorescent lamp powder	*Aspergillus niger*	Spent medium** (2w of cultivation), 250 ml Erlenmeyer flasks, 150 rpm, 1% (w/v)	Mainly gluconic and oxalic acids	Y (≈1%)	2d	
Fluorescent lamp powder	*Aspergillus niger*	Semi-continuous, 250 ml Erlenmeyer flasks, 150 rpm, 1% (w/v)	Mainly gluconic, citric and oxalic acids	Y (≈0.9%) Eu (≈0.3%)	≈42d	
Fluorescent lamp powder	*Aspergillus niger*	Semi-continuous, 250 ml Erlenmeyer flasks, static, 1% (w/v)	Mainly gluconic, citric and oxalic acids	Y (≈18.2%) Eu (≈10.6%)	≈42d	
Mixture of yttrium oxide and aluminum oxide	Mixed culture Kombucha	Two-step (10d of cultivation), beaker flask, 200 mL of Kombucha, static, 0.25% (w/v)	Mainly acetic and gluconic acids	Y (≈10%)	14d	Fritz et al. [27]
Mixture of yttrium oxide and aluminum oxide	Mixed culture Kombucha	Two-step (30d of cultivation), beaker flask, 200 mL of Kombucha, static, 0.25% (w/v)	Mainly acetic and gluconic acids	Y (≈12%)	14d	

*h: hours, d: days, w: weeks.

**Cell-free medium obtained from filtered supernatants of a grown culture.

Generally, extracting valuable substances from waste requires the dissolution or partial destruction of oxides, hydroxides, phosphates, carbonates, or silicates containing the desired metals. This dissolution occurs through secondary processes such as microbial acid production (dissolution promoted by protons or acidolysis), complexing agents (dissolution promoted by chelation or complexolysis), and reducers or oxidants (dissolution promoted by redox processes or redoxolysis) [21,28].

Among the variety of microorganisms capable of dissolving waste containing REEs, this study utilized *Acidithiobacillus thiooxidans*, a chemoautotrophic bacterium that tolerates acidic pH levels between 0.5 and 6.0, high concentrations of heavy metals, and can utilize sulfur as an energy source, secreting sulfuric acid as a metabolite [29–31]. Despite its enormous potential, few studies have evaluated the use of this microorganism for the recovery of REEs from secondary sources, with only twelve publications found [20,32–42]. Hopfe et al. [20] was the only study found that attempted to investigate *A. thiooxidans* for the recovery of REE from fluorescent lamp phosphor. However, they did not observe bioleaching, possibly due to the increase in pH outside the ideal growth conditions for the bacteria as a result of acid consumption by the residue.

Bioleaching using *A. thiooxidans* can promote the dissolution of REEs through both acidolysis and complexolysis. In addition to the strong acid released, sulfate is also produced, which can complex with REEs, increasing their solubility and thus preventing their precipitation [43–45]. Therefore, considering that extraction methods of REEs based on biological processes are more environmentally sustainable than conventional methods employed in the mining industry, such as acid leaching and solvent extraction, and

given the advantages of bioleaching using *A. thiooxidans* in promoting the dissolution of REEs through acidolysis and complexation, the use of *A. thiooxidans* in bioleaching fluorescent lamps powder was explored to solubilize REEs. This can be applied in higher value-added products, aiming for a circular economy and greater independence from foreign suppliers.

3.2 Material and methods

3.2.1 Fluorescent lamp recycling waste

Fluorescent lamps recycling waste (FLW) was donated by recycling company Tramppo (Brazil). Before the bioleaching and characterization assays, the sample was standardized in terms of particle size. To remove impurities such as metallic parts and large glass fragments, the sample was first sieved through a conventional 1 mm mesh. It was then ground for 1 minute at 3500 rpm using a SpeedMixer DAC 150.1 FVZ-K (Hauschild) automatic mixing device and subsequently passed through a 0.088 mm mesh granulometric sieve to ensure homogeneity.

3.2.2 Bacterial culture and bioleaching experiments

The FG-01 strain of *Acidithiobacillus thiooxidans* was used, which was originally isolated from effluents from uranium mines located in Brazil [46]. This strain was grown in modified 9K medium: 3.0 g L^{-1} of $(NH_4)_2SO_4$, 0.5 g L^{-1} of K_2HPO_4, 0.5 g L^{-1} of $MgSO_4 \cdot 7H_2O$, 0.1 g L^{-1} of KCl, and 10 g L^{-1} of S° [47]. The pH was adjusted to 2.8 with concentrated sulfuric acid. The basal salt solution was sterilized by autoclaving at 120°C for 20 minutes, while the sulfur was autoclaved at 110°C for 1 hour.

Bioleaching experiments were conducted in 250 mL glass Erlenmeyer flasks with a working volume of 100 mL, maintained in a thermostatic orbital shaker at 30°C and 150 RPM, in 9K medium, as specified in the following experimental conditions: (i) Abiotic control - Action of the sterile culture medium in contact with FLW. (ii) One-step bioleaching - Inoculated culture medium and FLW together from the beginning. (iii) Two-step bioleaching - *A. thiooxidans* cultured until pH ≈ 0.8 and then FLW is added. Bioleaching was carried out with 10% (v/v) inoculum volume, an initial cell concentration of 10^7 cells mL^{-1}, and 2% pulp density. Experiments were conducted in conventional Erlenmeyer flasks and in flasks with three baffles. Before collecting aliquots for analysis, evaporation losses were replenished with sterile deionized water. These samples were collected and centrifuged to measure pH, acidity by titration with standardized NaOH solution, and the concentration of REEs. The quantification of solubilized REEs was performed by ICP-MS [48].

3.2.3 Recovery of $Y_2O_3:Eu^{3+}$ phosphor from bioleaching solution

After bioleaching, an equal volume of oxalic acid aqueous solution (10% w/w) was added to the leachates to precipitate the solubilized REEs as rare-earth oxalates. The mixture was kept under magnetic stirring at 60 °C for 2 h. The precipitated oxalates were recovered by centrifugation, washed twice with deionized water using a resuspension–centrifugation method, and calcined at 800 °C for 2 h (heating rate 10 °C min^{-1}). The resulting oxides were washed with deionized water and centrifuged repeatedly until the

wash water reached pH 7 to remove excess CaO. Finally, the solid was annealed at 1000 °C for 4 h (heating rate 10 °C min^{-1}) to obtain $Y_2O_3:Eu^{3+}$ phosphor.

3.2.4 Bacterial inhibition experiments

Different REEs were considered to evaluate the growth inhibition of *A. thiooxidans* in flasks with baffles, using $La(NO_3)_3$, $Y(NO_3)_3$, $CeCl_3$, and $EuCl_3$ concentrations varying between 2.5 and 10 mmol L^{-1}. The growth of the microorganism in 9K medium (10% v/v inoculum, 10^8 cells mL^{-1}) was determined by measuring the cell concentration in the liquid phase by turbidimetry and indirectly by pH.

3.2.5 Analytical and characterization methods

To characterize the fluorescent lamp waste and recovered oxides, a X-ray Diffraction (XRD) was performed using a SmartLab SE diffractometer (Rigaku), operated with 40 kV radiation, 20 mA, Cu-Kα-1.54186 Å, scan axis: Θ/2Θ, scan range between 4° to 120°, scan step: 0.02, scan speed: 2°/min, length-limiting slit: 10 mm, incident slit: 1/2. Phase quantification was carried out by Rietveld method [49] with using GSAS-II software [50].

The concentration of REE in the initial fluorescent lamp waste and liquid aliquots from bioleaching assays was determined by inductively coupled plasma mass spectrometry (ICP-MS) (Perkin Elmer-Sciex, model Elan 6000), according the method proposed by Fontana et al. [48]. The fluorescent lamp wastes were digested using microwave ovens Ethos Plus (Milestone), and DGT 100PLUS (Provecto Analítica), according to the procedure described by Fontana et al. [48].

The photoluminescence (PL) excitation and emission spectra of $Y_2O_3:Eu^{3+}$ phosphor were acquired at room temperature on a Horiba-Jobin Yvon Fluorolog®-3 FL3-22 spectrofluorometer containing a Hamamatsu R928P photomultiplier as UV-visible detector. The excitation source consists of a 450 W continuous xenon short-arc lamp (UXL-450S-O, USHIO INC.). The PL emission spectra were corrected for the wavelength sensitivity of the detector and the excitation spectra were corrected to the intensity of the lamp in the excitation range. The absolute PL quantum yield (Φ_{PL}) measurements were carried out at room temperature on a Hamamatsu C13534-11 Quantaurus-QY Plus UV-NIR spectrometer equipped with an integrating sphere. The Φ_{PL} values are accurate within 10%. The sample is measured in triplicate and the reference (blank) is the empty quartz sample holder.

3.3 Results and discussion

3.3.1 Fluorescent lamps recycling waste characterization

Industrial fluorescent lamp recycling waste (FLW) was characterized by XRD combined with the Rietveld method to identify and quantify the crystalline phases present in this complex residue, which originates from the industrial recycling of various lamp models. Figure 1a shows the refined XRD pattern of the fluorescent lamp recycling waste, with good agreement between the calculated and observed diffractograms, as evidenced by both qualitative visual inspection of the residuals and low quantitative statistical factors (Rwp = 3.917% and GOF =1.55). The crystalline phase composition of the waste sample (Figure 1b) was found to include seven different crystalline phases with varying contents, confirming the

complex nature of the material. Halophosphate ($Ca_5(PO_4)_3Cl_{0.1}F_{0.9}$) was identified as the major crystalline phase. This compound is a lower-quality, non-REE-based white light phosphor used in older fluorescent lamp models [51]. Because it is easily leached in acidic media together with REE-based phosphors, releasing large amounts of Ca^{2+} ions [52], it can represent an important source of impurities in the recovered REEs oxides from FLW. Calcite ($CaCO_3$) was also found as an important impurity, originating from its use as a major component of the basing cement in fluorescent lamps [53]. Among the identified REE-based phosphors, the red YOX phosphor ($Y_{1.92}Eu_{0.08}O_3$) is the most abundant, accounting for approximately 17% of the crystalline components in the waste. The green CAT ($Ce_{0.63}Tb_{0.37}MgAl_{11}O_{19}$) phosphor and the blue BAM phosphor ($Ba_{0.86}Eu_{0.14}MgAl_{10}O_{17}$) are also present, though in slightly lower concentrations. LAP ($La_{0.60}Ce_{0.27}Tb_{0.13}PO_4$) green phosphor was also identified in lower concentration (<3%). The ratio between red, blue, and green REE-based triphosphor components is known to vary significantly depending on the target color index of each fluorescent lamp model [54,55]. Finally, small amount of quartz (SiO_2) is also present, which may be used as additive/binder and was previously identified in FLW [56].

The REEs content in fluorescent lamp waste was determined by ICP-MS, as shown in Figure 1c. Considering the total amount of REEs, it can be estimated that approximately 8.1% w/w of the industrial waste is composed of these elements. This concentration is higher than the average values typically found in mineral deposits under exploration, highlighting the significant potential of such waste as a secondary source of REEs through urban mining [57]. Of the total REEs content, about 90% corresponds to Y, which is expected since Y_2O_3 is the host matrix of one of the most abundant phosphors, while other REEs are present only in doping concentrations. Eu is the second most abundant (~6%), while Tb, Ce, and La occur in smaller amounts (1–2%). The presence of these elements is consistent with the crystalline phase composition determined by XRD (Figure 1c). Gd was also detected in trace amounts (~0.1%), likely associated with minor quantities of the less common green phosphor (Gd, Mg)B_5O_{12}:Ce,Tb [55,58], which may not have been detected by XRD due to its low concentration.

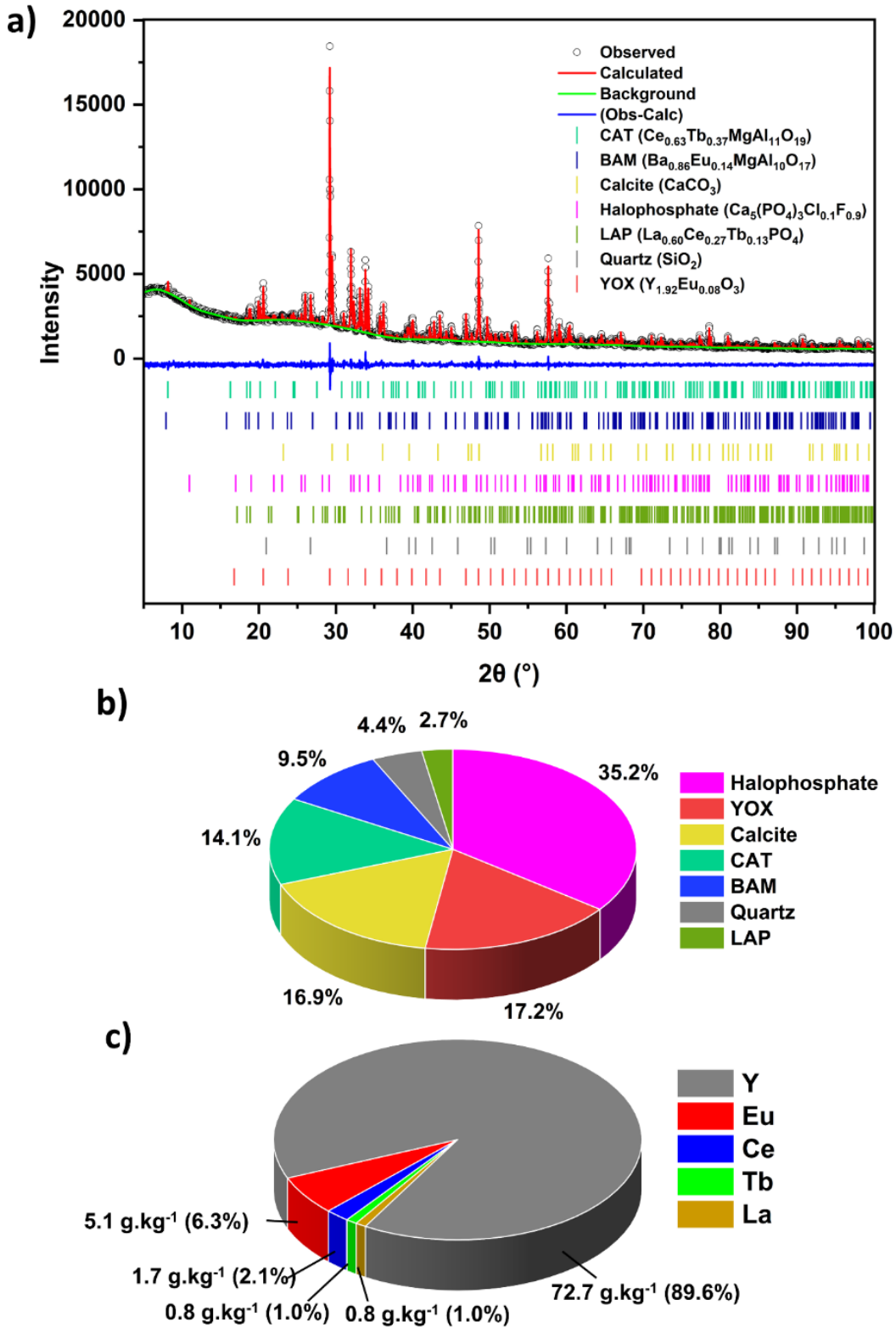


Figure 1 (a) Rietveld refinement of XRD data of industrial fluorescent lamp recycling waste, showing good agreement between experimental and calculated diffractograms (Rwp = 3.917% and GOF = 1.55). (b) Quantitative crystalline phase composition determined by Rietveld refinement, evidencing the complex multiphase nature of the material, with halophosphate as the major component and the presence of several REE-based phosphors (YOX, CAT, BAM, LAP), along calcite and quartz as minor impurities. (c) REE content determined by ICP-MS, expressed in $g.kg^{-1}$ and as percentages of the total REEs content. Gd was detected only in trace amounts and is omitted from the figure for clarity.

