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EXTRACTION OF RARE EARTH ELEMENTS FROM END-OF-LIFE LED LAMPS USING ACID LEACHING

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Advisors: Prof. Dr. Renato Ribeiro Siman and Prof.ª Dr.ª Luciana Harue Yamane

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Extraction of rare earth elements from end-of-life LED lamps using acid leaching

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RESUMO

A recuperação de elementos de terras raras (ETR) é uma preocupação crescente devido à sua importância em várias indústrias e a incerteza na oferta desses metais. Os resíduos de equipamentos elétricos e eletrônicos (REEE) representam uma fonte secundária potencialmente valiosa para a recuperação de ETR, porém, a falta de rotas consolidadas e a limitação dos estudos a alguns dos 17 ETR têm sido desafios evidentes. Afim de identificar lacunas no âmbito da recuperação de ETR a partir de REEE, uma revisão sistemática foi realizada descrevendo as condições e procedimentos aplicados a lâmpadas fluorescentes, fósforos de tubos de raios catódicos, ímãs de neodímio, baterias de níquel-metal hidreto, placas de circuito impresso, resíduos de LED e outras fontes secundárias. Os processos hidrometalúrgicos, com ácido sulfúrico como agente de lixiviação principal, foram amplamente utilizados. No entanto, há lacunas notáveis, como a falta de estudos sobre a recuperação sequencial de metais como cobre, ferro, prata, ouro e ETR, bem como a ausência de pesquisas abordando a recuperação de uma mistura de diferentes resíduos. Ainda, o uso de lâmpadas de LED como potencial fonte secundária de elementos de terras raras permanece relativamente pouco estudado na literatura, uma vez que não existem grandes quantidades de estudos que investiguem a recuperação de ETR, como cério e ítrio, a partir desse tipo de resíduo. A fim de explorar o processo hidrometalúrgico avaliou-se três agentes lixiviantes (ácido nítrico, ácido sulfúrico e a combinação de ácido sulfúrico e peróxido) para extração de elementos terras raras a partir de placas de circuito impresso (PCI) e componentes eletrônicos de lâmpadas LED inservíveis. Foram avaliadas as influências da temperatura, concentração de ácidos e relação sólido-líquido utilizando um delineamento experimental Box-Behnken, analisando três níveis em cada fator. A otimização do processo revelou que a melhor combinação de agentes lixiviantes consiste em ácido sulfúrico e peróxido de hidrogênio, com os parâmetros ideais de concentração de 2.5 $mol.L^{-1}$, temperatura de 55°C e uma relação sólido-líquido de 100 $g.L^{-1}$. Embora nenhuma das variáveis tenha demonstrado uma influência estatisticamente significativa dentro da faixa investigada, ao se utilizar ácido sulfúrico e peróxido de hidrogênio, no cenário mais favorável, tanto a temperatura quanto a relação sólido-líquido tiveram um impacto notável no processo de extração. Como direção para pesquisas futuras, sugerimos a exploração de novos intervalos de parâmetros com base nas condições mais favoráveis identificadas neste estudo e ainda complementar a avaliação com rotas de purificação/recuperação. Além disso, pode ser benéfico considerar a implementação de um procedimento em estágios múltiplos, possivelmente incorporando uma etapa de separação mecânica ou uma fase adicional de lixiviação. Essa abordagem poderia resultar no aumento da concentração de elementos de terras raras no material sólido, ao mesmo tempo em que permitiria a remoção de outros metais, tais como ferro, cobre e chumbo, tornando o processo mais atrativo.

Palavras-chave: Elementos Terras Raras, Cério, Ítrio, Lâmpadas de LED, REEE, Lixiviação.

ABSTRACT

The supply of rare earth elements (REE) is a growing concern due to their importance in various industries and the uncertainty in the supply of these metals. Waste electrical and electronic equipment (WEEE) represents a potentially valuable secondary source for REE recovery. However, the lack of consolidated routes and the limitation of studies to some of the 17 REE have been clear challenges. A systematic review was carried out describing the conditions and procedures applied to fluorescent lamps, cathode ray tube phosphors, neodymium magnets, nickel-metal hydride batteries, circuit boards printed, LED waste, and other secondary sources to identify gaps in the scope of ETR recovery from WEEE. Hydrometallurgical processes utilizing sulfuric acid as the primary leaching agent found extensive use. Nonetheless, there are notable gaps, such as the lack of studies on the sequential recovery of metal such as coper, iron, silver, gold, and REE metals. Additionally, there is an absence of research addressing a mixture of different wastes. LED lamps are a potential secondary source of rare earth elements, but they remain relatively little studied in the literature since there are not large numbers of studies that investigate the recovery of REE, such as cerium and yttrium, from this type of residue. Thus, to develop the first stage of the hydrometallurgical process, three leaching agents were assessed for extracting rare earth elements from printed circuit boards (PCB) and electronic components of end-of-life LED lamps: nitric acid, sulfuric acid, and a combination of sulfuric acid and peroxide. The influences of temperature, acid concentration, and solid-liquid ratio were evaluated using a Box-Behnken experimental design, analyzing three levels in each factor. Process optimization revealed that the higher results were using the combination of sulfuric acid and hydrogen peroxide, with the ideal parameters of concentration of 2.5 mol.L^{-1}, temperature of 55°C, and a solid-liquid ratio of 100 g.L^{-1}. Although none of the variables demonstrated a statistically significant influence within the range investigated when using sulfuric acid and hydrogen peroxide, in the most favorable scenario, both temperature and solid-liquid ratio had a notable impact on the extraction process. As a direction for future research, we suggest exploring new parameter ranges based on the most favorable conditions identified in this study and also complement the evaluation with purification/recovery routes. Additionally, it may be beneficial to consider implementing a multi-stage procedure, possibly incorporating a mechanical separation step or an additional leaching phase. This approach could increase the concentration of rare earth elements in the solid material while allowing for the effective removal of base metals, making the process more efficient and economically viable.

Keywords: Rare Earth Elements, Cerium, Yttrium, LED Lamps, RE, Leaching.

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ABBREVIATIONS LIST

% v/v, Volume/volume percentage

Al, Aluminum

ANOVA, Analysis of variance

Ce, Cerium

Cr, Chrome

Cu, Copper

Dy, Dysprosium

EEE, Electrical and electronic equipment

Er, Erbium

Eu, Europium

Fe, Iron

Ga, Gallium

Gb, Gadolinium

H2O2, Hydrogen Peroxide

H2SO4, Sulfuric Acid

HCl, Hydrochloric Acid

Ho, Holmium

ICP-OES, Optical Emission Spectrometry with Inductively Coupled Plasma

La, Lanthanum

LCD, liquid crystal display

LED, light-emitting diode

Lu, Lutetium

Nd, Neodymium

Ni, Nickel

Pb, Lead

PCB, Printed circuit board

Ppm, Parts per million

Pr, Praseodymium

REE, Rare Earth Element

Sm, Samarium

Sn, Tin

Tb, Terbium

Tm, Thulium

WEEE, Waste electrical and electronic equipment

Y, Yttrium

Yb, Ytterbium

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CHAPTER 1

GENERAL INTRODUCTION AND DISSERTATION SCOPE

Electrical and electronic equipment (EEE) are increasingly inserted in modern society, with global consumption estimated to increase by 2.5 million tons per year (Forti *et al.*, 2020). Once users discard these types of equipment, they are considered waste of electrical and electronic equipment (WEEE). Like new electrical and electronic devices, WEEE has an increasing generation flow. Baldé et al. (2022) predicts that WEEE generation will exceed 74 million tons in 2030 and it will reach 110 million tons per year in 2050.

The growing and expressive generation of WEEE raises concern about the forms of treatment, especially involving materials recovery, in line with the concept of circular economy (Gaustad et al., 2018; Kanwal; Li; Zeng, 2021; Tansel, 2016). However, the treatment process depends on the composition, as WEEE has a variety of components and materials, from hazardous to valuable, depending heavily on the design and functionality of the device (Shittu; Williams; Shaw, 2021).

WEEE treatment has economic and environmental benefits (Ahirwar; Tripathi, 2021). From an economic point of view, Forti et al. (2020) estimate that 57 billion dollars in secondary materials were present in the total WEEE generated in 2019, showing the potential value embedded in this waste. From an environmental standpoint, the irregular disposal of WEEE can cause the dispersion of pollutants, such as heavy metals or flame retardants, causing potential damage to water bodies, soil, and air, in addition to affecting human health. Additionally, it can disperse critical and secondary materials that can have economical value (Balaram, 2019; Dang; Zhang, 2021).

In addition, the growing demand for EEE has caused concern regarding critical materials supply, such as rare earth elements (Oliveira; Benvenuti; Espinosa, 2021). Thus, the recovery of secondary materials from WEEE becomes essential due to the depletion of primary sources, with recovery strategies being prioritized in several countries, especially in those with scarce mineral reserves (Chagnes et al., 2016; Shittu; Williams; Shaw, 2021).

Within the electronics category, there are various types of equipment, such as home appliances, computers, smartphones, photovoltaic panels, and LED lamps (Confederação Nacional da Indústria, 2017). LED lamps are considered WEEE, unlike traditional fluorescent lamps or sodium and mercury vapor lamps, although there are disagreements in this regard.

According to Liu and Keoleian (2020), LED brought advantages in energy savings, with LED lamps being 40% more energy efficient than fluorescent lamps. Additionally, features such as customizable colors, design flexibility, and enhanced economic and energy efficiency have enabled LED lamps to permeate and dominate the lighting sources market (Cenci et al., 2020b). Given the advantages and the consequent expansion of the market, a considerable increase in the generation of waste from LED lamps is estimated (Cenci et al., 2020a), which justifies the search for recycling processes for their components.

Thus, it is relevant to describe that LED lamps contain polymeric and metallic parts, including PCBs, electronic components, batteries, and cables (Cenci et al., 2020b). Valuable metals like gold, silver, aluminum, copper, and rare earth elements (REE) are present in the metallic fraction and PCB, as a result, LED lamp recycling has gained significant research focus (Martins; Tanabe; Bertuol, 2020; Rebello et al., 2020).

In addition to the financial potential, rare earth elements are essential for future technologies applied by the electronics industry, green technology, energy, mobility, aviation, lighting, and computing, among other areas (Patil *et al.*, 2021).

The criticality of REEs is related to the supply risk due to geological scarcity, regarding different proportions of some REE in ores, extraction difficulties, and dependence on some countries, with China holding 97% of their production (Lie; Liu, 2021a; Makarova et al., 2020; Yuksekdag et al., 2021). Thus, it is necessary to identify alternative secondary sources to promote the sustainable use of rare earth elements (Annoni et al., 2020; Marra; Cesaro; Belgiorno, 2019; Ruiz-Mercado et al., 2017).

The main routes established for rare earth elements recovery from WEEE are hydrometallurgical and pyrometallurgical (Lie; Lin; Liu, 2021). Nonetheless, when it comes to extracting metals from secondary sources, the preferred method is hydrometallurgy, mainly due to less energy demand and gas emissions (Ahirwar; Tripathi, 2021; Akcil et al., 2021; Marra; Cesaro; Belgiorno, 2019).

The extraction of rare earth elements by hydrometallurgical route is investigated for secondary sources, such as nickel metal hydride batteries (Ahn *et al.*, 2020; Vargas *et al.*, 2021), electronic waste grinding dust (Marra *et al.*, 2018; Talebi *et al.*, 2018), and neodymium magnets (Ciro *et al.*, 2019; Makarova *et al.*, 2020). However, varying compositions, specifically distinct secondary sources, return disparate leaching outcomes, even in cases where identical methodologies are employed (Innocenzi; De Michelis et al., 2013; Tunsu et al., 2016).

Hence, it is fundamental to explore separately the efficiency of the extraction. In this context, Oliveira, Benvenuti, and Espinosa (2021) propose employing hydrometallurgical methods for extracting rare earth elements from waste generated by LEDs.

Mineral acids, such as nitric and sulfuric acid, are extensively employed for leaching rare earth elements from secondary and primary sources (Marra; Cesaro; Belgiorno, 2019). Additionally, during the leaching stage of the hydrometallurgical process, common factors under investigation include the type and concentration of the leaching agent, the solid-to-liquid ratio, temperature, and reaction duration (Pimassoni *et al.*, 2023). Although extensive research has been conducted, a definitive consensus regarding the optimal reaction conditions for rare earth element extraction remains elusive. These conditions exhibit variability based on the specific waste type and even diverge among studies targeting the same secondary source. Such distinctions arise from factors variations such as models, manufacturers, production years, and other pertinent aspects.

Thus, the present research aimed to develop the leaching step of a hydrometallurgical process to recover rare earth elements from end-of-life LED lamps. Leaching agents (nitric acid, sulfuric acid, and sulfuric acid with hydrogen peroxide) were assessed. Evaluated parameters were temperature, acid concentration, solid-liquid ratio and leaching time.

Dissertation Scope

Chapter 2 presents a systematic literature review describing the process applied to recover REE from different types of WEEE. This Chapter presented a residue composition analysis, the processes used in fluorescent lamps, cathode-ray tube phosphors, NdFeB magnets, nickel-metal hydride batteries, WEEE crushing powder, printed circuit boards, LED residue, and other residues. Furthermore, the benefits and drawbacks of each primary process, along with a flow chart of the most successful processes applied, were provided. The Chapter was published in the Hydrometallurgy journal (Impact Factor (2020) 4.7 and QUALIS CAPES A1) with DOI:10.1016/j.hydromet.2023.106156.

Chapter 3 contains the experimental part of the research. In this Chapter three leaching agents were investigated: nitric acid, sulfuric acid, and the combination of sulfuric acid and hydrogen peroxide. The impact of temperature (25 to 55°C), acid concentration (1 to 4 mol.L^{-1}), and solid-liquid ratio (25 to 100 g.L^{-1}) in the extraction of yttrium and cerium was examined, leading to the optimal leaching conditions identification for each acid used. Chapter 4 is composed of the conclusions, limitations, and future research.

CHAPTER 2

THE RECOVERY OF RARE EARTH ELEMENTS FROM WASTE ELECTRICAL AND ELECTRONIC EQUIPMENT: A REVIEW

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Resumo

Elementos de terras raras (ETR) são considerados metais críticos devido ao seu risco de oferta e demanda crescente devido a importância econômica em diversos segmentos industriais. Resíduos de equipamentos elétricos e eletrônicos (RE) são um potencial material secundário para a recuperação de ETR que permanece inexplorada em escala comercial. Além disso, o processo carece de rotas consolidadas, e a literatura tem estudado apenas a recuperação de alguns dos 17 ETR. Esta revisão sistemática descreve as condições e procedimentos aplicados a lâmpadas fluorescentes, fósforos de tubos de raios catódicos, ímãs de neodímio, baterias de níquel-metal hidreto, placas de circuito impresso, resíduos de LED e outras fontes secundárias para identificar os desafios e lacunas da recuperação de ETR. Ítrio, neodímio e cério são os elementos mais comumente recuperados. Com a maior concentração de ETR em sua composição, os resíduos de imas de NdFeB são os mais investigados como fonte secundária de ETR. A literatura destaca o uso de processos hidrometalúrgicos para recuperar esses elementos e o ácido sulfúrico como o agente de lixiviação mais utilizado. É notória a ausência de estudos avaliando processos sequenciais de recuperação de metais básicos e preciosos, e elementos de terras raras. Observa-se também a falta de estudos investigando a recuperação de uma mistura de diferentes resíduos. Além disso, para tornar o processo mais atraente para o mercado, os pesquisadores devem realizar estudos sobre o aumento de escala e a viabilidade econômica desses processos.

Palavras-chave**:** elementos terras raras, metais críticos, mineração urbana, reciclagem, RE

Abstract

Rare earth elements (REE) are considered critical metals due to their supply risk and growing demand due to their economic importance in various industrial segments. Waste electrical and electronic equipment (WEEE) is a potential secondary source for recovering REE which remains unexplored on a commercial scale. Moreover, the process lacks consolidated routes, and the literature has only studied the recovery of some of the 17 REE. This systematic review describes the conditions and procedures applied to fluorescent lamps, cathode-ray tube phosphors, neodymium magnets, nickel-metal hydride batteries, printed circuit boards, LED waste, and other secondary sources to identify the challenges and gaps of recovering REE. Yttrium, neodymium, and cerium are the most commonly recovered elements. With the highest concentration of REE in its composition, NdFeB magnet residues are the most investigated as a secondary REE source. The literature highlights the use of hydrometallurgical processes to recover these elements and sulfuric acid as the most used leaching agent. The absence of studies evaluating sequential processes to recover base metals and precious and rare earth elements is well known. Note also the lack of studies investigating recovery from a mix of different residues. Additionally, to make the process more attractive to the market, researchers must conduct studies on the scale-up and economic viability of these processes.

Keywords**:** rare earth elements, critical metals, urban mining, recycling, WEEE.

2.1 INTRODUCTION

Rare earth elements (REE) belong to the group of lanthanides, plus yttrium and scandium, and have properties such as chemical stability regarding temperature and heat conduction. Besides, they show magnetic properties of interest in aviation, electronics, transportation, and lighting industries, among others (Buechler *et al.*, 2020). A variety of technology items, such as optical glasses, metallic additives, and catalyzers (Saratale, G. et al., 2020); healthcare, transport, aerospace, and defense devices (Prodius et al., 2020b); and electronic equipment, such as nickel metal hydrides, cathode-ray tube phosphors, neodymium magnets, LED equipment, among others employ these elements (Prodius et al., 2020a).

Demand for REE grows as the consumption of new electronic equipment increases (Brewer *et al.*, 2019). Estimates suggest that the REE market grows at an annual rate of 3.7 to 8.6% (Tan; Li, 2019), contributing to the criticality of these raw materials. Despite their relative abundance on the Earth's crust, REE are considered critical metals due to their poor distribution. They are found mainly in China, the United States, India, Australia, and Brazil (Saratale, G. et al., 2020). China holds 97% of the REE market (Yuksekdag *et al.*, 2021), and this dependence is another factor contributing to its criticality. Finally, the US Department of Energy and the European Commission categorize REE as critical due to their importance for clean energy economies and the possible interruption of their supply (European Commission communication, 2017; U.S. Department of Energy, 2011).

Due to their criticality, urban mining and the recovery of REE from secondary materials are essential to meet growing market demands (Lie; Liu, 2021a). Among secondary materials, waste electrical and electronic equipment (WEEE) remains a commercially unexplored REE source with the potential to fill the gap between industrial demand and the decrease in raw material availability (Brewer *et al.*, 2019).

Moreover, WEEE shows a growing generation rate. Estimates predict that the world will generate 120 million tons year^{-1} of WEEE by 2050 (World Economic Forum, 2019). Thus, recovering REE from WEEE contributes both to assure REE supply and recycling WEEE. However, REE recovery processes remain poorly explored, even on a laboratory scale.

Hydrometallurgical and pyrometallurgical processes are the main routes explored on a laboratory scale to recover REE from WEEE (Lie; Lin; Liu, 2021). Studies have extracted REE from secondary materials such as nickel-metal hydride batteries (Ahn *et al.*, 2020; Vargas *et al.*, 2021), electronic waste grinding powder (Marra *et al.*, 2018; Talebi *et al.*, 2018), neodymium magnets (Ciro *et al.*, 2019; Makarova *et al.*, 2020), among others by hydrometallurgical processes. Nevertheless, different compositions, such as secondary materials, can produce divergent leaching outcomes, even when utilizing the same method (Innocenzi et al., 2013b; Tunsu et al., 2016). As a result, it becomes essential to investigate extraction efficiencies individually.

For many years, research focused on recovering gold and silver (Caldas et al., 2021; Cerecedo-Sáenz et al., 2021; Pourhossein et al., 2021; Zhan et al., 2020; Zhang; Zhan; Xu, 2021). However, literature still lacks consolidation for efficient, economical, and environmentally viable processes for REE recovery. Thus, every year, new studies seek to develop them (Opare; Struhs; Mirkouei, 2021; Toache-Pérez et al., 2020). Hence, we find it relevant to review the theme, determine established processes, and identify the gaps and challenges to recover REE from WEEE.

The novelty of this article lies in the approach of fluorescent lamps, nickel-metal hydride batteries, phosphorus from cathode ray tubes, NdFeB magnets, WEEE grinding powder, and LED lamps, among others, as secondary materials of REE. Additionally, it provides a comprehensive analysis of the waste compositions, focusing on the most extensively researched REE. This article also includes flowcharts outlining the processes used to extract REE from these various secondary materials. The main contribution of this study is finding research gaps in REE recovery from WEEE.