3.3.2 Bioleaching of fluorescent lamp recycling waste

Acidithiobacillus thiooxidans is an acidophilic chemolithoautotrophic bacterium commonly used in the bioleaching of ores and urban waste. It is capable of oxidizing sulfur compounds to sulfuric acid, as shown in Equation 1 [22,29–31].

$$2S^{\circ} + 3O_2 + 2H_2O \rightarrow 2H_2SO_4 \quad (1)$$

A. thiooxidans cultures were employed for the bioleaching of REEs from FLW using either a one-step approach (in which the inoculated culture medium and FLW were combined from the beginning) or a two-step approach (in which *A. thiooxidans* was first cultured until the pH reached ≈ 0.8, after which FLW was added). Bioleaching assays under both approaches were conducted in conventional and baffled flasks to evaluate the influence of baffles on leaching performance due to improved mixing and aeration. Figure 2 summarizes the kinetic profiles for solubilization of REEs present in FLW during the bioleaching assays under the different conditions investigated, while Figure 3 displays the extraction efficiencies obtained under these conditions after 3 (Figure 3a) and 14 days (Figure 3b). Variation in pH and H^+ concentration during bioleaching assays are shown in Figure 4.

While Y, Eu, and Gd were efficiently solubilized, Tb, Ce, and La exhibited low extraction percentages (Figures 2 and 3). These results may be related to the crystalline phase composition of the waste determined XRD, which showed that these elements are present in the form of green phosphors LAP and CAT, known to be resistant to acid leaching under ambient conditions. Conversely, $Y_2O_3:Eu^{3+}$ (YOX) and $GdMgB_5O_{10}$ are more easily solubilized [13,59,60]. Among the tested conditions the two-step bioleaching method yielded the best leaching performance, particularly in flasks with baffles, which achieved complete solubilization of Y and Eu (98-100%) in about three days and approximately 80% extraction of Gd after 14 days. Nevertheless, it is important to indicate that together Y and Eu accounts for around 95% of total REE content, as shown by ICP-MS.

The one-step bioleaching with *A. thiooxidans* was significantly improved by the presence of baffles, achieving extraction values comparable to those of the two-step method in the later stages of the experiments (Figure 2). It has been reported that baffles facilitate aeration [61], allowing CO_2 and O_2 to reach the microorganisms. The promotion of CO_2 and O_2 access to *A. thiooxidans*, which uses these gases as a carbon source and final electron acceptor, influenced the pH values, as shown in Figure 4. Consequently, greater acid production was observed in the experiments conducted with baffles, both in the one-step and two-step methods (Figure 4b).

Figure 4 data show that the flasks with baffles not only increased acid production but also enhanced its kinetics. It took approximately three days for the *A. thiooxidans* culture to reach a pH of ≈ 0.8 in the flasks with baffles, compared to eight days in the conventional flasks. The waste material was then added on days 3.5 and 8 during the two-step bioleaching processes, with and without baffles, respectively. The greater acid production in the flasks with baffles also resulted in higher REEs extractions (Figures 2 and 3), as described by Equations 2, 3, 4, 5, and 6, which outline the acidic solubilization of the main components of the fluorescent lamp.

$$Y_2O_3:Eu^{3+}_{(s)} + 6H^+_{(aq)} \rightarrow 2Y^{3+}_{(aq)} + Eu^{3+}_{(aq)} + 3H_2O_{(l)} \quad (2)$$

$$BaMgAl_{10}O_{17}:Eu^{2+}_{(s)} + 34H^+_{(aq)} \rightarrow Ba^{2+}_{(aq)} + Mg^{2+}_{(aq)} + 10Al^{3+}_{(aq)} + Eu^{2+}_{(aq)} + 17H_2O_{(l)} \quad (3)$$

$$(La,Ce,Tb)PO_{4(s)} + 3H^{+}_{(aq)} \rightarrow (La,Ce,Tb)^{3+}_{(aq)} + H_2PO_4^{-}{}_{(aq)} + H^{+}_{(aq)} \quad (4)$$

$$(Ce,Tb)MgAl_{11}O_{19(s)} + 38H^{+}_{(aq)} \rightarrow (Ce,Tb)^{3+}_{(aq)} + Mg^{2+}_{(aq)} + 11Al^{3+}_{(aq)} + 19H_2O_{(l)} \quad (5)$$

$$(Gd,Ce)TbMgB_4O_{10(s)} + 8H^{+}_{(aq)} + 2H_2O_{(l)} \rightarrow (Gd,Ce)^{3+}_{(aq)} + Tb^{3+}_{(aq)} + Mg^{2+}_{(aq)} + 4H_3BO_{3(aq)} \quad (6)$$

Microorganisms facilitate metal mobilization by secreting metabolites and altering environmental pH. Acids and other metabolites can chelate metal ions, detaching them from the solid phase via acidolysis, redoxolysis and complexolysis [62,63]. Conversely, microbial acid generation can directly dissolve matrices through acidolysis (Equations 2-6).

As shown in Equations 7-10, the dominant dissolution mechanism, whether acidolysis or complexolysis, is governed by the solution pH relative to the acid dissociation constant (pK_a) of the involved ligands and the stability constants ($\log_k$) of the resulting complexes. Complexation of REEs by key lixiviants produced by autotrophic sulfur-oxidizing bacteria [21]:

$$H_2SO_{4(aq)} \rightleftharpoons HSO_4^{-}{}_{(aq)} + H^{+}_{(aq)} \qquad pK_a = 1.99 \quad (7)$$

$$HSO_4^{-}{}_{(aq)} \rightleftharpoons H^{+}_{(aq)} + SO_4^{2-}{}_{(aq)} \qquad pK_a = -1.99 \quad (8)$$

$$REE^{3+}_{(aq)} + HSO_4^{-}{}_{(aq)} \rightleftharpoons REE(HSO_4)^{2+}_{(aq)} \qquad \log_k = 3.4\text{-}3.3 \quad (9)$$

$$REE^{3+}_{(aq)} + 2HSO_4^{-}{}_{(aq)} \rightleftharpoons REE(HSO_4)_2{}^{+}_{(aq)} \qquad \log_k = 5.1\text{-}5.3 \quad (10)$$

At pH levels below a ligand's pK_a, protonation weakens metal-ligand complexes, favoring acidolysis. At higher pH, deprotonated ligands facilitate stable complex formation, making complexolysis the dominant mechanism and preventing the precipitation of solubilized REEs.

Additionally, the two-step experiments yielded better results because the FLW material was added during the logarithmic phase of microorganism growth, avoiding direct contact with the waste from the beginning, as occurs in the one-step process. Consequently, in the one-step process, the growth of *A. thiooxidans* may be inhibited by the presence of REEs (as discussed in section 3.3) and by the acidic consumption of the residue. Furthermore, a distinct initial leaching kinetic was observed between flask types in the 1-step process (Figures 2 and 3A). The normal flask yielded higher efficiencies for Y, Eu, and Gd after 7 days compared to the baffled flask. We hypothesize that this difference stems from a transient lag phase experienced by the microorganisms upon inoculation into the baffled flask, where modified hydrodynamic conditions may have temporarily impaired metabolic activity. In contrast, the 2-step protocol circumvented this issue by adding the residue during the logarithmic growth phase, thus using an active culture that was unaffected by the reactor configuration.

The control flask reached a pH of ≈ 6.5 in about three days (Figure 4b). This increase in pH can be attributed to the presence of calcium halophosphate, the major crystalline phase identified in the FLW material, which consumes H_2SO_4 to produce $CaSO_{4(s)}$ and weaker acids, as shown in Equation 11.

$$Ca_5(PO_4)_3(OH,Cl,F)_{(s)} + 5H_2SO_{4(aq)} \rightarrow 5CaSO_{4(s)} + 3H_3PO_{4(aq)} + H(OH, Cl, F)_{(aq)} \quad (11)$$

The increase in the alkalinity of the medium was reported by Hopfe et al. [20] as the reason for not observing bioleaching of fluorescent lamps by *A. thiooxidans*. They used a pulp density of approximately 2.8% at 300 RPM and ambient temperature in a one-step experiment, which involved twice the rotation speed and a higher pulp density compared to this study. Therefore, these conditions may have led to greater acid consumption in a shorter time, thereby inhibiting the microorganisms.

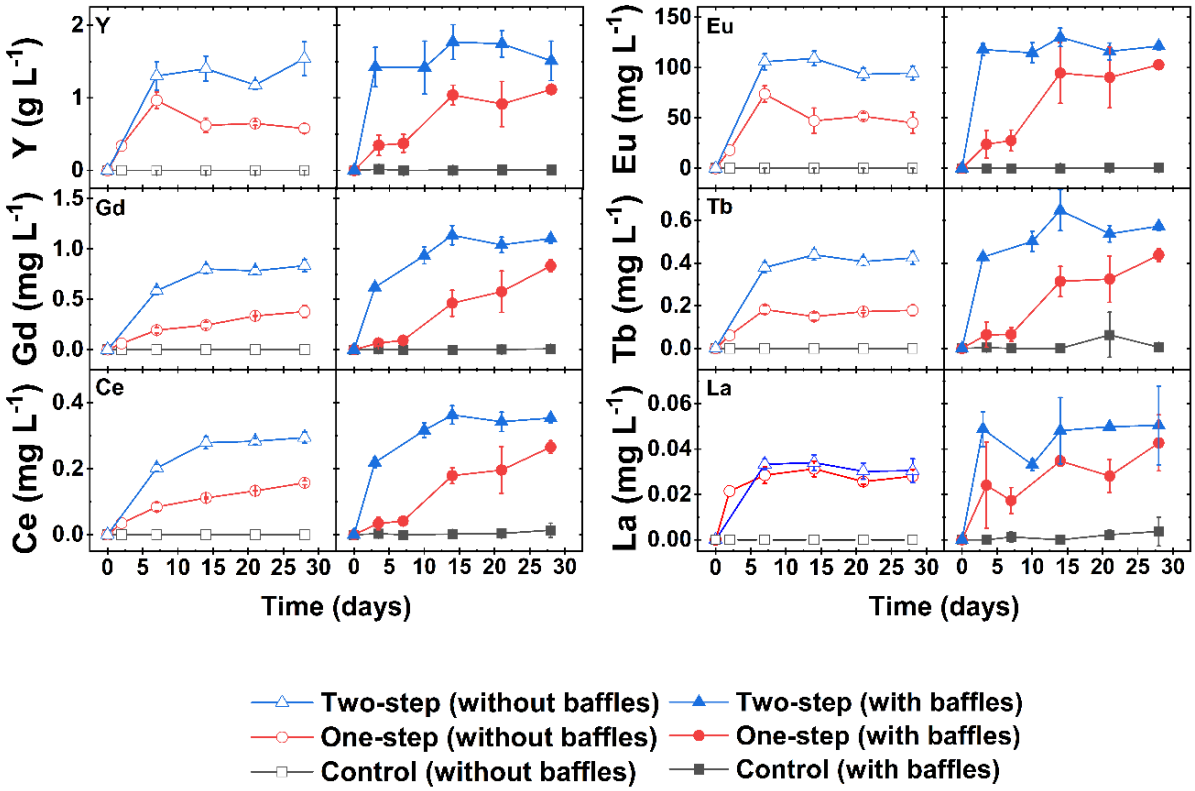


Figure 2. Kinetic profiles of REEs (Y, Eu, Gd, Tb, Ce and La) solubilization from industrial fluorescent lamps recycling waste under one-step and two-step bioleaching, in conventional and baffled flasks.

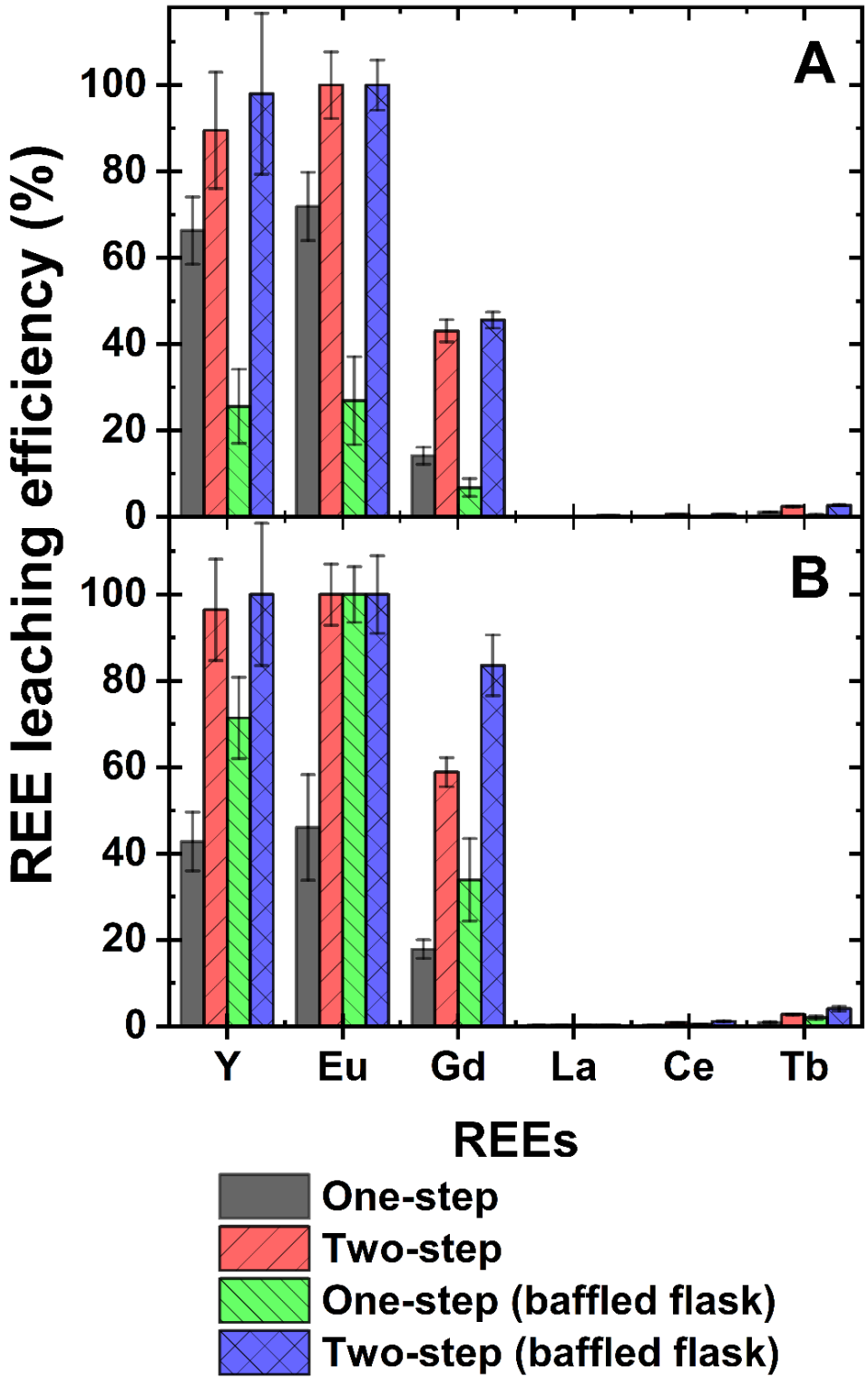


Figure 3. REE leaching efficiency during the bioleaching experiments. A: After three days for the two-step condition with baffles and seven days for the others; B: after 14 days.