Among previous reviews, Oliveira; Benvenuti; Espinosa (2021) evaluated technologies to recycle REE, focusing on recovering gallium and REE from LED lamps. This paper is a broader review encompassing other REE and secondary materials. Also emphasizing LED residues (but not specifically on REE), Rahman et al. (2021) reviewed recycling processes according to the 10R-strategy perspective, presenting the identified methods in the form of flowcharts.

Schaeffer et al. (2018) comprehensively reviewed the recovery of various metals from electronic waste but focused on processes using ionic liquids. Sethurajan et al. (2019)

reviewed hydrometallurgical processes to recover critical and precious metals from LCD waste, batteries (Lithium-ion, NiMH), LED components, fluorescent lamps, and printed circuit boards (PCB). However, their analysis did not encompass pyrometallurgical methods.

Given the above, we find the need for a comprehensive review to elucidate what studies have aimed to recover REE from secondary materials, such as WEEE, showing the compositions, processes, and recoveries achieved and evaluating the challenges and possible gaps in the subject.

Thus, we conducted a systematic review of studies on the recovery of REE from fluorescent lamps (which, although Brazilian classifications exclude from the WEEE category, expressively appear in searches in English for the terms used), nickel-metal hydride batteries, cathode-ray tube phosphors, NdFeB magnets, WEEE grinding powder, LED residues, among others, showing their compositions side by side, critically analyzing the most investigated REE, and schematizing the processes applied to these secondary materials.

2.2 METHODOLOGY

This is a systematic review of bibliographic sources. In total, two searches were conducted in the Web of Science and Scopus databases without a temporal filter and with the search terms shown in The chosen studies were then analyzed to identify their secondary source, recovered REE, applied process, process sequence, leaching conditions (if applicable), waste composition, obtained yields, and whether they evaluated scale-up and economic viability.

Table 1.

Results of these two searches were unified and duplicates, excluded. Titles and abstracts were read to choose studies that carried out experimental research which was relevant to the scope of this study. Studies which neither assessed the recovery of at least one REE or started from a residual matrix were excluded.

The chosen studies were then analyzed to identify their secondary source, recovered REE, applied process, process sequence, leaching conditions (if applicable), waste composition, obtained yields, and whether they evaluated scale-up and economic viability.

Table 1 - Search terms used to form our final study portfolio.

Research 1 – to find studies which somehow relate electronic equipment and REE	*“e-waste” OR “electronic waste” OR “electrical and electronic waste” OR “waste of electric and electronic equipment” OR “WEEE” OR “electro-electronic equipment” AND “rare earth element*” OR “rare earth metal*” OR “REE”*
Research 2 – to find studies which use electrical and electronic equipment as a secondary REE source and hydrometallurgical processes to recover them.	*“e-waste” OR “electronic waste” OR “electrical and electronic waste” OR “waste of electric and electronic equipment” OR “WEEE” OR “electro-electronic equipment” AND “rare earth element*” OR “rare earth metal*” OR “REE” OR “yttrium” OR “cerium” AND “hydrometallurgy” OR “hydrometallurgical* process*” OR “acid leaching” OR “leaching”*

Source: Authors

2.3 RESULTS AND DISCUSSION

2.3.1 WEEE as secondary REE sources

Waste electrical and electronic equipment have heterogeneous compositions with up to 60 chemical elements in the periodic table (World Economic Forum, 2019). Their composition varies due to brand, model, manufacturer year, and function. Table 2 summarizes the metallic content of WEEE used as secondary REE sources. Each entry in the Table 2 represents an interval obtained from the lowest and highest concentration reported in the literature. A single value indicates that other authors did not assess the element.

The most critical REE in Table 2 are yttrium, neodymium, europium, and dysprosium due to their importance in cleaner energy and their supply risk (Deng *et al.*, 2022). Those elements (except dysprosium) stand out in most residues in Table 2 and occur in larger quantities than other REE.

Nickel-metal hydride batteries (NiMH) and neodymium (NdFeB) magnets contain a greater amount of REE. They constitute the most studied secondary material. Figure 1 shows the number of studies for each residue. In addition to the amount of REE in waste, those two components are featured in different electrical and electronic equipment. Studies have investigated the waste of these components for a longer time, given their usage since the 1990s (Erust et al., 2019; Takano; Asano; Goto, 2022).

Neodymium is the most evaluated REE in research with NdFeB magnets, and lanthanum is the most investigated recovery from NiMH batteries. We may easily explain this by observing that neodymium and lanthanum are the most abundant REE in these residues.

Moreover, hybrid devices, images of magnetic components, cordless power tools, cell phones, surveillance, protection, guidance, and other magnetic systems employ neodymium (Jyothi *et al.*, 2020). Rechargeable batteries, cell phones, surveillance equipment, and solar transducers contain lanthanum. Estimates predict that demand for neodymium will grow by 700% over the next 25 years (Kumari et al., 2021a), justifying the interest in recovering this element.

However, research efforts have not only concentrated on recovering the most abundant rare earth element (REE) present in the chosen residue, but have also explored the simultaneous extraction of other elements and assessed REE in lower proportions.

Table 2 - Concentration of metals (%w/w) from different waste electrical and electronic equipment used as a secondary material to recover rare earth elements.

Elements	LED Lamps[1]	LED Chips [2]	Cathode ray tube phosphors[3]	PCB (computer and laptop)[4]	NdFeB[5]	NiMH[6]	Fluorescent lamp[7]	E-scrap[8]
Arsenic	0.0066-0.02	0.00054-0.013	0.02	NE	NE	NE	0.002	NE
Barium	0.24	ND – 0.0024	NE	0.19-0.51	NE	NE	0.11-0.41	0.3347
Boron	NE	NE	NE	NE	0.95-2.14	NE	NE	NE
Bromine	NE	NE	0.001	NE	NE	NE	0.005	NE
Cadmium	<0.0002	NE	0.12-0.3126	0.001-0.47	NE	0.83-2.07	0.01	0.0027-0.0236
Calcium	0.032-3.067	NE	1.35	NE	NE	0.17	1.05-29.49	0.0006-37.6
Lead	0-6.406	0.0005-0.8103	0.2955	1.5-5.5	NE	0.03	NE	0.1623-2.21
Cobalt	0.01	NE	0.09	0.00041 – 0.084	0.95-1.9	5.4-6.3	0.0479-0.09	0.0092
Copper	1.59-35.027	0.00318-0.54	0.004-0.005849	6.9-24.69	0.2-2.15	0.51	0.04	0.1007-3.3501
Chromium	NE	0.00279-0.0213	0.01	0.004-0.356	NE	NE	0.21	0.0694
Sulfur	NE	NE	7.22	NE	NE	0.09	0.04	NE
Erbium	NE	NE	0.00015	NE	NE	NE	NE	0.00541
Tin	9.975-13.802	1.025	0.02	NE	NE	NE	0.01	NE
Strontium	0.017-0.1	NE	1.64	NE	NE	NE	0.26	NE
Iron	0.027-40.203	25.64-39.86	0.00024-0.82	10.8	64-84	0.99-2.9	0.02-0.61	1.15-58

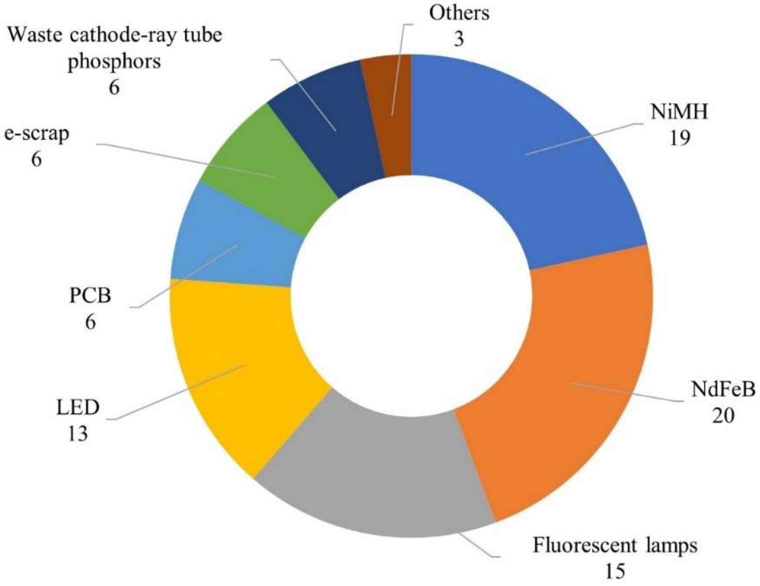
Elements	LED Lamps[1]	LED Chips [2]	Cathode ray tube phosphors[3]	PCB (computer and laptop)[4]	NdFeB[5]	NiMH[6]	Fluorescent lamp[7]	E-scrap[8]
Phosphor	0.008-0.058	0.00584-0.01142	0.03	NE	NE	0.21	0.53-9.4	0.0776-15.7
Gallium	0-0.530	0.00015-0.01356	0.01	NE	NE	NE	0.001	NE
Lithium	NE	NE	NE	NE	NE	NE	NE	0.0142
Magnesium	0.182-0.48	NE	2	NE	NE	0.38	0.08-17.58	0.26-0.84
Manganese	NE	NE	0.36	0.0079-0.112	NE	2.37-8.67	0.02-0.59	0.3298-3.12
Mercury	NE	ND	0.003	NE	NE	NE	NE	NE
Molybdenum	NE	NE	0.03	0.00078-0.007	NE	NE	0.01	0.0098
Nickel	0.064-0.271	0.1541-0.4797	0.003-0.008	0.13-1.0	0.6-1.8	44.98-56.52	0.02	0.043-1.16
Gold	0.014 – 0.03485	0.00301-0.01763	0.000234	0.0086-0.13	NE	NE	NE	0.00087
Palladium	NE	NE	0.000046	0.009	NE	NE	NE	0.0023
Platinum	NE	NE	NE	0.007	NE	NE	NE	0.00013
Potassium	NE	NE	0.003	NE	NE	2.17-4.27	0.03-0.39	NE
Silver	0.0014-0.0384	0.0248-0.18	0.01-0.1039	0.057-0.271	NE	NE	0.001	0.0271
Rubidium	NE	NE	0.01	NE	NE	NE	0.004	NE
Selenium	NE	NE	0.002	0.0035-0.0047	NE	NE	0.0004	NE
Silicon	0.008	NE	11.41	NE	NE	0.2	13.48-24.65	0.59-1
Tellurium	NE	NE	0.01	NE	NE	0.04	0.003	0.00383
Titanium	0.068-1.10	NE	0.01	NE	NE	NE	0.004	0.5179
Vanadium	NE	NE	0.01	0.00079-0.001261	NE	NE	0.003	NE