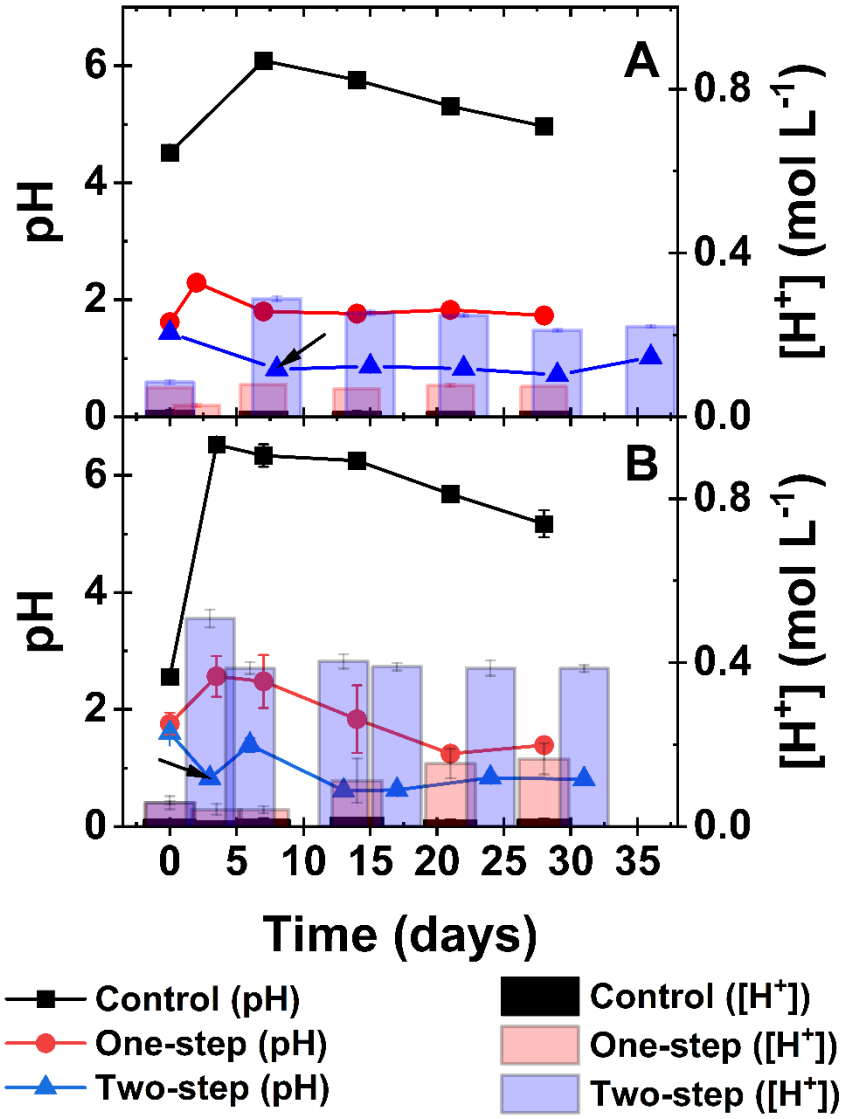


Figure 4. Variation in pH and H^+ concentration ($[H^+]$) over time during bioleaching, without (A) and with baffles (B). The arrow indicates when the residue was added in the two-step experiments.

3.3.3 Inhibition of A. thiooxidans by REEs

Growth of *A. thiooxidans* was investigated in the presence of different REE ions to better understand bioleaching behavior (Figure 5). pH and cell number analysis (Figure 5) shows that *A. thiooxidans* was inhibited by the presence of Y and La, but not by Eu and Ce. Concentrations of only 2.5 mmol L^{-1} of Y or La were sufficient to reduce the cell number and acid production compared to the control. In contrast, no inhibition was observed even with 10 mmol L^{-1} of Eu or Ce. Considering the experimental conditions and the total solubilization of the REEs, their concentrations in mmol L^{-1} in the aqueous phase would be approximately 16.4 (Y), 0.675 (Eu), 0.246 (Ce), and 0.111 (La). Thus, it is possible that the growth rate of *A. thiooxidans* in the one-step experiments was reduced due to the bioleaching of the waste material and the consequent solubilization of Y, which reached approximately 6.5 and 12.6 mmol L^{-1} after 28 days in flasks without and with baffles, respectively. These concentrations are above 5 mmol/L, which showed some level of inhibition of *A. thiooxidans*. This also explains why the two-step experiments demonstrated greater REEs solubilization and higher acid production (Figures 2, 3 and 4).

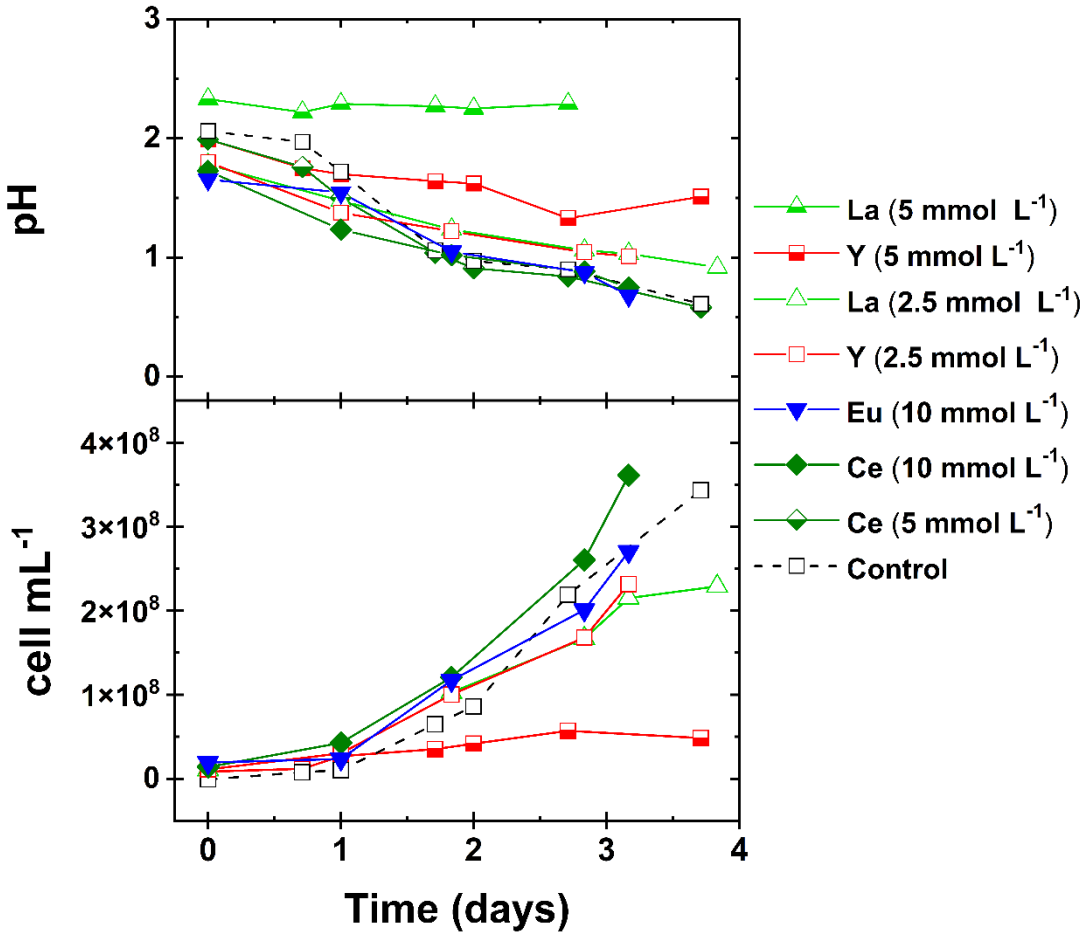


Figure 5. Growth of *A. thiooxidans* in the presence of different REE ions.

Sulfur-oxidizing microorganisms possess multiple enzymatic pathways for sulfur oxidation. These include a sulfur oxidation multienzyme complex, sulfide quinone oxidoreductase, thiosulfate quinone oxidoreductase, and tetrathionate hydrolase. These bio-oxidation reactions require various cofactors and release electrons, which are subsequently transferred to the respiratory chain to generate energy for cellular growth [64]. Thus, at sufficient concentrations, rare earth metals (e.g., Y, La) can become toxic by permeating the cell membrane. This intrusion can lead to the displacement of essential intracellular ions in enzymatic or nutrient transport systems, ultimately causing metabolic impairment through intracellular accumulation and enzyme inhibition.

3.3.4 Comparison with reported bioleaching methods and process sustainability

Bioleaching is widely recognized as an environmentally friendly alternative to conventional hydrometallurgical methods for metal recovery [20,22,25,65]. Its primary advantages include the in-situ biological production of lixiviants, which reduces the need for continuous reagent input and minimizes the use of harsh chemicals, thereby lowering the environmental footprint associated with waste treatment and carbon emissions. This aligns with the principles of a circular economy, promoting resource recovery from complex waste streams [22,27,66].

In order to compare the bioleaching performance of the present study with other methods applied to fluorescent lamp waste or similar materials, we systematically reviewed the literature on bioleaching

approaches for the extraction of REEs from fluorescent lamp recycling waste. To the best of our knowledge, all studies identified that assess the bioleaching of REEs from fluorescent lamp waste are summarized in Tables 1 and 2 [20,22–27].

Table 2. Summary of the Results of this study using fluorescent lamp powder as waste type and sulfuric acid bioproducted by *A. thiooxidans*.

Experiment type	REE leaching efficiency	Time
One-step, 250 ml Erlenmeyer flask, 150 rpm, 2.0% (w/v)	Y (66.3%) Eu (71.9%) Gd (14.2%) La (0.2%) Ce (0.2%) Tb (1.1%)	7 days
Two-step (8d of cultivation), 250 ml Erlenmeyer flask, 150 rpm, 2.0% (w/v)	Y (89.5%) Eu (100%) Gd (43.1%) La (0.2%) Ce (0.6%) Tb (2.4%)	7 days
One-step, 250 ml baffled Erlenmeyer flask, 150 rpm, 2.0% (w/v)	Y (25.6%) Eu (26.9%) Gd (6.8%) La (0.1%) Ce (0.1%) Tb (0.4%)	7 days
Two-step (3.5d of cultivation), 250 ml baffled Erlenmeyer flask, 150 rpm, 2.0% (w/v)	Y (98.0%) Eu (100%) Gd (45.6%) La (0.3%) Ce (0.6%) Tb (2.7%)	3 days

It is important to highlight that, to date, the only reported attempt to use *A. thiooxidans* for the bioleaching of fluorescent lamp waste was the study by Hopfe et al. [20], which, as already mentioned, employed a one-step approach in which alkalinization by the waste material led to microorganism inhibition and no bioleaching was observed. In contrast, the present study demonstrates for the first time that both one-step and two-step approaches can be successfully applied for the efficient bioleaching of REEs from fluorescent lamp waste, thereby expanding the applicability of *A. thiooxidans* in this field. In fact, most of the reported studies on bioleaching of fluorescent lamps waste materials were conducted using organic acid-producing microorganisms, which show significantly lower efficiency than the sulfuric acid produced by *A. thiooxidans*. Notably, our two-step process using baffled flasks achieved nearly complete extraction of Y and Eu (>98%) within three days. In contrast, Castro et al. [26] reported a maximum bioleaching of approximately 13% for Y, 12% for Eu, and 1% for La, Ce, and Tb with *Aspergillus niger* over four to seven days. Similarly, Hopfe et al. [20,25], under their optimal conditions, recovered 12.6% Y and 12.1% Eu using spent medium from a mixed Kombucha culture, along with 12.6% of total REEs through single-step bioleaching with *K. xylinus* after 14 days of incubation. All of the studies using organic acid-

producing microorganisms summarized in Tables 1 and 2 show similar efficiencies, all of which are outperformed by *A. thiooxidans*-based bioleaching reported in the present study.

When compared with another chemolithotrophic microorganism, the oxidizing action of Fe^{3+} produced by *A. ferrooxidans* has also been reported to result in relatively high extraction percentages (Tables 1 and 2). For example, in a one-step bioleaching process using a mixed culture, Beolchini et al. [22] achieved 70% Y extraction from cathode-ray tube powders within 16 days. Likewise, Auerbach et al. [24] reported complete Y extraction and 25% Eu recovery after bioleaching a mixture of pure red YOX fluorescent phosphor with *A. ferrooxidans*. Nevertheless, compared to our study, these reports still show lower efficiency and were conducted on less complex waste materials. Overall, the results highlight the superior potential of *A. thiooxidans*-based bioleaching, demonstrating enhanced efficiency for the recovery of REEs from real, complex fluorescent lamp waste derived from the recycling industry, and paving the way for more sustainable and scalable strategies for REE recovery from complex waste streams.

Unlike heterotrophic bacteria and fungi, which require organic supplements for growth and energy supply, *A. thiooxidans*, being a chemoautotrophic bacterium, has the advantage of not needing expensive organic compounds as a source of energy and carbon. For example, the study by Jin et al. [67] demonstrates that utilizing agricultural waste as a substrate for *G. oxydans* to produce a bio-lixiviant presents a potentially cost-effective route for metal recovery. Similarly, *A. thiooxidans* shows strong potential for scale-up in e-waste bioleaching. Its key advantage lies in not requiring an external carbon source, which could further streamline the process economics and operational logistics. Furthermore, these organisms are capable of proliferating under extreme environmental conditions, including low pH (< 1) and high metal concentrations [21,30]. Since it produces sulfuric acid during the process, the use of these microorganisms eliminates the need to transport often hazardous reagents, thereby reducing costs.

This inherent efficiency and operational safety make chemoautotrophic microorganisms like *A. thiooxidans* particularly compelling candidates for sustainable industrial bioleaching processes. Their biological function directly translates into core principles of green chemistry: using less hazardous materials, designing for energy efficiency, and preventing waste through in-situ reagent synthesis. However, environmental benefits must be balanced with economic viability for industrial adoption.

The recovery of REEs from end-of-life products like fluorescent lamps is of significant interest. The growing adoption and market share of LED lighting, a trend projected to continue, consequently, the implementation of recycling processes that offer both economic and environmental benefits is essential to manage the ongoing generation of FL waste, with the phosphor fraction representing the primary value [13]. For bioleaching, some studies indicate potential profitability, especially when using low-cost substrates like agricultural waste [27,67], while others highlight challenges from high feedstock costs, energy consumption, and slower kinetics at higher pulp densities [62].

Our study, conducted at a 2% pulp density for proof-of-concept, confirms the technical feasibility of recovering a high-purity Y_2O_3:Eu^{3+} product. To assess true economic potential, future research must prioritize scaling to industrially relevant pulp densities. As highlighted in recent reviews, improving economic viability requires concerted efforts to reduce costs via non-sterile operation, strain optimization, and efficient downstream processing [62,65,68].

3.3.5. Recovery of $Y_2O_3:Eu^{3+}$ phosphor

To further demonstrate the applicability of the *A. thiooxidans* bioleaching approach for the recovery of REEs from fluorescent lamp recycling waste, we attempted the recovery of $Y_2O_3:Eu^{3+}$ phosphor through a facile procedure involving selective precipitation of Y^{3+} and Eu^{3+} oxalates, followed by thermal decomposition at 800ºC to yield the corresponding REEs oxide. It is important to note that, due to the high concentration of Ca^{2+} ions in the leachate, originating from the concomitant solubilization of halophosphate, and their chemical similarity to REEs, Ca^{2+} oxalates can also precipitate, forming CaO as an impurity in the final oxide. To partially remove such impurities, the initially calcined oxide was washed with deionized water to promote hydration of CaO into soluble $Ca(OH)_2$ (Equation 12). Washing was continued until neutral pH was reached, indicating the end of hydroxide ion release from $Ca(OH)_2$ dissolution (Equation 13). Washed oxide was then annealed at 1000ºC to improve crystallinity.

$$CaO_{(s)} + H_2O_{(l)} \rightarrow Ca(OH)_{2(s)} \quad (12)$$

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \quad (13)$$

The recovered oxide was characterized by XRD and Rietveld refinement, as shown in Figure 6a. A well-crystallized Y_2O_3 cubic phase was identified as the major crystalline component (96.1 wt%), with a minor presence of CaO (3.9 wt%), demonstrating the recovery of REE oxide with reasonably high purity from the complex initial waste. It should be noted that the control sample, prepared without additional washing to remove CaO, exhibited an increased amount of CaO impurities (15.5 wt %, Figure S1), indicating the effectiveness of the washing procedure in removing CaO impurities. As expected, Eu^{3+} ions did not form a separate oxide phase due to their high solubility in the Y_2O_3 lattice, where they act as dopants. In turn, although the formation of a gadolinium oxide phase was anticipated, it was not identified by XRD. This is likely due to its low concentration in the initial waste, which is also reflected by its low concentration (~1 ppm) in the leachate, as shown in Figure 2.

To confirm the presence of Eu^{3+} ions in the recovered oxide and to evaluate its luminescent properties as a REE-based phosphor, the material was studied by photoluminescence (PL) spectroscopy. PL excitation spectra of recovered $Y_2O_3:Eu^{3+}$ phosphor as well as U719-$Y_2O_3:Eu^{3+}$ Philips Standard are depicted in Figure 6b. In both samples the emission was monitored at 614.0 nm, in the $^5D_0 \rightarrow {}^7F_2$ hypersensitive *f-f* transition. The spectra were normalized by the intensity at 592.0 nm, $^5D_0 \rightarrow {}^7F_1$ magnetic dipole allowed transition. Based on the excitation spectra presented in Figure 6b, PL emission spectra were collected under excitation at 265.0 nm, $O^{2-} \rightarrow Eu^{3+}$ charge transfer band (CTB), as shown in Figure 6c. It is possible to verify that the profile of excitation spectra for the recovered $Y_2O_3:Eu^{3+}$ phosphor and $Y_2O_3:Eu^{3+}$ Standard are similar. This similarity also occurs in the emission spectra of Figure 6c. Therefore, the Eu^{3+} ion is replacing Y^{3+} ion in the same symmetry sites of Y_2O_3 cubic crystalline phase for both recovered and Standard $Y_2O_3:Eu^{3+}$. To better quantitatively evaluated the PL features of the recovery $Y_2O_3:Eu^{3+}$ phosphor, absolute PL quantum yield (Φ_{PL}) was obtained, Figure 6d. Under excitation at 265.0 nm, $O^{2-} \rightarrow Eu^{3+}$ CTB, Φ_{PL} values of 32.7±3.3% for the recovered $Y_2O_3:Eu^{3+}$, indicating a reasonably high luminescence quantum yield for a inorganic phosphor. Overall, XRD and PL measurements indicate that functional $Y_2O_3:Eu^{3+}$ phosphor can be successfully recovered from leachate derived from bioleaching of FLW complex material.

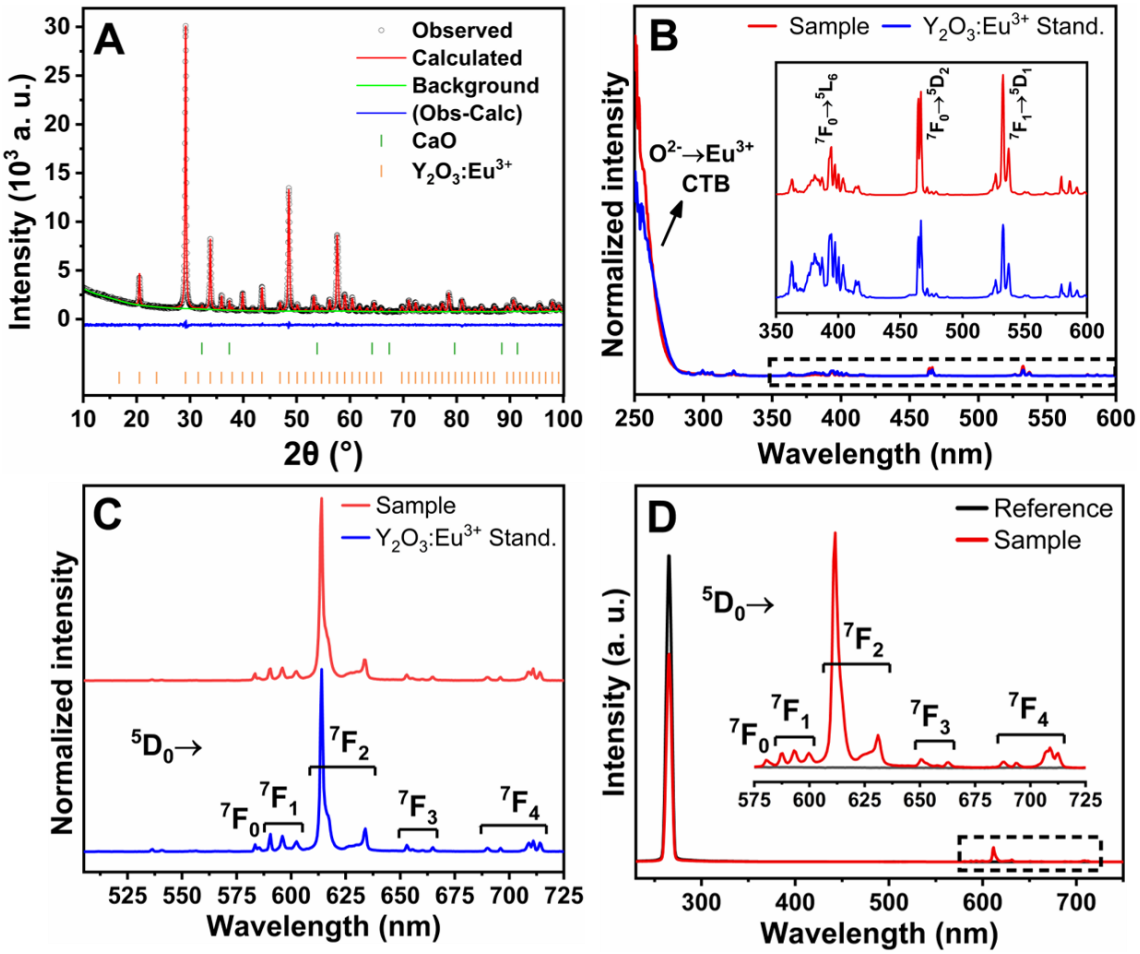


Figure 6. (a) Rietveld refinement of XRD data of recovered $Y_2O_3:Eu^{3+}$ phosphor annealed at 1000 ºC (Rwp = 3.394% and GOF = 1.37). (b) Excitation and (c) emission spectra of recovery (sample) and standard $Y_2O_3:Eu^{3+}$. (d) Absolute PL quantum yield spectra of blank (reference) and recovered $Y_2O_3:Eu^{3+}$ phosphor.

3.4 Conclusion

XRD and Rietveld refinement of the FLW material revealed its complex nature, composed of seven different crystalline phases, including halophosphate, REE-based phosphors, and other impurities. ICP-MS analysis determined the REE content to be approximately 8 wt.%, with Y and Eu together accounting for 95% of the total.

Bioleaching by *A. thiooxidans* demonstrated the capability to extract Y, Eu, and Gd from fluorescent powder due to the production of sulfuric acid under ambient conditions. Two-step bioleaching using baffled flasks yielded superior results, achieving complete solubilization (>98%) of Y and Eu in approximately three days and around 80% extraction of Gd after 14 days. La, Ce, and Tb remained insoluble in the residue, suggesting the potential for their separation from Y, Eu, and Gd through alternative methods such as high-temperature acid leaching or alkaline fusion treatment. The growth of *A. thiooxidans* was partially inhibited in the presence of 5 mmol L^{-1} of Y, and 2.5 mmol L^{-1} of Y and La, and completely inhibited by 5 mmol L^{-1} of La, but not by 10 mmol L^{-1} of Ce and Eu. Such inhibition behavior of *A. thiooxidans* in the presence of REEs was not previously investigated in the literature, and may indicate why one-step bioleaching approach is less efficient compared to two-step approach.

Moreover, europium-doped yttrium oxide (Y_2O_3:Eu^{3+}) was successfully recovered from the bioleachate via oxalate precipitation and calcination, achieving a final purity of 96%. The presence of Eu^{3+} ions and the luminescent properties of the recovered material were confirmed by photoluminescence spectroscopy. The excitation and emission spectral profiles of the recovered Y_2O_3:Eu^{3+} were similar to those of the commercial standard, indicating that Eu^{3+} ions occupy Y^{3+} sites in the same cubic phase symmetry. The recovered phosphor exhibited a promising absolute quantum yield of 32.7% under 265 nm excitation, validating its functionality as a red-emitting phosphor.

Therefore, we position this research as a focused contribution towards a sustainable alternative and a necessary step in developing a viable, lower-impact supplemental source, rather than as a definitive solution. The goal is to build a bridge toward a more circular economy for REEs, where bio-based recycling from waste mitigates the ecological cost of virgin material extraction. Our proof-of-concept study, conducted at a 2% pulp density, confirms the technical feasibility of recovering high-purity Y_2O_3:Eu^{3+}. To assess its true economic potential, future work must prioritize scaling to industrially relevant pulp densities. As noted in recent reviews, improving viability will require concerted efforts to reduce costs through non-sterile operation, strain optimization, and efficient downstream processing.

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3.6 Author contributions: CRediT

Ailton Guilherme Rissoni Toledo: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision. **Warley Pimenta de Sá:** Validation, Investigation, Data Curation. **Beatriz Sanches Gonçalves:** Validation, Investigation, Data Curation. **Felipe Bortolazzo Fernandes:** Validation, Investigation, Data Curation. **Klaiani Bez Fontana:** Investigation. **Fábio José Caixeta:** Investigation, Writing - Review & Editing. **Eduardo Sidinei Chaves:** Investigation, Writing - Review & Editing. **Elias Paiva Ferreira Neto:** Formal analysis, Resources, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition. **Sidney Jose Lima Ribeiro:** Writing - Review & Editing, Project administration, Funding acquisition. **Denise Bevilaqua:** Conceptualization, Methodology, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

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During the preparation of this work the authors used ChatGPT 4.0 (Open AI) and DeepSeek-V3.1 (DeepSeek) Large Language Models in order to improving grammar and language of this manuscript. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

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3.10 Supplementary Material

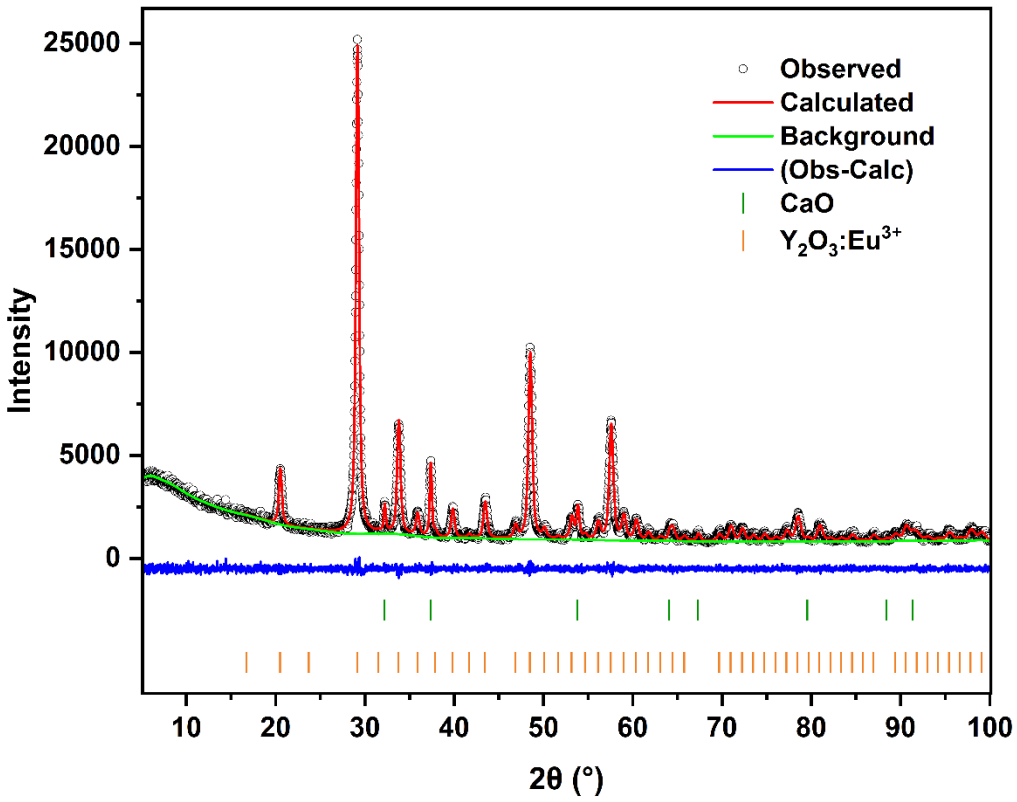

Figure S1. Rietveld refinement of XRD data for recovered $Y_2O_3:Eu^{3+}$ phosphor obtained prior to washing and subsequent annealing (Rwp = 4.934%, GOF = 2.10), indicating a CaO content of 15.5 wt%.