Elements	LED Lamps[1]	LED Chips [2]	Cathode ray tube phosphors[3]	PCB (computer and laptop)[4]	NdFeB[5]	NiMH[6]	Fluorescent lamp[7]	E-scrap[8]
Zinc	0	0.00365-0.00662	19.7117-24.6	0.07-4.48	NE	1.56-7.25	0.05	0.7279-7.5
Zirconium	NE	NE	0.2	NE	NE	NE	NE	NE
Rare Earth Elements								
Cerium	0.001629-0.020	ND	<DL	0.0007-0.007	NE	2.49-6.7	0.112-0.23	0.0072-0.2047
Dysprosium	NE	NE	NE	0.00002-0.005	0.12-1.55	0.16	NE	0.0101-0.03
Scandium	NE	NE	<DL	0.0019-0.0025	NE	0.05	NE	NE
Europium	NE	NE	0.6057	0.0001	NE	NE	0.559-0.8	0.0002-0.00191
Gadolinium	NE	NE	0.000305	0.000166	NE	NE	0.138-0.15	0.138
Indium	NE	0.00017-0.0124	0.001	NE	NE	NE	0.0003	NE
Ytterbium	NE	NE	<DL	0.000012-0.000016	NE	NE	NE	NE
Yttrium	0.0021-1.425	ND	1.2017-13.74	0.00019-0.00021	NE	0.19	2.14-11.18	0.0042-0.0664
Lanthanum	NE	NE	0.000166	0.00039-0.003	NE	6.74-23.7	0.070-0.14	0.0087-0.0903
Lutetium	NE	NE	< DL	NE	NE	NE	NE	0.0004
Neodymium	NE	NE	0.000012	0.00016-0.093	7.77-31.4	1.58-3.6	NE	0.0088-0.99
Praseodymium	NE	NE	<DL	NE	3.5-3.97	0.07-0.45	NE	0.0239-0.16
Samarium	NE	NE	0.005089	0.000037-0.000042	NE	NE	NE	0.0148-0.07

Elements	LED Lamps[1]	LED Chips [2]	Cathode ray tube phosphors[3]	PCB (computer and laptop)[4]	NdFeB[5]	NiMH[6]	Fluorescent lamp[7]	E-scrap[8]
Total REE	0.003729-1.445	0.00017-0.0124	1.2017 - 14.352272	0.004231 – 0.112658	11.39 – 36.92	11.28 – 34.45	3.0103 – 12.5	0.0783 – 1.75131

NE = not evaluated, ND = not detected, DL= detection limit, LED = light-emitting diode, PCB= printed circuit board, REE= Rare Earth Elements. Source: [1]Cenci et al. (2020a; 2020b), Rebello et al. (2020), Vinhal et al. (2022); [2]Lim et al. (2011); Pourhossein and Mousavi (2018); [3]Cesaro et al. (2018); Innocenzi et al. (2013a); [4]Priya and Hait (2018, 2020); Tunali, Tunali and Yenigun (2021); [5]Bonin, Fontaine and Larivière (2021); Ciro et al. (2019); Maât et al. (2016); Piotrowicz et al., (2020) [6]Lie, Lin and Liu (2021); Maroufi, Assefi and Sahajwalla (2018); Zielinski et al. (2020); [7]Botelho Junior, Espinosa and Tenório (2021); Čížková et al., (2021); Innocenzi et al. (2013b); Pavón et al. (2021); [8]García-Balboa et al. (2022); Marra, Cesaro and Belgiorno (2019); Peelman et al. (2018); Peelman, Sietsma and Yang (2018).

Figure 1 - Number of studies in different types of secondary materials among the portfolio assembled with searches in the Scopus and Web of Science databases up to 2022.



Fonte: Authors

On the other hand, studies have scarcely assessed PCB — also present in multiple electrical and electronic equipment — as a secondary REE source. As per Figure 1, only six studies analyzed it. Its composition depends on the electrical and electronic equipment housing it. Analyzing the concentrations in Table 2, we observe that gold and silver are 10^2 times greater than REE, whereas copper is about 10^5 times greater. As a result, this component holds a higher value as a source of base and precious metals.

Table 2 shows the composition of PCB for laptops and computers. Among REE, neodymium and cerium show the highest mass percentages. Also, Priya and Hait (2018) investigated the composition of PCB in 16 WEEE types, finding 15 REE, of which scandium and cerium had the greatest percentages. We should note that recycling PCB is already commercially consolidated. Therefore, REE presence further increases the value of this type of waste, encouraging the adaptation and improvement of current processes to increase the range of recovered metals.

In addition, in six studies in our portfolio, e-scrap (powder from the mechanical processing of WEEE in recycling plants) shows a composition which strongly depends on the specific processed electrical and electronic equipment. This variability accounts for the range of metal concentrations observed in this residue. It is of interest to integrate the research on the recovery of REE from e-scrap with other recycling processes, such as the recovery of copper, silver and gold, posing the challenge of operationalizing these flowsheets.

The e-scraps residues mentioned thus far (NiMH batteries, NdFeB magnets, PCB and e-scraps) consist of diverse electrical and electronic equipment that find application in a wide range of fields. However, new electronics emerge constantly and consolidated ones receive further uses (such as LED lamps). As residue generation increases, research analyzing its recycling starts to surface.

The amount of REE in LED lamps and chips vary across models, brands, and light colors, as specified by Vinhal *et al.* (2022), and may include yttrium, cerium, indium, and (in larger proportions) gallium. Studies have investigated the recovery of cerium and yttrium, but gallium is the most assessed due to its higher concentration. Compared to other electrical and electronic equipment listed in Table 2, LED residues and cathode-ray tube phosphors exhibit the highest percentage of gallium. Moreover, NiMH batteries and cathode-ray tube phosphors have a cerium and yttrium mass percentage 10^3 to 10^4 times greater than that in LED waste.

Moreover, regarding lighting devices, fluorescent lamps (although ignored as WEEE in some countries) were featured in 15 studies in our portfolio. They focused on the fluorescent phosphor powder in the residue, highlighting the presence of yttrium. By itself or with other REE, 12 studies recovered this element.

Cathode-ray tube phosphors may be recycled with fluorescent lamps, as described by Innocenzi et al. (2013b), or separately, as in seven other studies. Comparing the composition of cathode-ray tube phosphors and fluorescent lamps shows that both have expressive yttrium and europium amounts and similar percentages of other abundant components, such as aluminum and silicon.

According to Franz and Wenzl (2017), the descending demand for REE features cerium, lanthanum, neodymium, yttrium, praseodymium, dysprosium, and others. These elements are among the most abundant REE in technologies and equipment. Researchers investigated the following REEs in descending order: yttrium, cerium, neodymium, lanthanum, and praseodymium. Thus, we found that data showed agreement, as studies aimed to develop processes to obtain the most used and demanded REE on the market.

Besides REE, Table 2 shows other critical elements, such as antimony, cobalt, scandium, phosphorus, magnesium, nickel, and vanadium (European Commission communication, 2017; U.S. Department of Energy, 2011).

The evaluated studies ignored them as they focused on REE. Still, Takano, Asano and Goto (2022), Maroufi, Assefi, and Sahajwalla (2018), Sobianowska-Turek (2018), Vargas et al. (2021) studied cobalt extraction. Table 2 demonstrates that multiple residues, particularly NiMH batteries, contain cobalt as a part of their composition. Its industries use more than 40% of the global cobalt production, but the element still lacks a commercially established recovery (European Commission communication, 2017; Prodius et al., 2020a).

All residues in Table 2Table 2 - Concentration of metals (%w/w) from different waste electrical and electronic equipment used as a secondary material to recover rare earth elements. contain nickel, of which NiMH batteries show the highest mass percentages (as with cobalt). Demand for it tends to grow with the development of electric vehicle technologies (U.S. Department of Energy, 2011). Since nickel represents around 50% of the composition of this residue, 14 out of the 19 studies that utilized NiMH batteries simultaneously examined nickel and REE. Studies with LED waste (Pourhossein e Mousavi, 2018, 2019), e-scrap (Diaz *et al.*, 2016), and NdBFe magnet (Walton *et al.*, 2015) also recovered it.

End-of-life products do not undergo recovery processes for phosphorus and scandium. Antimony, magnesium, and vanadium have a 28%, 9%, and 44% recycling percentages, respectively (European Commission communication, 2017). However, as it lies outside our portfolio, we shall ignore their recovery.

Residue composition influenced the selection of recovery processes and rates. Research treats metals in quantities higher than REE percentages (such as base metals) as contaminants. Thus, the study of REE recovery must observe the behavior of these contaminants. Additionally, it is crucial to assess the sequence of their removal during REE recovery, whether it involves mechanical separation before hydrometallurgical processes or purifying the leach liquor. For example, Innocenzi et al. (2013a) simultaneously recovered zinc and yttrium. Sobianowska-Turek (2018) extracted 100% of the zinc from their residues, along with cerium. So, the following step considers the presence of this metal in precipitation or solvent extraction.

Extraction processes (often distinct from each other) to recover REE are defined by each residue and their specific compositions. Therefore, the next topic details the processes applied to different WEEE.

2.3.2 REE recovery processes from WEEE

There are mainly three types of processes used to recover REE from WEEE. They are hydrometallurgy, pyrometallurgy, and bioleaching. Among these, hydrometallurgical processes are the most used. Compared to pyrometallurgical methods, this approach exhibits reduced greenhouse gas emissions and operates at lower temperatures, resulting in lower energy consumption and associated costs (Lisińska *et al.*, 2018). Compared with the biological approach, hydrometallurgy stands out for being less time-consuming (Magoda; Mekuto, 2022).

Regarding the recovery step, multiple choices exist, such as solvent extraction, adsorption (using different types of adsorbents), and precipitation. The determination of which one to use varies according to the leaching reagent system, metal concentration, impurities, and economy of the process (Jadhav; Hocheng, 2015). Table 3 presents a comparative analysis of the advantages and disadvantages of these specific recovery methods.

Table 3 - Advantages and Disadvantages of different recovery methods.