4 Manuscrito II:

Beyond Conventional Mining: Bioleaching of Rare Earth Elements from Spent Fluid Catalytic Cracking and Drill Cuttings for a Sustainable Supply Chain

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Abstract

The escalating global demand for rare earth elements (REEs), driven by their critical role in advanced technologies and the renewable energy transition, underscores the need for sustainable and alternative sources. This study addresses this challenge by investigating the potential of two underutilized waste streams from the oil and gas industry, drill cuttings (DC) and spent fluid catalytic cracking catalyst (SFCCC), as secondary resources for REE recovery via bioleaching with *Acidithiobacillus thiooxidans*. For SFCCC, both one-step and two-step bioleaching proved highly effective, achieving exceptional extraction yields of up to 92.0% for La and 95.1% for Ce within just three days. The process was characterized by remarkable rapidity and stability, with over 70% extraction within the first 24 hours and no observable re-precipitation over nine days. X-ray diffraction (XRD) analysis revealed that the SFCCC originates from a Y ultra-stable zeolite and confirmed the breakdown of this zeolitic structure after bioleaching, providing direct mechanistic evidence for the efficient REE liberation. These results surpass the highest recovery rates reported in the literature. In contrast, the application of a two-step bioleaching process to drill cuttings achieved a total REE recovery of approximately 40%, with individual efficiencies of 53.4% for Y, 45.2% for Ce, 44.7% for Nd, 42.5% for Pr, and 14.0% for Sc. The significant difference in efficiency between the two matrices is attributed to the complex mineralogy and high buffering capacity of the drill cuttings. To the best of our knowledge, this is the first comprehensive study dedicated to the bioleaching of REEs from drill cuttings. This research demonstrates a viable, lower-energy pathway for REE recovery, offering the dual benefit of transforming environmental liabilities into valuable resources and contributing to a more secure and circular supply of these critical elements.

Keywords: Bioleaching, Drill Cuttings, SFCCC, Rare Earth Elements, Circular Economy, Resource Recovery, *Acidithiobacillus thiooxidans*.

4.1 Introduction

The growing demand for rare earth elements (REEs), essential components in modern technologies such as electronics, renewable energy systems, and the automotive industry, has intensified the search for efficient and sustainable extraction methods. These methods aim to mitigate the environmental impacts associated with traditional mining practices (Joshi et al., 2025). In this context, spent fluidized catalytic cracking catalyst (SFCCC) and drill cuttings, materials typically considered waste from petroleum refining and drilling operations, are now being viewed as a promising yet underexplored secondary source for recovering these critical elements (Costa et al., 2023; Huang et al., 2025; Rasool et al., 2025).

The disposal of drill cuttings and SFCCC presents several environmental challenges, primarily due to the potential for leaching of harmful substances into the soil and surrounding water bodies (Costa et al.,

2023; Fontana et al., 2025; Wang et al., 2021). When heavy metals are present in drilling waste, they can seep into the soil and contaminate groundwater, leading to serious ecological and health problems (Albert and Prosser, 2023; de Costa de Azevedo et al., 2025; Hu et al., 2021; Lelchat et al., 2020).

In addition to contaminants, drill cuttings can contain REEs (generally between 100 and 400 ppm), which can be recovered. The occurrence of REEs in these materials, often adsorbed by ions or incorporated into organic matrices and mineral clays, opens up prospects for a novel extraction process. This alternative source offers the advantage of potentially requiring less energy and causing less ecological damage (Costa et al., 2023; Fontana et al., 2021; Rasool et al., 2025; Wu et al., 2024). Since they are already brought to the surface during the drilling activity itself, the need for additional mining stages to access them is eliminated. This condition establishes them as a low-cost raw material with a reduced environmental impact, worthy of further investigation for REE recovery (Rasool et al., 2025).

As for SFCCC, which are crucial for converting crude oil into gasoline in the petroleum refining industry, represent a significant source REEs. These catalysts are formulated with rare earth-exchanged zeolites and a silica-alumina matrix, containing lanthanum (La) and cerium (Ce) as their primary REEs (Huang et al., 2025). Global oil refineries generate between 700,000 and 900,000 metric tons of this spent catalyst annually. The REE content in SFCCC is considerable, with oxides of lanthanum and cerium constituting approximately 1.5 to 2.2 wt% of the material, making La a primary target for recovery operations (Chen et al., 2024; Mouna and Baral, 2019; Swain, 2023).

REEs possess unique magnetic, optical, and electronic properties, making them indispensable for countless high-technology applications. They are crucial components in products such as wind turbines, solar panels, electric vehicles, LED and LCD screens, hard disks, and various catalysts. In addition to their roles in clean energy technologies, REEs are essential in military and aerospace applications, contributing to the production of aircraft, missiles, satellites, and communication systems (Gaustad et al., 2021; Jowitt et al., 2018; Sousa Filho et al., 2019). Thus, the market demand for REEs continues to grow due to their application in emerging technologies (Joshi et al., 2025; Tejaswini et al., 2022).

Conventional mining and extraction methods pose significant environmental challenges, including the generation of toxic waste and pollution. The extraction and processing of REEs have substantial environmental repercussions. These mining operations generate substantial amounts of waste and may require high temperatures, high pressures, and significant reagent consumption (Chen et al., 2024; Joshi et al., 2025). Therefore, biohydrometallurgy can present a more sustainable alternative by converting drill cuttings and SFCCC, often classified as residues, into valuable resources (Huang et al., 2025; Owusu-Fordjour and Yang, 2023; Rasool et al., 2025).

Bioleaching is a promising technology that involves the use of microbial processes to extract metals from solid materials, which can include drill cuttings and SFCCC. This method capitalizes on the natural ability of certain microorganisms to dissolve metals from solid substrates, potentially providing an environmentally friendly alternative to conventional metal extraction methods (Brown et al., 2023; Joshi et al., 2025; Toledo et al., 2025, 2023). In the context of drill cuttings and SFCCC, bioleaching could not only aid in the recovery of valuable rare earth elements but also help mitigate the environmental impacts associated with these wastes by reducing its toxic component content (Costa et al., 2023; Piszcz-Karaś et al., 2016; Rasool et al., 2025; Wang et al., 2021).

Metal bioleaching relies on three primary mechanisms: acidolysis, complexolysis, and redoxolysis. In acidolysis, microorganisms produce acids that directly dissolve the metal from the mineral matrix. Complexolysis involves the formation of soluble metal complexes that help solubilize metals from the solid phase. Finally, redoxolysis is characterized by oxidation-reduction (redox) reactions, which oxidize components and increase the solubility of the target metals (Glombitza and Reichel, 2013; Rasoulnia et al., 2021).

The success of bioleaching depends significantly on the choice of microorganisms. For instance, chemolithoautotrophic bacteria, such as those from the genus *Acidithiobacillus*, play a crucial role in the process by catalyzing oxidation reactions (Hopfe et al., 2018; Rasoulnia et al., 2021). The effectiveness of this process is influenced by various environmental factors, such as pH, temperature, and the chemical composition of the wastes, requiring careful optimization for successful implementation.

This study evaluated the bioleaching of REEs from drill cuttings and SFCCC via a biotechnological process utilizing *Acidithiobacillus thiooxidans*, a bacterium capable of oxidizing elemental sulfur into sulfuric acid to extract REEs (Boden and Hutt, 2019; Bosecker, 1997). To the best of our knowledge, this is the first study on the bioleaching of REEs from drill cuttings.

As research and technological advancements continue to progress, bioleaching has the potential to transform the landscape of REE extraction from drill cuttings and SFCCC, aligning with broader sustainability goals and contributing to the circular economy. By recovering valuable metals from waste materials, biohydrometallurgy reduces the need for primary mining and its associated ecological damage (Chen et al., 2024; Joshi et al., 2025). Furthermore, as global demand for REEs continues to increase, especially in the context of clean energy technologies, bioleaching presents a viable alternative to ensure resource security and reduce the environmental footprint of metal production.

4.2 Material and methods

4.2.1 Drill cuttings and SFCCC samples

The drill cuttings and SFCCC samples were provided by a Brazilian oil and gas company. The drill cuttings were obtained from offshore exploration well sampling at 3453 m. The drill cuttings were manually homogenized, stored in 500 mL plastic vials under refrigeration at 8 ± 2 °C, the SFCCC were stored in plastic vials at room temperature (25 ± 5°C). Previously, for the characterization analysis and bioleaching experiments all samples were dried (at 90 ± 5 °C until constant weight), manually milled, and sieved to guarantee a particle size under 1 mm.

4.2.2 Bacterial culture and bioleaching experiments

The bioleaching experiments utilized the bacterial strain *Acidithiobacillus thiooxidans* FG-01, initially isolated from uranium mine effluents in Brazil (Garcia Jr., 1991). The microorganisms were cultivated in an adapted 9K medium, prepared with the following components per liter: 3.0 g of $(NH_4)_2SO_4$, 0.5 g of K_2HPO_4, 0.5 g of $MgSO_4 \cdot 7H_2O$, 0.1 g of KCl, and 10 g of elemental sulfur (S°) (Silverman and Lundgren, 1959). The pH of the medium was set to 2.8 using concentrated sulfuric acid. Sterilization was performed by autoclaving the basal salt solution at 120°C for 20 minutes, whereas sulfur was sterilized separately at 110°C for 60 minutes. All trials were conducted with a 10% (v/v) inoculum, an initial cellular density of 10^7 cells per mL, and a pulp density of 2%. Erlenmeyer baffled flasks were employed in the experimental setup.

The bioleaching tests were performed in 250 mL Erlenmeyer flasks containing 100 mL of working volume, agitated at 150 rpm and 30°C in an orbital shaker. Three distinct experimental conditions were established: (i) an abiotic control, consisting of sterile medium in contact with the fine-grained leaching material (DC); (ii) an one-step process, wherein inoculated medium and DC were combined at the start of the experiment; and (iii) a two-step process, in which *A. thiooxidans* was pre-cultured until the pH reached approximately 0.8 before the introduction of DC (three days of cultivation).

The acidophilic and chemolithoautotrophic bacterium *A. thiooxidans* is frequently employed in bioleaching processes for both mineral ores and municipal solid waste (Bevilaqua et al., 2002; Bosecker, 1997; Chen et al., 2024). Its metabolic activity is characterized by the oxidation of reduced sulfur compounds, resulting in the production of sulfuric acid. This key reaction is represented in Equation 1 (Boden and Hutt, 2019).

$$2S°_{(s)} + 3O_{2(g)} + 2H_2O_{(l)} \rightarrow 2H_2SO_{4(aq)} \quad (1)$$

4.2.3 Analytical measurements

The mineralogical composition of the drill cuttings and SFCCC was determined using X-ray diffraction (XRD) analysis. Measurements were carried out on a Smartlab SE diffractometer equipped with Cu-Kα radiation (λ = 1.54186 Å) operated at 40 kV and 20 mA. The scanning parameters included a Θ/2Θ axis, a range from 4° to 120° with a step size of 0.02°, and a speed of 5°/min. A length-limiting slit of 10 mm and an incident slit of 1/2° were used during data acquisition. For chemical composition the samples were analyzed by Energy Dispersive X-ray fluorescence (EDXRF) in an S2 Ranger spectrometer (Bruker, Germany) using powder pellets as sample preparation (1.2 g of the samples and 0.8 g of boric acid as a binder). The granulometry of the samples for powder pellets as sample preparation was defined as lower than 100 µm, and pressed using a PE-MAN hydraulic press (Breitlander, Germany) at 2×10^2 MPa for 2 min. The S2 Ranger measurements were carried out using a Pd X-ray tube and maximum power of 50 W. An automatic sampler and EQUA ALL software were used for instrument control, data collection, and analysis (Bruker, Germany).

The concentration of REEs in the samples were determined after acid digestion (total concentration) and in the supernatant after bioleaching experiments were determined by ICP-MS. The acid digestion was performed using a microwave-assisted acid digestion procedure adapted from Fontana et al. (2021). Briefly, sample aliquots (30-50 mg) were weighed into the digester flask, and 4.0 mL of HNO_3, 1.0 mL of HCl, 1.0 mL of H_2O_2, and 0.5 mL of HF were added. Subsequently, the samples were subjected to microwave oven-assisted digestion, the HF then was removed by reaction with boric acid. The sample solutions obtained were cooled to room temperature (25 ± 3 °C) and transferred to polypropylene vials and filled up to 50.0 mL with ultrapure water. For the bioleaching experiments, to account for evaporation during the experiments, sterile deionized water was added to the samples prior to aliquot collection. The collected samples were subsequently centrifuged. The pH, acidity (determined by titration with a standardized NaOH solution) and REEs concentration of the supernatant were determined. For REEs quantification, all the measurements were performed in triplicate using an Elan 6000 ICP-MS (Perkin Elmer-Sciex, Thornhill, Canada) with argon as a carrier gas (99.996%, White Martins, São Paulo, Brazil). The optimal instrumental conditions were obtained using RF power of 1100W, nebulizer gas flow of 1,09 L min^{-1} and sample introduction by a crossflow nebulizer coupled to a double pass Schott spray chamber. Multielement calibration curves with REEs concentration ranging from 1.0 µg L^{-1} to 80 µg L^{-1} in 1% (v/v) of HNO_3 and 5.0 µg L^{-1} of Rh as the internal standard were employed for quantifying the REEs in the different samples and bioleaching supernatant solutions.

4.3 Results and discussion

4.3.1 Characterization of SFCCC and drill cuttings samples

Drill cuttings was characterized by XRD combined with the Rietveld method to identify and quantify the crystalline phases present in this drilling industry residues (Figures 1) (O tratamento de dados da caracterização do SFCCC ainda está sendo feita). Figure 1a shows the refined XRD pattern of the drill cuttings, with good agreement between the observed and calculated diffractograms.

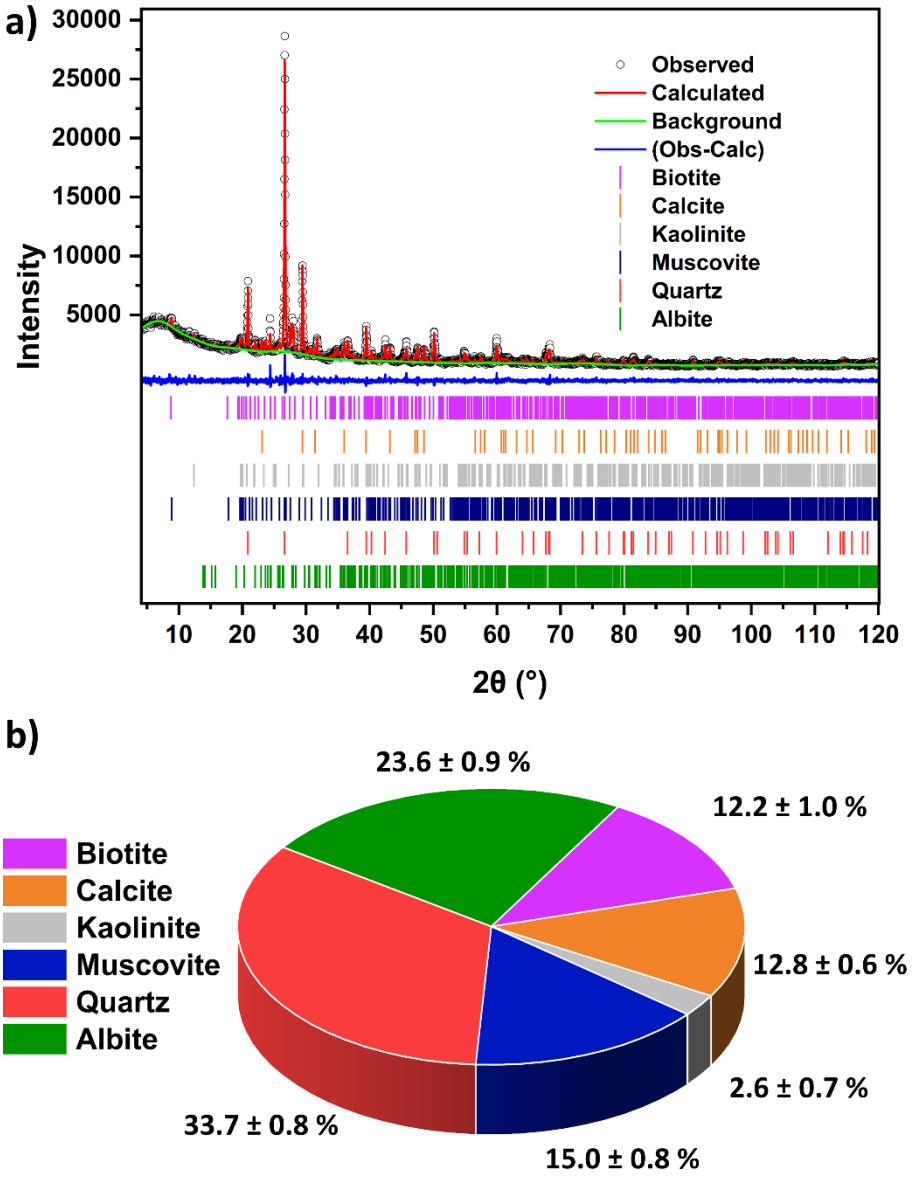


Figure 1. (a) Rietveld refinement of XRD data from drill cuttings, showing good agreement between the experimental and calculated diffractograms. (b) Quantitative crystalline phase composition determined by Rietveld refinement, illustrating the complex multiphase nature of the material, with quartz as the major component and the presence of albite, muscovite, biotite, and calcite, along with kaolinite as a minor phase.

The chemical composition of the drill cuttings, as determined by EDXRF, reveals that SiO_2 and Al_2O_3 are present in the highest percentages (Table 1). This finding is consistent with the presence of albite, muscovite, biotite, and kaolinite (aluminosilicates), as well as SiO_2, identified by XRD.

Table 1. EDXRF results for the chemical composition of drilling cuttings (% w/w).

Components	Percentages (% w/w)
Na_2O	2.4
MgO	3.1
Al_2O_3	15.54
SiO_2	53.54
K_2O	3.44
Fe_2O_3	5.81
TiO_2	0.94
MnO	0.09
CaO	9.85
BaO	0.12

The elemental analysis of the drill cuttings, obtained by EDXRF (Table 1), revealed that the sampled lithologies are predominantly composed of aluminosilicate phases, with SiO_2 (53.54%) and Al_2O_3 (15.54%) as the major constituents, followed by CaO (9.85%). Minor fractions of Na_2O, MgO, K_2O, Fe_2O3, TiO_2, MnO, and BaO were also detected. Similar compositional patterns, marked by elevated SiO_2 and Al_2O_3 contents linked to aluminosilicate minerals, were reported by Fontana et al. (2025) and Soares et al. (2022) in drill cuttings generated during offshore oil and gas exploration in in ultra-deep waters off the Brazilian coast.

The drill cuttings contained a total quantified REE content of 146 ppm, as shown in Table 2.

Table 2. Concentration of REEs in drill cuttings determined by ICP-MS (mg/kg).

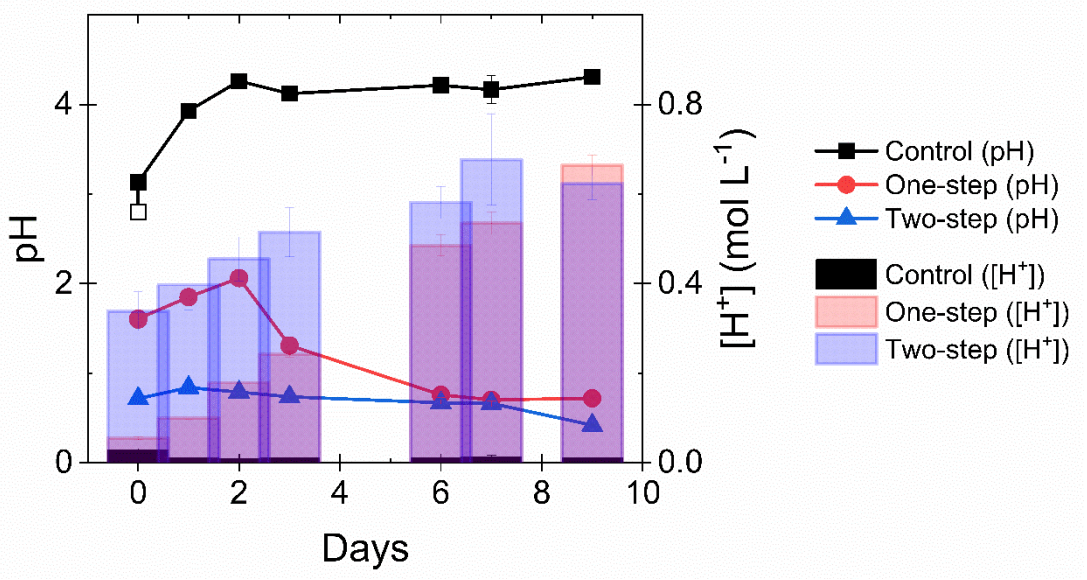
REEs	Concentration (mg/kg)
Ce	60.22 ± 1.63
Sc	33.10 ± 11.03
Nd	30.27 ± 0.27
Y	14.57 ± 0.64
Pr	8.44 ± 0.08

Other REEs, such as La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, were also identified, but their concentrations were below the Limit of Quantification (LOQ). Although drill cuttings possess low REE concentrations (100–400 ppm), which are insufficient for conventional mining, their value as a potential source of these elements lies in their unique economic advantages: high availability, zero mining cost (as they are a waste by-product), and immediate accessibility. This eliminates the substantial capital expenditures typically associated with exploration, excavation, and transportation of ores (Rasool et al., 2025).

4.3.2 Bioleaching of SFCCC

Following the addition of SFCCC, acid consumption was observed. During the initial 30 minutes, the pH of the control increased by approximately 2.8-3.1 units. In contrast, the one-step and two-step experiments showed almost no change in pH during this time period (Figure 2). The initial pH of the two-step experiment was 0.8 due to prior microbial cultivation, while the pH of the one-step experiment was lower than that of the control, a consequence of adding the inoculum at pH 0.8.

Figure 2. Changes in pH and hydrogen ion concentration ([H^+]) throughout the bioleaching process. The open symbols represent the acidity prior to the addition of the SFCCC.



The increase in acidity observed in both the one-step and two-step experiments demonstrates that microbial activity was not inhibited by the presence of SFCCC (Figure 2). As a result, both bioleaching methods proved effective for the extraction of lanthanum and cerium, as illustrated in Figures 3 and 4.

Figure 3. Kinetic profiles of La and Ce solubilization from spent fluidized catalytic cracking catalyst under one-step and two-step bioleaching.

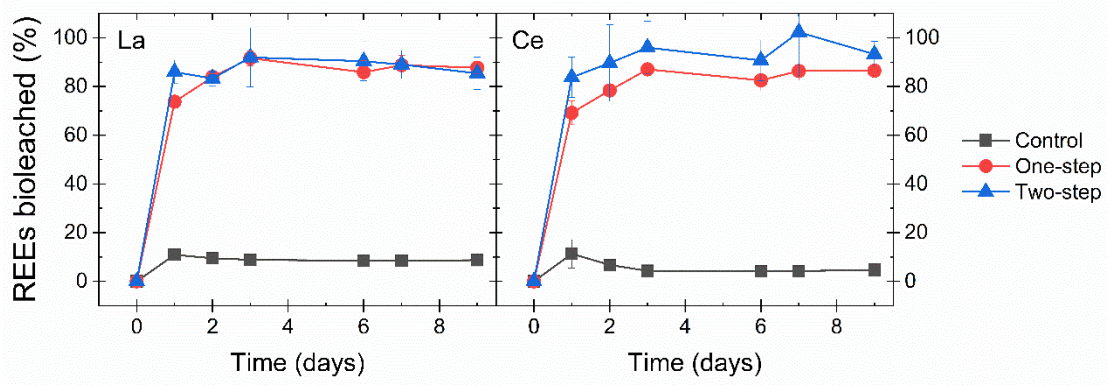
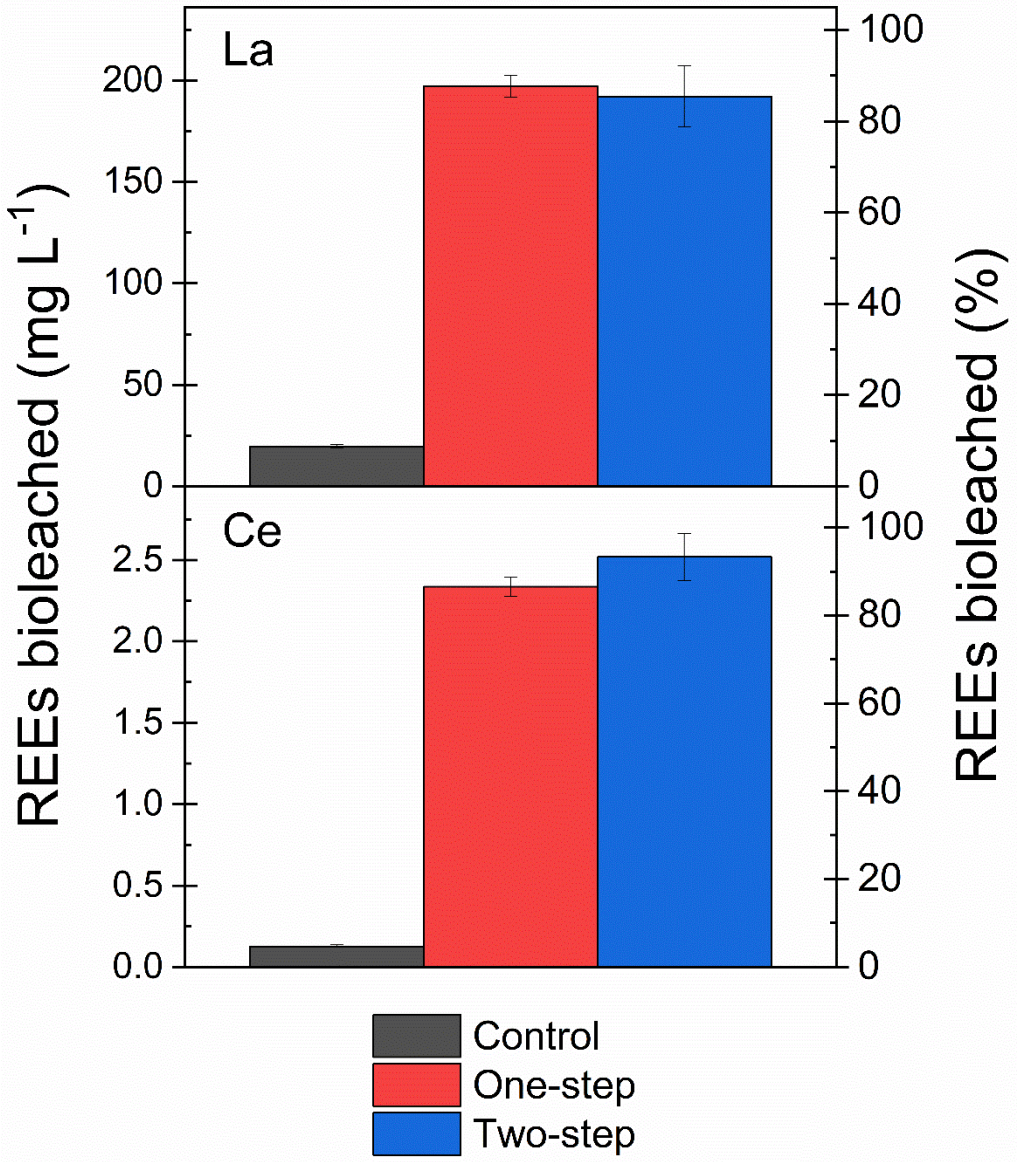


Figure 4. Rare earth elements (La and Ce) recovery yields from spent fluidized catalytic cracking catalyst under one-step and two-step processes after a nine-day bioleaching period.