Process	**Advantages**	**Disadvantages**
Precipitation	- Highly efficient - Simple - Low cost	- Limited Selectivity Range - Generates a waste product
Solvent extraction	- High selectivity - Produces high purity single rare earth solutions and compounds - Used commercially	- High cost - Only applied to non-dilute metal ion solutions - Time-consuming - High solvent requirement
Adsorption	- Economical process - Easy in operation - Efficient removal in dilute solutions	- Less loading capacity on multiple cycles - Slow kinetics

Source: Awual et al. (2019); Darban et al. (2022); Lie and Liu, (2021b); Liu, C. et al. (2022); Opare, Struhs and Mirkouei (2021); Parga et al. (2012); Provazi et al. (2011); Vaughan et al. (2021).

Precipitation is considered a cost-effective method since it requires simpler equipment and fewer chemicals compared to other separation techniques such as solvent extraction. When optimized effectively, this method can yield high-purity products. However, it may not be suitable for scenarios where multiple components in the leach liquor have similar properties, as undesired co-precipitations can occur (Liu, Z. *et al.*, 2022; Provazi *et al.*, 2011).

In contrast, the solvent extraction method exhibits the capability to selectively extract individual rare earth elements (REE) from complex mixtures, resulting in the production of high-purity compounds. However, the solvent extraction method has limitations when applied to diluted solutions and can be time-consuming. The high solvent requirement can be mitigated using solvent recycling and proper treatment when it is no longer usable. Moreover, it is worth mentioning that researchers often employ a precipitation step following the solvent extraction method (Parga et al., 2012; Peelman et al., 2018; Peelman; Sietsma; Yang, 2018; Vaughan et al., 2021).

The advantages of efficiency in dilute solutions and costs should be an incentive for new research focusing on minimizing the slow kinetics and low selectivity, in complexed solutions, of adsorption processes, which are significant disadvantages compared to other methods (Awual *et al.*, 2019; Darban *et al.*, 2022).

Recovery processes vary according to the secondary material used and even for the same source. Most studies include the following mechanical treatments: milling, grinding, sieving, homogenization, and their various combinations. For the most part, mechanical treatment aims at comminution and the influence of these processes on leaching and recovery is rarely analyzed. Thus, we will assess REE recovery from different residues separately and generically list mechanical processes as mechanical treatment.

2.3.2.1 Fluorescent lamps

The amount of REE found in fluorescent lamps is ten times higher than in primary ores explored on an industrial scale (Zhang; Anawati; Azimi, 2022). As shown before, 15 papers analyze this residue as a secondary material of many REE.

Studies on this source lack a thorough investigation of pre-treatment mechanical processes, and it influences on the following processes. Only two compared materials with and without pre-treatment. Most show the mechanical treatment required to obtain the comminuted residue needed for the evaluated processes, listing the equipment used but ignoring their influence on recovery yields. He et al. (2018) and Song et al. (2017) analyzed the mechanical activation influence on the recovery and concluded that the proposed activation positively influences results, leaching more than 80% of cerium, terbium, yttrium, and europium from waste.

Most studies used hydrometallurgy as a recovery process. Yttrium recovery constituted the focus of 93% of our portfolio [He et al. (2018) are the only exception]. We found that sulfuric acid stands out as a leaching agent (Botelho Junior; Espinosa; Tenório, 2021; He et al., 2018; De Michelis et al., 2011; Song et al., 2017; Tunsu et al., 2016) applied primarily when studies aimed to recover only yttrium. Furthermore, we observed the association of sulfuric acid with hydrogen peroxide (Innocenzi et al., 2013b), hydrochloric acid (Patil *et al.*, 2021; Pavón *et al.*, 2018), and aqua regia (Artiushenko *et al.*, 2021).

Overall, optimal leaching conditions with sulfuric acid as a leaching agent include concentrations around 2 mol.L^{-1}, solid-liquid ratios ranging from 50 to 200 g.L^{-1}, temperatures from 20 to 90°C (a wide range), and reaction times from 1 to 168 hours.

Using sulfuric acid at a 2 mol.L^{-1} concentration, Botelho Junior, Espinosa and Tenório (2021) leached 95% of the yttrium, applying a 50 g.L^{-1} solid concentration at 45°C. However, to accomplish this, the reaction took seven hours, a long period compared to studies such as Saratale, G. et al. (2020) which used one hour at 60°C and recovered 99% of yttrium by applying a lower sulfuric acid concentration of 1.5 mol.L^{-1} at a higher solid loading of 400 g.L^{-1}.

Still aiming to recover only yttrium, De Michelis et al. (2011) also applied sulfuric acid at a 2 mol.L^{-1} concentration, leaching 85% of yttrium at a higher temperature (90°C) — the highest in studies with fluorescent lamps as a secondary source. The addition of an oxidizing agent to the reactions appears to have satisfactory results with higher leaching yields at lower temperatures. By associating sulfuric acid with hydrogen peroxide, Innocenzi et al. (2013a) used a 2 mol.L^{-1} concentration, 10% v/v of hydrogen peroxide (30% v/v) at 200 g.L^{-1} and 70°C, leaching 100% of yttrium after three hours.

Thus, among the studies focusing only on yttrium recovery, we found that the process Saratale, G. et al. (2020) developed seems to be the most attractive due to high yields under more economically favorable conditions since a 1% difference in yield is insufficient to justify extra costs by increasing temperatures, acid concentrations, and reagents.

Studies used fluorescent lamps to recover yttrium and other REE, such as europium, cerium, terbium, lanthanum, and gadolinium. Song et al. (2017) simultaneously leached 96.3%, 91.1%, and 77.3% of yttrium, europium, and cerium, respectively, by using 2 mol.L^{-1} of sulfuric acid under a 12.5 g.L^{-1} solid-liquid ratio at 70°C for one hour.

Focusing on cerium and terbium recovery, He et al. (2018) also used sulfuric acid as a leaching agent at a 2 mol.L^{-1} concentration and 200 g.L^{-1} solid-liquid ratio in a 2-hour reaction time at 80°C. The Authors achieved leaching percentages of 89.8% for terbium and 85% for cerium from waste that had undergone prior mechanical activation treatment.

Studies also applied other acids for leaching. Inorganic acids (sulfuric, hydrochloric, and nitric) had their results compared at 20°C and a 100 g.L^{-1} solid-liquid ratio. Sulfuric acid was found as the most suitable leaching agent (Tunsu *et al.*, 2016). The acid presents optimal energetic conditions, having an intermediate solid-liquid ratio and low temperature. However, despite leaching more than 90% of yttrium, europium, terbium, cerium, and gadolinium, the Authors proposed a 168-hour reaction, which is less attractive for larger-scale processes.

The use of hydrochloric acid is related to multiple leaching steps. Patil et al. (2021) evaluated the recovery of europium, lanthanum, cerium, yttrium, and terbium via sequential leaching (nine steps in a row) and a progressively increasing hydrochloric acid concentration (0 to 10 mol.L^{-1}) at a 100 g.L^{-1} solid concentration at 25°C. The Authors leached more than 95% of all analyzed REE.

With fewer steps and lower acid concentrations, Pavón et al. (2018) used two rounds of hydrochloric acid leaching (1 and 2 mol.L^{-1}) as the first step of their hydrometallurgical process. Then, the leach liquor underwent precipitation, calcination, dissolution, and solvent extraction. Despite omitting their results, the Authors concluded that their process resulted in high purity extractions (>99%), making it viable for recovering REE.

Finally, Artiushenko et al. (2021)applied aqua regia to recover yttrium, europium, terbium, ytterbium, lanthanum, gadolinium, samarium, neodymium, cerium, and erbium, recovering 80% of yttrium, 85% of europium, and a total 83% for all REE.

In addition to hydrometallurgical processes, studies employed biohydrometallurgical treatment (Hopfe *et al.*, 2017, 2018), solid-state chlorination (Hopfe *et al.*, 2017), and processes using supercritical fluids (Zhang; Anawati; Azimi, 2022). As a form of final recovery, authors used solvent extraction (Patil et al., 2021; Pavón et al., 2018; Saratale, R. et al., 2020; Tunsu et al., 2016) and precipitation (Góralczyk; Uzunow, 2013; Innocenzi et al., 2013b; De Michelis et al., 2011). Table 4 summarizes the sequential processes (unit operations) used in research with fluorescent lamps as a secondary REE source.

Table 4 - Processes flow to recover rare earth elements from fluorescent lamps.

Process flow and unit operations	**Leaching or final recovery yields***		**References**
	Metal	**Recovery (%)**	
Mechanical activation → Supercritical fluid extraction	*Y	70	(Zhang; Anawati; Azimi, 2022)
	*Eu	70	
	*Tb	50	
Bioaccumulation of REE in *G. phlegrea* biomass	NI		(Čížková et al., 2021)
Leaching → Adsorption → Desorption	*Y	80	(Artiushenko et al., 2021)
	*Eu	85	
	*Tb	79	
	*Yb	67	
	*La	52	
	*Gd	85	
	*Sm	87	
	*Nd, Ce, Er	68-93	
	*Total	83	
Leaching	Y	95	(Botelho Junior et al., 2021)
Heat treatment (Hg removal) → nine sequential leaching steps → liquid-liquid extraction	Y	96.2	(Patil et al., 2021)
	Eu	99	
	Gd	55.1	
	Tb	95.6	
	La	99	
	Ce	99	
magnetic separation → leaching → solid-state chlorination → leaching	*Y	95.7	(Pavón et al., 2021)
	*Eu	92.2	
pH adjustment → iron precipitation → filtration → pH adjustment (liquid phase) → solvent extraction → stripping	*Y	99	(Saratale, R. et al., 2020)
Cultivation of microorganisms → bioleaching	REE	12.6	(Hopfe et al., 2018)
Alkali mechanical activation → leaching → centrifugation	Tb	89.8	(He et al., 2018)
	Ce	85	
Leaching (2x) → precipitation → calcination → dissolution in acid → solvent extraction	*Ce	100	(Pavón et al., 2018)
	*Y	100	
	*Eu	100	
Mechanical activation → Leaching	Y	96.3	(Song et al., 2017)
	Eu	91.1	
	Ce	77.3	
Autoclave (mercury reduction) → cultivation of microorganisms → bioleaching	REE	7.9	(Hopfe et al., 2017)
Mechanical treatment → leaching → solvent extraction	Y	98.2	(Tunsu et al., 2016)
	Eu	97.1	
	Tb	88.7	
	Ce	78.5	

Process flow and unit operations	Leaching or final recovery yields*		References
	Metal	Recovery (%)	
	La	17.4	
	Gd	89.2	
Disassembly → leaching → cooling → precipitation → drying	Y	85	(De Michelis et al., 2011)
Leaching → purification → precipitation → calcination	Y	100% → *55%	(Innocenzi et al., 2013b)

NI = percentage not informed. * Final recovery yields
Source: Authors

Addressing other elements within this residue, Zhang, Anawati and Azimi (2022) found that calcium and aluminum compete with REEs in the solvent extraction step. Saratale, R. et al. (2020) presented the occurrence of coprecipitation of iron and calcium. The Authors optimized the pH range to remove the iron before the solvent extraction. On the other hand, the extractant used by Artiushenko et al. (2021) suffers a low influence of the iron and copper in the leach liquor. Also dealing with calcium, De Michelis et al. (2011) developed a process that extracted 85% of yttrium with only 5% of calcium, showing a solution for the negative effect that this contaminant may have in the following steps.