The bioleaching kinetics for both lanthanum and cerium were remarkably rapid, with solubilization exceeding 70% within the first day. Notably, the solubilized rare earth elements (REEs) remained stable in solution without any observable precipitation for up to nine days (Figures 3 and 4). After three days, the extraction yields for La reached approximately 91.6 ± 3.1% (206.1 ± 6.9 mg L^{-1}) and 92.0 ± 12.1% (206.9 ± 27.3 mg L^{-1}) for the one-step and two-step processes, respectively. Similarly, the three-day Ce extraction yields attained 87.1 ± 2.2% (2.35 ± 0.06 mg L^{-1}) in the one-step and 95.1 ± 10.8% (2.59 ± 0.29 mg L^{-1}) in the two-step process. These results exceed the bioleaching values for REEs from SFCCC reported in the scientific literature (Table 3).

Table 3. Overview of REEs bioleaching studies from Spent fluidized catalytic cracking catalysts (SFCCCs).

Microorganism used for leaching	Experiment type*	Major leaching agents	Total REE leaching yield	Time	Reference
G. oxydans	Spent medium (4d of cultivation), 50mL	Gluconic acid	≈49%	1d	Reed et al. (2016)

	tubes, 150rpm, 1.5% (w/v), 30°C				
A. calcoaceticus	Spent medium (4d of cultivation), 50mL tubes, 150rpm, 1.5% (w/v), 30°C	Gluconic acid	≈27%	1d	
P. frederiksbergensis	Spent medium (4d of cultivation), 50mL tubes, 150rpm, 1.5% (w/v), 30°C	Gluconic acid	≈25%	1d	
G. oxydans	Spent medium (36-40h of cultivation), 50mL conical tubes, 150rpm, 1.5%-50% (w/v), 30°C	Gluconic acid	≈49% (1.5% w/v); ≈40% (18% w/v); ≈28% (50% w/v)	1d	Thompson et al. (2018)
G. oxydans	Two-step (12 or 36h of cultivation), stirred bioreactor, 150rpm, 1.5% (w/v), 30°C	Gluconic acid	≈56%	1-2d	
G. oxydans	Spent medium (>100h of cultivation in continuous stirred bioreactor, dilution rate: 0.05-0.38h^{-1}), 50mL conical tubes, 150rpm, 1.5% (w/v), 30°C	Gluconic acid	≈51% (0.05% h^{-1}); ≈49% (0.16% h^{-1}); ≈42% (0.38% h^{-1})	1d	
G. oxydans	Spent medium (36-40h of cultivation), column bioleaching, 1.5 and 50% (w/v), 30°C	Gluconic acid	≈46% (1.5% w/v); ≈31% (50% w/v)	1d	
Y. lipolytica	Spent medium (48h of cultivation), 500mL erlenmeyer flasks, 150rpm, 1% (w/v), 30 and 50°C	Citric acid	≈53% (La, 50°C); ≈100% (Ce, Nd, 50°C); ≈27% (La, 30°C)	1h	Azevedo et al. (2019)
G. oxydans	Spent medium (from refined glucose, corn stover and potato wastewater, 36-42h of cultivation), 50mL conical tubes, 150rpm, 50% (w/v), 30°C	Gluconic acid	≈25.7% (potato wastewater); ≈25.1% (refined glucose); ≈23.3% (corn stover)	1d	Jin et al. (2019)
G. oxydans	Spent medium (from refined glucose, corn stover and potato wastewater, 36-42h of cultivation), 50mL conical tubes, 150rpm, 1.5% (w/v), 30°C	Gluconic acid	≈40% (potato wastewater); ≈47% (refined glucose); ≈30% (corn stover)	1d	
A. niger	Two-step (3d of cultivation), 250mL	Citric acid	≈63% (La)	21d	

	Erlenmeyer flask, 130rpm, 1% (w/v), 30°C				Mouna and Baral (2019)
A. niger	Two-step (3d of cultivation), 250mL Erlenmeyer flask, 130rpm, 3% (w/v), 30°C	Citric acid	≈52% (La)	21d	
A. niger	Two-step (3d of cultivation), 250mL Erlenmeyer flask, 130rpm, 5% (w/v), 30°C	Citric acid	≈33% (La)	9d	
A. niger	Spent medium (25d of cultivation), 250mL Erlenmeyer flask, 130rpm, 1% (w/v), 30°C	Citric acid	≈30.8% (La)	21d	
A. niger	Spent medium (14d of cultivation), 300mL Erlenmeyer flasks, 120rpm, 5% (w/v), 30°C	Citric acid	≈74% (La)	3d	Dewi et al. (2020)
A. ferrooxidans	Two-step (1d of cultivation), 250mL Erlenmeyer flask with 2g L^{-1} Fe^{2+}, 130rpm, 1-20% (w/v), 30°C	Fe^{3+}	≈51% (La, 1% w/v); ≈20.2% (Ce, 1% w/v); ≈26% (La, 20% w/v); ≈11.3% (Ce, 20% w/v)	10d	Muddanna and Baral (2021)
A. ferrooxidans	Two-step (1d of cultivation), 250mL Erlenmeyer flask with 8.8g L^{-1} Fe^{2+}, 130rpm, 1-20% (w/v), 30°C	Fe^{3+}	≈83% (La, 1% w/v); ≈14.3% (Ce, 1% w/v); ≈40% (La, 20% w/v); ≈8.3% (Ce, 20% w/v)	8d	
G. oxydans	Spent medium (36-40h of cultivation), 50mL conical tubes, 150rpm, 1.5% (w/v), 30°C	Gluconic acid	≈36%	1d	Aston et al. (2022)
Y. lipolytica	Spent medium (48h of cultivation), 500mL Erlenmeyer flask, 150rpm, 0.1-1% (w/v), 50°C	Citric and oxalic acids	≈92% (La, 0.4% w/v); ≈51% (La, 1.0% w/v)	45m	Ferreira et al. (2022)
A. caldus	One-step, 500mL Erlenmeyer flasks, 150rpm, 1-5% (w/v), 45°C	H_2SO_4	≈53.8% (La, 1% w/v); ≈59.6% (Ce, 1% w/v); ≈35.9% (La, 5% w/v); ≈39.7% (Ce, 5% w/v)	14d	Wang et al. (2023)

A. caldus	Two-step (5d of cultivation), 10L bioreactor, 150rpm, 10% (w/v), 35-40°C	H_2SO_4	≈44.6% (La) ≈40.3% (Ce)	10d	
A. thiooxidans	Spent medium (until pH 0.8), flasks, 135rpm, 5% (w/v), 30°C	H_2SO_4	≈50% (La) ≈47% (Ce)	8h	Zhang and Xin (2025)
Mixed bacterial cultures	Spent medium (until pH 0.8), flasks, 135rpm, 5% (w/v), 30°C	H_2SO_4 and Fe^{3+}	≈48% (La) ≈44% (Ce)	8h	
A. thiooxidans	Two-step (until pH 0.8), flasks, 135rpm, 5% (w/v), 30°C	H_2SO_4	≈47% (La) ≈43% (Ce)	8h	
Mixed bacterial cultures	Two-step (until pH 0.8), flasks, 135rpm, 5% (w/v), 30°C	H_2SO_4 and Fe^{3+}	≈44% (La) ≈41% (Ce)	8h	
A. thiooxidans	Two-step (until pH 0.8), flasks, 135rpm, 5% (w/v), 30°C	H_2SO_4	≈47% (La) ≈43% (Ce)	8h	
A. thiooxidans	Spent medium (until pH 0.8), flasks, 160rpm, 5% (w/v), 30°C	H_2SO_4	≈83% (La) ≈79% (Ce)	8h	
A. thiooxidans	One-step, 250mL baffled Erlenmeyer flasks, 160rpm, 2% (w/v), 30°C	H_2SO_4	≈91.6% (La) ≈87.1% (Ce)	3d	This work
A. thiooxidans	Two-step (3d of cultivation), 250mL baffled Erlenmeyer flasks, 150rpm, 2% (w/v), 30°C	H_2SO_4	≈92.0% (La) ≈95.1% (Ce)	3d	

*Cell-free medium obtained from filtered supernatants of a grown culture.

The presence of microbial cells during bioleaching did not impair the extraction of rare earth elements (REEs). In fact, Thompson et al. (2018) and Mouna and Baral (2019) reported that the two-step bioleaching method yielded higher efficiency compared to the spent medium approach (Table 3). Consequently, process scale-up can avoid the costs associated with microbial cell filtration.

Another significant cost factor in these processes is the carbon source. Most studies reported in the literature have employed heterotrophic microorganisms (Table 3), which require an organic carbon source that can increase process costs. To address this issue, Jin et al. (2019) evaluated agricultural wastes as a substrate for fermentation to develop a more cost-effective bioleaching process. In comparison, *A. thiooxidans* offers the advantage of being an autotrophic microorganism, obtaining carbon from CO_2 and producing minimal biomass. Excessive biomass production, as seen in heterotrophic systems, could interfere with the recovery of solubilized REEs.

Unlike our findings, in which the REE concentration reached a plateau and remained constant over time, Mouna and Baral (2019) observed a decrease in the concentration of solubilized REEs. This was likely attributable to re-precipitation as La-citrate, gluconate, or oxalate complexes, as well as bioaccumulation and adhesion of lanthanum to *A. niger*. Similarly, Dewi et al. (2020) suggested the

potential precipitation of lanthanum as lanthanum oxalate, achieving better results with an organic acid-producing process that excluded oxalic acid.

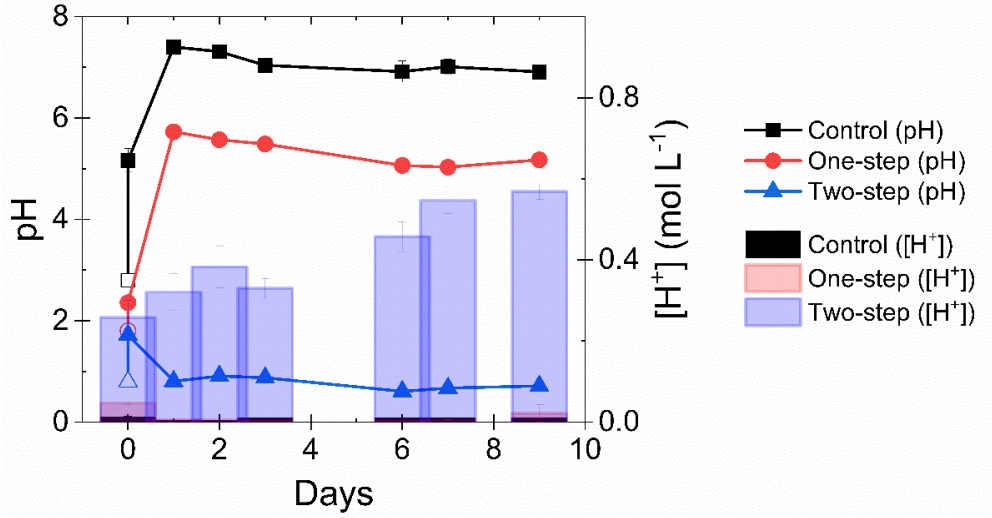
Our one and two-step processes achieved the highest La and Ce recovery percentages reported to date. Furthermore, by assessing one-step bioleaching with *A. thiooxidans* for the first time, we demonstrated the feasibility of extracting REEs in a single step, which could enable upscaling in continuous reactors. Among the studies found in the literature (Table 3), the previously highest reported recoveries were by Muddanna and Baral (2021) using an autotrophic bacterium, with a maximum of 83% for La (1% w/v pulp density, 5 days, two-step) and 23% for Ce (5% w/v pulp density, 10 days, two-step), Ferreira et al. (2022) using a heterotrophic microorganism, achieving approximately 92% La solubilization (0.4% w/v pulp density, 45 minutes, spent medium), and by Zhang and Xin (2025) also using *A. thiooxidans* with 83% for La and 79% for Ce (5% w/v pulp density, 8 hours, spent medium).

The efficacy of the bioleaching process is further corroborated by X-ray diffraction (XRD) analysis, the diffractograms identified the primary solid phase of the SFCCC as a Y ultra-stable zeolite. A significant decrease in the intensity of the characteristic crystalline peaks was observed following bioleaching, indicating a partial breakdown of the zeolitic framework. This structural alteration provides a direct mechanistic explanation for the high REE liberation, as the dissolution of the host matrix directly releases the incorporated rare earth elements into the solution.

4.3.3 Bioleaching of drill cuttings

The variation in acidity during bioleaching of drill cuttings is shown in Figure 5:

Figure 5. Changes in pH and hydrogen ion concentration ($[H^+]$) throughout the bioleaching process. The open symbols represent the acidity prior to the addition of the drill cuttings.



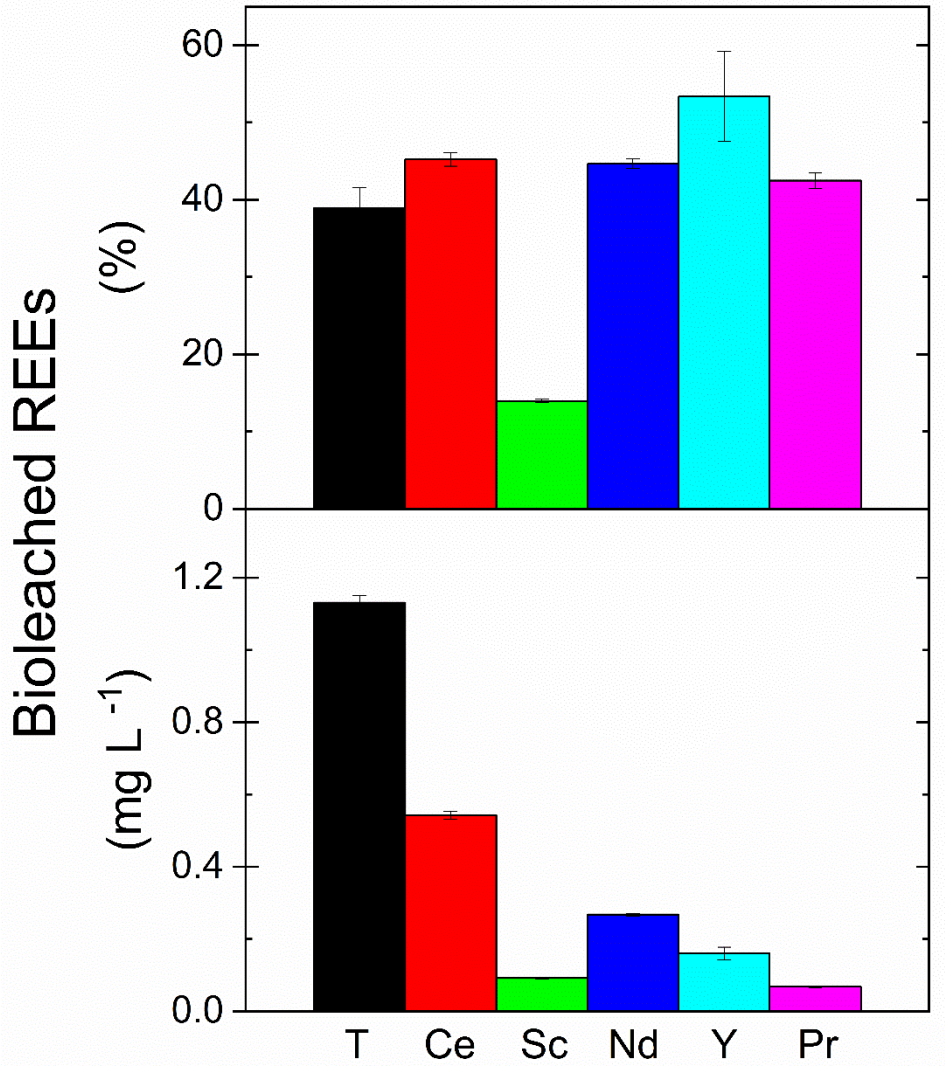
Following the addition of the drill cuttings, rapid acid consumption occurred in all assays, with a higher acid consumption than that of the SFCCC (Figures 2 and 5). During the initial 30 minutes, the pH increased by approximately 2.8-5.2, 1.8-2.4, and 0.8-1.7 units for the control, one-step, and two-step experiments, respectively.