2.3.2.2 Cathode-ray tube phosphors

As with fluorescent lamps, most of the studies extracted yttrium from this residue, mainly recovering it by hydrometallurgical processes. Research only used sulfuric acid as a leaching agent, either by itself (Lie; Ismadji; Liu, 2019; Lie; Liu, 2021a; 2021b; Tian et al., 2018) or associated with hydroxide peroxide (Innocenzi et al., 2013a; Innocenzi et al., 2013b; Yin et al., 2018). Table 5 shows the process flows employed to recover yttrium and europium from cathode-ray tube phosphors.

Studies achieved final recoveries above 80%, and leaching yields close to it, showing that sulfuric acid performs satisfactorily for this residue. We highlight that high-leaching yields have been achieved by utilizing sulfuric acid at a concentration of 2 mol.L^{-1}, with a solid-liquid ratio of 50 to 100 g.L^{-1}, temperatures ranging from 50 to 70°C, and a duration of up to 3 hours.

The use of isolated sulfuric acid as a leaching agent was associated with microwave application. Lie, Ismadji and Liu (2019) and Lie and Liu (2021b) adopted sulfuric acid at a 2 mol.L^{-1} concentration, a 10 g.L^{-1} solid-liquid ratio for one and half hour-reactions, respectively. They obtained similar leaching results: 100% europium and 78-87% yttrium. It is possible to note that the low solid-liquid ratio could lead to a high-cost process since an expressive amount of leaching agent would be necessary to treat small quantities of residue. Moreover, cost-benefit analyses need to be made when adding an energy consumption process such as microwave use.

Associating sulfuric acid with hydrogen peroxide, Yin et al. (2018) point out the following conditions to return a higher leaching percentage: 3 mol.L^{-1} H_2SO_4, 4% v/v H_2O_2, 55°C, 1 hour of reaction, and a 50 g.L^{-1} solid concentration. They leached 99% of yttrium and europium and 45% and 100% of zinc and aluminum (one of the main impurities in the residue), respectively. Innocenzi et al. (2013a), on the other hand, used a lower acid concentration (2 mol.L^{-1}) and a higher percentage of hydrogen peroxide (10%v/v). After reacting for three hours with a 100 g.L^{-1} solid concentration at 70°C, they leached 100% of the yttrium in the residue. The Authors then precipitated the solution, first removing the zinc from it, then precipitating the yttrium, obtaining 80% yields.

It is possible to say that the leaching proposed by Yin et al. (2018) would be preferred when analyzing only the obtained yields by time of reaction and temperature. However, economic and environmental assessments would be necessary to determine the most suitable process for a large-scale operation.

Table 5 - Processes flow to recover rare earth elements from cathode-ray tube phosphors.

Process flow and unit operations	**Leaching or final recovery yields***		**References**
	Metal	**Recovery (%)**	
Microwave leaching → chemical precipitation → calcination	Y	86.7 → *96.9	(Lie and Liu, 2021b)
	Eu	100 → *86.6	
Microwave leaching	Y	78	(Lie; Ismadji; Liu, 2019)
	Eu	100	
Mechanical treatment → leaching → solvent extraction	*Y	100	(Tian et al., 2018)
	*Eu	100	
Leaching → extraction by ionic liquid	Y	99 → *99	(Yin et al., 2018)
	Eu	99 → *87.8	
Leaching → zinc precipitation → Y precipitation → calcination	Y	100 → *80	(Innocenzi et al., 2013a)
Leaching → purification → precipitation → calcination	Y	100 → *95	(Innocenzi et al., 2013b)

NI = percentage not informed. * Final recovery yields
Source: Authors

Aluminum and zinc appear in the research alongside REE. Tian et al. (2018) factored the presence of these elements when selecting the best extractant. Yin et al. (2018) achieved significant leaching yields of these metals. However, the solvent extraction resulted in only 8% of zinc and 0% of aluminum recovered. These low results make the process very selective and a suitable alternative for the final recovery of REE. Finally, Innocenzi et al. (2013a) focused on removing the zinc before yttrium precipitation, showing high yields for both (99% of zinc and 80% of yttrium).

In another study, Innocenzi et al. (2013b) applied the same process (2 mol.L^{-1} H_2SO_4, 10% v/v H_2O_2, 70°C, and 3 hours of reaction) but with a 200 g.L^{-1} solid concentration, analyzing residues from fluorescent lamps, cathode-ray tube phosphors, and a mixture of both. Cathode-ray tube phosphors showed higher leaching yields than the other two assessed residues. Despite the lower results, studies with multiple residues are necessary to determine the possibility of industrial plants being able to process different waste streams. The more heterogeneous the residue composition simultaneously evaluated is, the lower the expected yields. However, since the REE of interest was the same and their major contaminants were similar, verifying this possibility is an interesting idea, as per Innocenzi et al. (2013b).

2.3.2.3 NdFeB magnets

The NdFeB magnets are the most investigated secondary source in REE recovery. The studies evaluating it used traditional hydrometallurgical, pyrometallurgical, mechanical processes, and even some without acids. Table 6 shows the sequential steps employed to recover REE from NdFeB magnets. We find a search for environmentally friendly processes for NdFeB magnets, avoiding inorganic acids or toxic solvents. For example, Prodius et al. (2020b) evaluated CSEREOX as an extraction method, applying it after leaching with oxalic acid. The CSEREOX process extracts elements with water as its only solvent. Thus, some of the REE forms oxalates. According to the Authors, in addition to the advantage of only using the universal solvent, its separation time and the number of minimum cycles for recovery are lower than other methods, such as TriNOx and DEHPA.

Table 6 - Process flow to recover rare earth elements from NdFeB magnets.

Process flow and unit operations	**Leaching or final recovery yields***		**References**
	Metal	**Recovery (%)**	
Leaching → solvent extraction	REE	10	(Liu, C. et al., 2022)
Mechanical treatment → leaching → precipitation → solvent extraction	Dy	99.8 → *100	(Erust et al., 2019)
	Nd	99.8 → *100	
Leaching → dilution → diffusion dialysis	NI		(Hammache et al., 2021)
Mechanical treatment → infrared leaching	REE	100	Bonin, Fontaine and Larivière (2021)
Mechanical treatment → electrochemical leaching → solvent extraction	Nd	65.6	(Kumari et al., 2021a)
	Pr	18.7	
	Dy	1.4	
Chlorination roasting → leaching	Nd	70	(Kumari et al., 2021b)
	Pr	77	
	Dy	42	
Mechanical treatment → leaching → recovery with a metal-binding protein	*Sc	96	(Deblonde et al., 2020)
	*Y	96	
	*REE	99.8	
Mechanical treatment → electrochemical leaching	REE	35	(Makarova et al., 2020)
hydrogen decryption	NI		(Piotrowicz et al., 2020)
Addition of copper(II) nitrate hemi(pentahydrate) → addition of an aqueous ammonia solution → addition of oxalic acid → calcination of the precipitate	*REE	98	(Prodius et al., 2020a)
Mechanical treatment → leaching → CSEREOX	*Dy	68	(Prodius et al., 2020b)
Mechanical treatment → leaching → pH adjustment → centrifugation → biosorption	*REE	91	(Brewer et al., 2019)
Mechanical treatment → leaching → precipitation	*Nd	98	(Ciro et al., 2019)
	*Pr	98	
	*Dy	98	
Mechanical treatment → leaching → precipitation → microfilm synthesis	NI		(Maroufi; Assefi; Sahajwalla, 2018)
Mechanical treatment → extraction with a supercritical liquid	*Nd	94	(Zhang et al., 2018)
	*Pr	91	
	*Dy	98	
Mechanical treatment → oxidation → grinding → carbothermic reduction	REE separated in the oxide phase		(Maroufi et al., 2017)
Hydrothermal treatment → magnetic separation	*Nd	95	(Maât et al., 2016)
Mechanical treatment → magnetic separation → leaching → precipitation → oxidation	*Nd	66.7	(Diaz et al., 2016)
	*Pr	91.7	
	*Dy	54.9	
	*Nd	56	

Process flow and unit operations	Leaching or final recovery yields*		References
	Metal	Recovery (%)	
Mechanical treatment → microwave irradiation → leaching → precipitation	*Dy	56	(Tanvar; Kumar; Dhawan, 2019)
Hydrogen processing → rotation in a porous drum	NI		(Walton et al., 2015)

NI = percentage not informed. * Final recovery yields
Source: Authors

Seeking alternative methods, Prodius et al. (2020a) aimed to develop an acid-free leaching process, thus applying copper salts. Their process used oxalic acid in precipitation, recovering 98% of the REE in their residue. Maât et al. (2016) proposed a hydrothermal treatment that applies only water and a low concentration of sodium chloride as a catalyst, intensifying the oxidative power of water and forming neodymium and iron crystals separated by electromagnetic separation.

Walton et al. (2015) proposed a mechanical process to separate REE-containing powder for later recovery and reuse. For that, they distorted the residue, put it in contact with hydrogen at 2 atm pressure, placed it into a porous drum, and released and recovered the formed hydrogenated powder. Piotrowicz et al. (2020) also evaluated a pre-treatment, hydrogen decryption, which may serve as a direct reuse and an effective recycling method to transform magnets into a demagnetized powder for further processing.

Electrochemistry intensified the dissolution and increased purity when using organic acids and lowered concentrations of inorganic acids. As a way of improving the results of leaching with citric acid (0.5 mol.L^{-1}) for 5 hours at room temperature (25°C), the method positively affected the yields, although still not reaching 80% of extraction (Kumari et al., 2021b). When applied with even lower acid concentrations, sulfuric (0.5 mol.L^{-1}) and oxalic acids (0.05 mol.L^{-1}) for 2 hours at 22°C, presented unsatisfactory results (35%), highlighting the need to improve leaching conditions (Makarova *et al.*, 2020).

Zhang et al. (2018) conducted a supercritical fluid extraction using carbon dioxide as a solvent and TBP-HNO3 as a chelating agent, all within a single container. At the end of the process, they recovered more than 90% of neodymium, praseodymium, and dysprosium. Despite using more available, inert, and less toxic solvents, the process has the disadvantage of requiring special equipment to support supercritical conditions and high energy expenditure to achieve these conditions.

As seen from the above, the search for green processes is strongly present in the recovery of REE from this residue. Combining lower acid concentrations with auxiliary mechanisms, such as electrochemical processes, appears effective. Similarly, relying solely on mechanical alternatives has also shown positive results.

The conventional hydrometallurgical process is also assessed. Studies with leaching processes lack a consensus on the agent returning the best leaching yields. They include hydrochloric acid (Bonin; Fontaine; Larivière, 2021; Liu, C. et al., 2022; Maroufi; Assefi; Sahajwalla, 2018; Tanvar; Kumar; Dhawan, 2019), sulfuric acid (Bonin; Fontaine; Larivière, 2021; Diaz et al., 2016; Erust et al., 2019) band ammonium persulfate (Ciro *et al.*, 2019), with concentrations between 1 and 4 mol.L^{-1}, resembling studies with other residues. It is worth noting that, in the case of this secondary material, the majority of studies primarily concentrate on recovery rather than leaching processes.

Bonin, Fontaine and Larivière (2021) developed an infrared leaching process. Using sulfuric acid for 7.5 minutes and hydrochloric acid for 5 minutes, they leached 100% of neodymium, praseodymium, dysprosium, and terbium. Moreover, Ciro et al. (2019) used ammonium persulfate as a leaching agent at a 1.3 mol.L^{-1} concentration at 75°C. After 15 minutes of reaction, they leached 98% of REE.

These researches have shown an interesting common factor that is the reduced time necessary to reach complete or almost complete recoveries. Kumari et al. (2021a) evaluated chlorination roasting followed by water leaching at 95°C for one hour, leaching 100% of REE. Despite requiring a longer reaction duration, the research is promising due to the utilization of a universal solvent as a leaching agent.

In their assessment of a combined leaching and final recovery process, Liu, C. et al., (2022a) developed a method that involved the simultaneous addition of hydrochloric acid and ionic liquids in the same vessel, combining leaching and solvent extraction. Although they failed to obtain significant results (10%), they completely leached the iron in the residue, separating it from REE. The Authors highlight that acidity negatively affects REE extraction and that increasing ionic liquid concentration and contact time would slightly improve this extraction.

Precipitation stands out in the final recovery stage. Diaz et al. (2016) used it to recover REE from the leached liquor with sulfuric acid (1 mol.L^{-1}). As a result, they recovered 91.7%, 66.7%, and 54.9% of praseodymium, neodymium, and dysprosium, respectively. Tanvar, Kumar and Dhawan (2019) obtained similar results, recovering, via precipitation, 56% of dysprosium and neodymium, after leaching with hydrochloric acid (0.5 mol.L^{-1}).

Only Erust et al. (2019) explored the solvent extraction process after leaching by using sulfuric acid (2 mol.L^{-1}) as a leaching agent, precipitating the iron from the liquor before recovering 100% of neodymium and dysprosium by solvent extraction. The Authors concluded that the proposed process is economically feasible, being part of a scarce group that makes this analysis within the experimental results paper.

It is worth mentioning that Diaz et al. (2016) developed a process that also recovers base and precious metals by using electro-recycling to separate tin and copper, followed by a precious metal leaching of the undissolved material using acidic thiourea, resulting in the extraction of gold, silver, and palladium. Since it obtains different value streams from the e-waste, this process can be considered the most complete, and the next step should be the evaluation of scale-up possibilities.

Few articles go beyond the recovery stage to the application stage of the recovered material. An example of its use is demonstrated by Maroufi, Assefi and Sahajwalla, (2018), who leached residues with sulfuric acid (2 mol.L^{-1}), precipitated the REE, and applied the precipitate to form nanosheets.

We also found alternative processes to solvent extraction and recovery of REE via precipitation. Brewer et al. (2019) applied biosorption after leaching with sulfuric acid (0.1 mol.L^{-1}) at 20°C for 14 days, recovering more than 95% of scandium, yttrium, and other lanthanides. Deblonde et al. (2020) used a metal-binding protein after leaching with sulfuric acid (0.4 mol.L^{-1}) at 20°C, recovering 91% of REE. Furthermore, Hammache et al. (2021) used diffusion dialysis, which places the diluted leachate in contact with a membrane-repelling REE and enables other components to pass, concentrating REE.

Maroufi, Khayyam Nekouei and Sahajwalla (2017) used pyrometallurgy to concentrate REE in the oxide fraction of residues, separating it from other metals such as iron, cobalt, and nickel. Biohydrometallurgy was yet not used to recover REE from NdFeB magnets.

The research conducted with this secondary material focuses on different processes, a distinction that is not observed in the other sources presented in this paper. One possible reason is that the research has reached an advanced stage of investigation, aiming to improve the most used processes in the field of metallurgy. Additionally, it is also noteworthy that lower concentrations of acids were utilized compared to other residues when applied in these processes.

2.3.2.4 Nickel-Metal Hydride Batteries

The NiMH batteries are one of the most evaluated secondary REE source. Table 7 shows the processes to recover several REE from it. Note the predominance of hydrometallurgical leaching and precipitation in the final recovery. Among REE, studies evaluated cerium and lanthanum, employing sulfuric acid as the primary leaching agent. Hydrochloric and nitric acid were less commonly used.

Table 7 - Processes flow to recover rare earth elements from nickel-metal hydride batteries.

Process flow and unit operations	**Leaching or final recovery yields***		**References**
	Metal	**Recovery (%)**	
Leaching → precipitation	Y	97% → *54	(Takano; Asano; Goto, 2022)
	Ce	100 → *99	
	La	100 → *99	
Leaching	Nd	99.48	(Lie; Lin; Liu, 2021)
	Ce	96.43	
	La	99.14	
Leaching (2x) → precipitation	*Nd	85.97	(Lie; Liu, 2021a)
	*Ce	90.75	
	*La	82.59	
Leaching → precipitation → oxidation → solvent extraction	*Ce	84.7	(Schaeffer *et al.*, 2021)
Leaching → aqueous biphasic system (3x)	*Ce	8.5	(Vargas et al., 2021)
	*La	47	
Leaching → precipitation → heat treatment	*Nd	97.53	(Ahn et al., 2020)
	*Ce	99.6	
	*La	98.76	
Leaching → precipitation → hydroxide conversion + wet oxidation → selective dissolution	*Ce	97-98	(Porvali; Agarwal; Lundström, 2020)

Process flow and unit operations	Leaching or final recovery yields*		References
	Metal	Recovery (%)	
Leaching → precipitation	La	95.8 → *99.49	(Porvali *et al.*, 2020)
	Ce	89.9→ *99.14	
	Pr	96.3→ *99.12	
	Y	97→ *41.79	
	Sm	98.6 → *95.71	
Mechanical treatment → leaching	La	91.6	(Zielinski et al., 2020)
Mechanical treatment → leaching → evaporation and recirculation → pH adjustment → precipitation	La	99	(Zhang et al., 2019)
	Ce	99	
Mechanical treatment → leaching	La	68.08	(Diáz-López et al., 2018)
	Ce	84.61	
	Pr	32.36	
	Sm	61.07	
	Nd	65.95	
Mechanical treatment → thermal oxidation → thermal reduction	REEs separated in the oxide phase		(Maroufi *et al.*, 2018)
Leaching → precipitation	La	66.4% → *98%	(Porvali; Wilson; Lundström, 2018)
	Ce	88.8% → *99%	
	Pr	59.3% → *99%	
Supercritical fluid extraction	*REE	90	(Yao; Farac; Azimi, 2018)
Supercritical fluid extraction	*REE	90	(Yao; Farac; Azimi, 2017)
Leaching	Ce	97.7	(Sobianowska-Turek, 2018)
	La	88.7	
Mechanical treatment → leaching → precipitation	La	69.5	(Meshram; Pandey; Mankhand, 2016)
	Ce	89.4	
	Pr	95.5	
	Sm	98.4	
	Nd	98.1	
Leaching → electrochemical purification → precipitation	Ce	96	(Alonso et al., 2015)
	La	96	
	Nd	96	
Mechanical treatment → washing with water → leaching → filtration → precipitation	REE	98 → *97	(Liu *et al.*, 2019)

NI = percentage not informed. * Final recovery yields
Source: Authors

Before assessing a biphasic aqueous system, Vargas et al. (2021) leached waste with nitric acid under rough conditions, a 4 mol.L^{-1} of nitric acid at 70°C for 16 hours. The Authors omitted their leaching results, as they used it as a step to evaluate the following process. The developed processes initially involved the removal of iron, manganese, and cobalt using an aqueous biphasic system (ABS), followed by the recovery of nickel by precipitation. As a result, they recovered 47% and 8.5% of lanthanum and cerium, respectively.

In general, the variation in leachate type and concentration is small for this secondary material, with greater changes in temperature and reaction time. As for other secondary materials, sulfuric acid in concentrations up to 2 mol.L^{-1} resulted in satisfactory results. Higher temperatures better leached and recovered lanthanum and cerium

Diáz-López et al. (2018) and Lie, Lin and Liu (2021) applied hydrochloric acid in very different concentrations, 1 and 4 mol.L^{-1}, respectively. Lie, Lin and Liu (2021) used a higher temperature (45°C), lower solid (20 g.L^{-1}), and lower acid concentrations than Diáz-López et al. (2018) (25°C and 50 g.L^{-1}). Several studies show this balance between acid concentration and temperature, even with different secondary materials. Among those, lower concentrations and higher temperatures leached 99% of lanthanum and neodymium and 96% of cerium (Lie; Lin; Liu, 2021), compared to 68%, 66%, and 84% of lanthanum, neodymium, and cerium (Diáz-López et al., 2018). It is worth mentioning that, in addition to REE, Diáz-López et al. (2018) recovered nickel (94.32%) and cobalt (72.44%), then applied these metals in electroplating processes.