Between days 1 and 2, the residue consumed a substantial quantity of acid from the medium, evidenced by a rise in pH to approximately 7.4 and 5.7 in the control and one-step experiments, respectively (Figure 5). This neutralizing effect aligns with observations in soils amended with drill cuttings, which exhibit high innate buffering capacity attributable to their physicochemical properties, including elevated pH (~10), and high carbonate, calcium, and organic matter content (Kujawska and Pawłowska, 2022;

Stuckman et al., 2019). In contrast, the acidity in the two-step experiment increased due to microbial metabolism, which was not inactivated by the sharp pH increase outside its optimal growth range. Beyond the second day, the acid concentration remained relatively stable for the duration of the experiment across all conditions.

Microbial acid generation in the two-step system promoted the bioleaching of REEs from the drill cuttings (Figure 6). In contrast, no REE solubilization was detected in either the control or one-step experiments, attributable to the elevated pH environment caused by the acid-neutralizing capacity of the residue. Due to its high buffering capacity, a consequence of the significant lime and aluminosilicate content (Table 1), the material proved unsuitable for one-step bioleaching.

Figure 6. The recovery of the total amount and of each individual rare earth element (Ce, Sc, Nd, Y and Pr), obtained from drill cuttings under two-step processes after a nine-day bioleaching period. La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu, were also identified, but their concentrations were below the Limit of Quantification (LOQ).

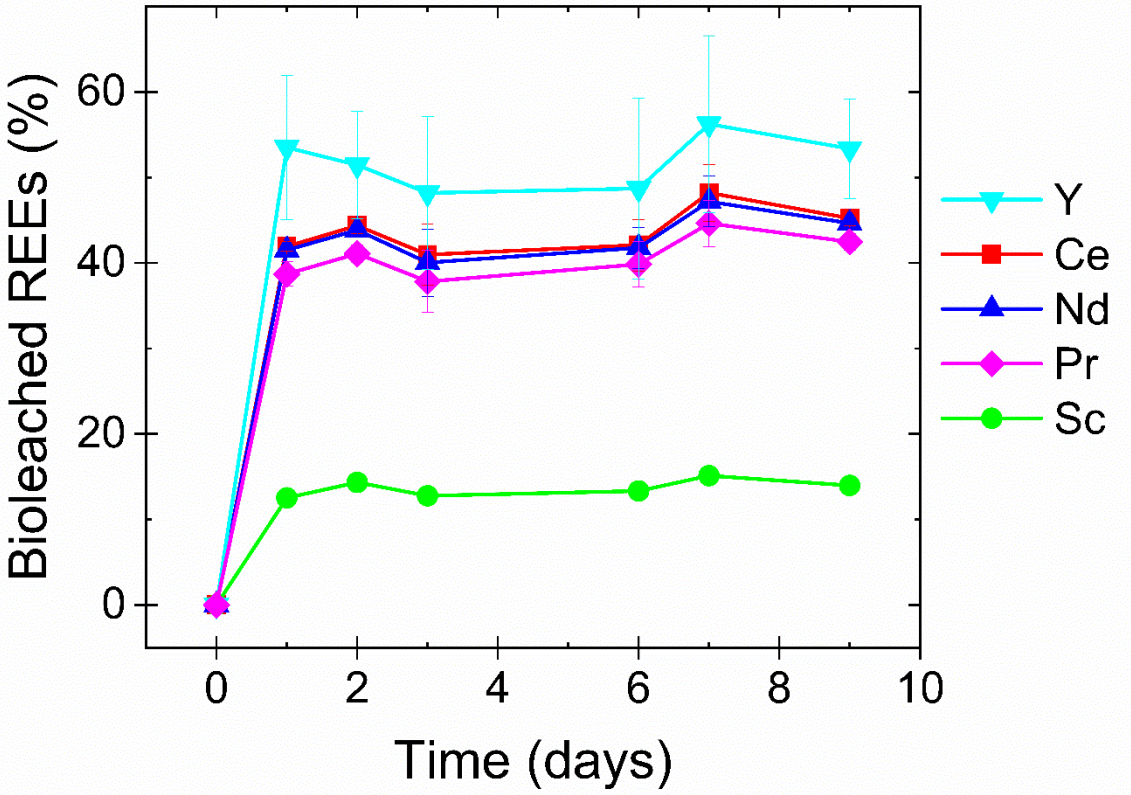


Approximately 40% of all REEs shown in Figure 6 were solubilized, corresponding to a concentration of 1.13 ± 0.02 mg L^{-1}. The extraction efficiencies for individual elements were 45.2 ± 0.9% for Ce, 14.0 ± 0.2% for Sc, 44.7 ± 0.6% for Nd, 53.4 ± 5.9% for Y, and 42.5 ± 1.0% for Pr. Bioleaching was conducted at a 2% pulp density, with the drill cuttings containing a total quantified REE content of 146 ppm.

A study investigating the association of rare earth elements (REEs) with different shale phases and their release into the environment also reported low REE solubilization yields, specifically, Bhattacharya et al. (2022) analyzed the Haynesville and Marcellus Shale, reporting total REE concentrations ranging from 295 to 342 ppm. Despite this REE content, the average leaching efficiency was markedly low, attaining only approximately 20% for the Haynesville Formation and a mere 9% for the Marcellus Formation. The authors attributed the low recovery to a substantial refractory fraction predominantly composed of aluminosilicate and clay minerals. Their findings further indicate that conventional sequential extraction techniques are largely ineffective for REE liberation from these organic-rich, aluminosilicate-bearing shales.

The presence of ion-adsorbed clays, such as muscovite and kaolinite at 15.0 ± 0.8% and 2.6 ± 0.7%, respectively (Figure 1), which can be more readily leached (Moldoveanu and Papangelakis, 2016; Rasool et al., 2025; Wu et al., 2023), may have contributed to the rapid REE solubilization observed in this study (Figure 7), with total REE extraction reaching 37.6% after the first day. Furthermore, as shown in Figure 1, the presence of albite (23.6 ± 0.9%) and biotite (12.2 ± 1.0%), which are less resistant to weathering than muscovite (Goldich, 1938; Wu et al., 2023), may also have promoted the kinetics of REE solubilization.

Figure 7. Kinetic profiles of REEs (Y, Ce, Nd, Pr and Sc) solubilization from drill cuttings under two-step bioleaching.



Low recovery efficiencies can be explained by REEs incorporated into mineral crystal lattices (Rasool et al., 2025). Fontana et al. (2025) evaluated REE fractionation in sediments from Brazilian offshore drilling wells, separating REEs into four fractions (F1–F4) with distinct mobility behaviors. The residual fraction (F4) contained the largest proportion of REEs, accounting for 45–80% of the total recovered. In this fraction, REEs are bound within the crystalline structures of primary minerals, rendering them geologically stable, resistant to leaching, and thus considered unavailable.

4.4 Conclusion

This study establishes the technical feasibility of bioleaching with *A. thiooxidans* for recovering rare earth elements (REEs) from two distinct oil and gas industry wastes: spent fluid catalytic cracking catalyst (SFCCC) and drill cuttings. The research demonstrates that the optimal process strategy is highly dependent on the specific chemical and mineralogical characteristics of the waste matrix.

For SFCCC, both one-step and two-step bioleaching proved highly effective, achieving exceptional extraction yields of up to 92.0% for La and 95.1% for Ce within just three days. A key finding was the remarkable rapidity and stability of the process, with over 70% extraction occurring within the first 24 hours and no observable re-precipitation of REEs over nine days. These results not only confirm the non-inhibitory nature of SFCCC in the conditions studied but also surpass the highest recovery rates reported in the literature. The XRD analysis provided critical insight into the underlying mechanism, revealing that the SFCCC originates from a Y ultra-stable zeolite. The observed decrease in the intensity of the crystalline phases after bioleaching suggests the breakdown of the zeolitic structure, which subsequently led to the release of rare earth elements into the solution. This direct evidence of matrix alteration underscores the efficacy of the bioleaching process in disrupting the host material and facilitating efficient REE liberation.

In contrast, the processing of drill cuttings required a two-step bioleaching approach to be effective. The material's high content of lime and aluminosilicates conferred a strong buffering capacity, rendering one-step bioleaching ineffective. The successful two-step process achieved a total REE recovery of approximately 40%, a notable efficiency for such a refractory matrix. The variability in individual element recovery, higher for Y (53.4%), Ce (45.2%), Pr (42.5%), and Nd (44.7%) than for Sc (14.0%), reflects the diverse modes of occurrence of REEs within the cuttings. The rapid initial kinetics suggest a labile, such as ion-adsorbed clays, easily accessible fraction, while the overall recovery limit points to a significant refractory fraction locked within silicate crystal structures. Moreover, this is the first study to investigate the bioleaching of drill cuttings.

This work provides a novel proof-of-concept for valorizing these underutilized waste streams. Future research should focus on pre-treatment methods to destroy carbonates and disrupt refractory silicates, coupled with the exploration of more robust microbial consortia. Such optimizations are crucial for developing economically viable processes that can transform these environmental liabilities into secondary resources, ultimately contributing to a circular economy for critical metals.

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Writing - Review & Editing. **Klaiani Bez Fontana:** Methodology, Validation, Investigation, Data Curation, Writing - Review & Editing. **Warley Pimenta de Sá:** Validation, Investigation, Data Curation. **Tatiane de Andrade Maranhão:** Writing - Review & Editing. **Eduardo Sidinei Chaves:** Writing - Review & Editing. **Elias Paiva Ferreira Neto:** Formal analysis; Data Curation; Resources, Writing - Review & Editing, Visualization, Supervision, Project administration, Funding acquisition. **Sidney Jose Lima Ribeiro:** Writing - Review & Editing, Project administration, Funding acquisition. **Denise Bevilaqua:** Conceptualization, Methodology, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

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5 Orientações

Continuo (co)orientando 1 TCC (aluno: Felipe Bortolazzo Fernandes), tendo completado a coorientação como supervisor científico de 1 TCC (Sá, 2025) e a coorientação de uma dissertação de mestrado (Ribeiro, 2025).

6 Disciplinas Ministradas

6.1 Professor de Bioquímica prática e teórica do Departamento de Bioquímica e Química Orgânica, do Instituto de Química – UNESP – Campus Araraquara (2023). Carga horária: 120.

6.2 Professor de Disciplina de pós-graduação: "Biomineração, extração e recuperação de metais de minérios e rejeitos" nos programas de Química e Biotecnologia, do Instituto de Química – UNESP – Campus Araraquara (2023). Carga horária: 60.

7 Lista de publicações no período

1. Toledo, A. G. R.; Thomeo, Y. M.; Dussán, K. J.; Benedetti, A. V.; Bevilaqua, D. Electrochemical insights into chalcopyrite leaching: Applying semiconductor theory for enhanced recovery. **Minerals Engineering**, v. 233, p. 109662, 2025.

2. Toledo, A. G. R.; Benedetti, A. V.; Bevilaqua, D. Semiconductor Aspects of Chalcopyrite and its Relevance for Copper Bioleaching: A Review. **Mineral Processing and Extractive Metallurgy Review**, v. 45, p. 1-23, 2024.

3. Bevilaqua, D.; **Toledo, A. G. R.**; Crocco, L. G.; P., R. N.; Costa, R. B.; Benedetti, A. V.; Tuovinen, O. H. **Chalcopyrite Dissolution: Challenges**. Advances in Science, Technology & Innovation. 1ed.Cham: Springer International Publishing, 2024, p. 23-39.

4. Toledo, A. G. R.; Costa, R. B.; Delforno, T. P.; Arena, F. A.; Bevilaqua, D. Exploring chalcopyrite (bio)leaching mechanisms under thermophilic conditions. **Minerals Engineering**, v. 204, p. 108417, 2023.

5. Toledo, A. G. R.; Bevilaqua, D.; Panda, S.; AKCIL, A. Hydrometallurgical Processing of Sulfide Minerals from the Perspective of Semiconductor Electrochemistry: A Review. **Minerals Engineering**, v. 204, p. 108409, 2023.

8 Outros

8.1 Congressos

- XXXV e XXXVI Congressos de Iniciação Científica da UNESP (CIC-2023 e 2024, apresentações em pôster pelos alunos de IC Beatriz Sanches Gonçalves e Warley Pimenta de Sá, que coorientei);

-47ª Reunião Anual da Sociedade Brasileira de Química (SBQ-2024, apresentação em pôster pela aluna de IC Beatriz Sanches Gonçalves, que coorientei);

- *Key Technologies in the Bioeconomy* (KTB-2024, *oral presentation*);

-XIII Four Biotec (2025, apresentação em pôster);

Participei como avaliador nos Congressos de Iniciação Científica (XXXV (2023), XXXVI (2024) e XXXVII (2025) da UNESP. Também participei da organização dos Eventos de Educação em Química (EVEQ) XXI (2023) e XXII (2024) (congressos da área de Educação em Química).

8.2 Startup

Fundador da startup *Biorecycling Solutions*, visando empreender futuramente os resultados dos estudos publicados.

9 Bibliografia

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