Furthermore, a study compared hydrochloric and sulfuric acid in pilot-scale lanthanum leaching (Zielinski *et al.*, 2020). The Authors obtained the highest dissolution selectivity with hydrochloric acid, keeping the solution at a pH of 3 and 25°C. As a disadvantage of applying sulfuric acid, the Authors point out the simultaneous precipitation of double lanthanide sulfates and nickel salts. Nevertheless, it is noteworthy that sulfuric acid remains the most widely utilized leaching agent in other studies.

Studies used sulfuric acid concentrations between 1 and 2 mol.L^{-1}, either by itself or with other reagents, such as ozonation (Alonso *et al.*, 2015) and the addition of sodium sulfate (Porvali; Wilson; Lundström, 2018). A study considered ozone leaching beneficial, associated with a 1 mol L-1 acid concentration at 25°C. After three hours, the process leached 96% of cerium, lanthanum, and neodymium (Alonso et al., 2015).

The recovery of REE by precipitation occurred after nickel and cobalt were separated from the solution using an electrochemical reactor.

On the other hand, adding sodium sulfate failed to improve leaching results. Porvali, Wilson and Lundström (2018) report a 2 mol.L^{-1} concentration at 30°C for three hours as optimal conditions. The Authors obtained lower yields than those who added ozone, extracting 66.4%, 88.8%, and 59.3% of lanthanum, cerium, and praseodymium, respectively.

Sulfuric acid alone leached more than 60% of all investigated REE and 100% of cerium and lanthanum (Takano; Asano; Goto, 2022; Zhang et al., 2019). For such a yield, both studies used one hour of reaction, a 2 mol.L^{-1} sulfuric acid concentration at 90°C. Ahn et al. (2020) also achieved a remarkable recovery of 99% of REE by leaching at 90°C. Such temperature was associated with a 1 mol.L^{-1} acid concentration and 4 hours of reaction.

However, 90°C was not the highest temperature used. Lie and Liu (2021a) investigated applying sulfuric acid (1 mol.L^{-1}) at 125°C for half an hour. The Authors omitted their leaching yields but recovered 82%, 90%, and 85% of lanthanum, cerium, and neodymium after precipitation, respectively. Again, note the balance between leaching agent concentration, temperature, and reaction time. An alternative to assess the better option is to economically and environmentally evaluate the proposed processes.

Liu et al. (2019) and Meshram, Pandey and Mankhand (2016) associated 75°C with 2 and 1.25 mol.L^{-1} of sulfuric acid, respectively. Meshram, Pandey and Mankhand (2016) recovered 98%, 98%, 95%, 89%, and 69% of neodymium, samarium, praseodymium, cerium, and lanthanum after two hours of reaction, the lowest leaching of lanthanum. In addition, the Authors recovered more than 90% of base metals, including nickel, cobalt, manganese, and zinc. Liu et al. (2019) obtained 98% of REE after leaching them for 40 minutes, also recovering manganese, cobalt, and nickel before the precipitation step.

Considering the similarities in the leaching processes, it can be argued that the method proposed by Liu et al. (2019) presents itself as a more economically viable option due to its lower time requirement and acid concentration.

Still, Porvali et al. (2020) leached 95 and 89.9% of lanthanum and cerium using 50°C and 2 mol.L^{-1} of sulfuric acid. Schaeffer et al. (2021) also used 2 mol.L^{-1} of sulfuric acid but at room temperature (25°C), obtaining a final material containing 84% cerium. The Authors proceeded to precipitation (double sulfate), cerium oxidation (NaOH), separation (ionic liquids), recovery (NaOH), and ionic liquid regeneration (NaNO3), stating that the processes have high selectivity towards cerium.

2.3.2.5 WEEE crushing powder

As recycling plants mechanically crush, grind, and sieve (among other processes) electronic waste, they generate crushing powder, i.e., e-scrap Marra, Cesaro and Belgiorno (2019). These fine particles, lost in the mechanical steps, contain recoverable metals. Table 8 summarizes the process flows used to recover REE from it. As with other waste, hydrometallurgy is the most applied process (67%). All studies applying only hydrometallurgical methods, used sulfuric acid by itself or associated with hydrogen peroxide.

Table 8 - Processes flow to recover rare earth elements from WEEE crushing powder.

Process flow and unit operations	**Leaching or final recovery yields***		**References**
	Metal	**Recovery (%)**	
Selection of microorganisms → bioleaching → bioaccumulation	NI		(García-Balboa *et al.*, 2022)
Leaching (2x) (REE) → filtration → leaching (gold)	Ce	100	(Marra; Cesaro; Belgiorno, 2019)
	Eu	100	
	Nd	100	
	Y	92	
	La	48	
Microbial growth → bioleaching → centrifugation → filtration	Ce	99	(Marra *et al.*, 2018)
	Eu	99	
	Nd	99	
	Y	80	
	La	80	
Leaching → solvent extraction → stripping	*Ce	100	(Talebi *et al.*, 2018)
	*La	100	
	*Y	100	
Melting → leaching → precipitation	*Nd	90	(Peelman *et al.*, 2018)
Mechanical treatment → oxidation → leaching → precipitation	*Nd	99	(Peelman; Sietsma; Yang, 2018)

NI = percentage not informed. * Final recovery yields
Source: Authors

Marra, Cesaro and Belgiorno (2019) and Talebi et al. (2018) combined 2 $mol.L^{-1}$ of sulfuric acid and 10% v/v of hydrogen peroxide (30% v/v), and a 100 $g.L^{-1}$ solid-liquid ratio at 25°C. Marra, Cesaro and Belgiorno (2019) leached residues twice and obtained yields of 100% of neodymium, cerium, and europium, 92% of yttrium, and only 48% of lanthanum. Talebi et al. (2018) studied leaching followed by solvent extraction, recovering 100% of yttrium, lanthanum, and cerium.

Additionally, the inclusion of pyrometallurgical techniques as pre-leaching phases produced positive outcomes. Peelman et al. (2018) melted and oxidized their residues prior to leaching with nitric acid (2 $mol.L^{-1}$) at 70°C for 6 hours. The Authors reported leaching 99% of neodymium and recovering 90% after precipitation. They highlighted that the approach generates substantial energy expenditure but no secondary waste. The Authors also investigated a leaching process without the pyrometallurgical step, using sulfuric acid as a leaching agent. The process recovered 91% of neodymium with lower energy expenditure. However, a disadvantage included the formation of $Fe(OH)_3$ due to the high iron content in the residue.

Peelman, Sietsma and Yang (2018) also examined the oxidation of WEEE shredding powder before acid leaching and precipitation. Their pre-treatment oxidizes the iron in the residue to Fe^{3+}, making it less soluble during leaching and reducing its simultaneous extraction. As a result, the Authors extracted 30-40% less iron with neodymium after applying sulfuric acid in a stoichiometric ratio at 70°C, recovering 99% of neodymium overall.

Marra et al. (2018) added biohydrometallurgy to these methods, recovering 80% of lanthanum and yttrium and 99% of cerium, europium, and neodymium. The main disadvantage of this method is time, eight days. Additionally, as a crucial step in recommending a scale-up, the Authors suggest a sequence to recover REE and base and precious metals.

This waste stream contains many base and precious metals. Marra, Cesaro and Belgiorno (2019) extracted 50% of gold from the residue in a second leaching step. Marra et al. (2018) found similar results using a biological approach, immobilizing 48% of gold. Moreover, adopting bioleaching, García-Balboa et al. (2022) recovered over

99% of copper, cobalt, aluminum, and zinc. Peelman et al. (2018) obtained over 90% of iron by associating pyrometallurgy with hydrometallurgy.

The processes applied to these residues had satisfactory results, yielding above 90% in most research. However, improvements are possible, such as reducing the time necessary for biohydrometallurgy processes, optimizing variables for economic use of energy and acids, and assessing the integrations of these processes in the existing recycling plants that produce them.

2.3.2.6 Printed circuit boards (PCB)

Printed circuit boards (PCB) are platforms to mount microelectronic components, such as semiconductor chips and capacitors. Most electrical and electronic equipment contain them (Hadi *et al.*, 2015). Although extensively explored to extract precious metals, studies have scarcely investigated PCB as a secondary REE source. Table 9 shows the process flows in our portfolio.

Since the results did not reach more than 80% of REE leached and recovered, much improvement is necessary before using this secondary source. Neither step is well developed, so it may be better to begin with the first step of the hydrometallurgical process. Considering the processes employed for other residues, it is suggested to utilize sulfuric acid as a leaching agent and further optimize the operating conditions.

Table 9 - Processes flow to recover rare earth elements from printed circuit boards.

Process flow and unit operations	**Leaching or final recovery yields***		**References**
	Metal	**Recovery (%)**	
Electrothermal activation (FJH System) → acid leaching	REE	33-67	(Deng *et al.*, 2022)
Leaching → pH adjustment (base+H2O2) → nano filtration → supported liquid membrane → ceramic membrane distillation	Ce	43.2	(Yuksekdag *et al.*, 2022)
	Dy	53.2	
	Er	47.5	
	Eu	21.2	
	Gd	48.9	
	Ho	29.7	
	La	38.5	
	Lu	76	
	Nd	57.5	
	Pr	71.7	
	Sm	29	
	Tb	66.5	
	REE	49.37	

Process flow and unit operations	Leaching or final recovery yields*		References
	Metal	Recovery (%)	
Mechanical treatment → leaching	Greater recoveries: Nd, Y, Dy		(Yuksekdag *et al.*, 2021)
Mechanical treatment → bioleaching → chemical precipitation of base metals	La	27	(Priya; Hait, 2020)
	Ce	27	
Size reduction by cutting → pyrolysis	REE concentrated in the carbonaceous fraction rich in slag		(Khanna *et al.*, 2018)
Leaching → chemical precipitation (3x) → biomineralization (Mn and Ca)	*Nd	70	(Kim; Seo; Roh, 2018)
	*Pr	50	

NI = percentage not informed. * Final recovery yields
Source: Authors

Starting even before the leaching step, mechanical treatments had their influences evaluated. For PCB, they generally consist of grinding/crushing and sieving (Priya; Hait, 2020; Yuksekdag et al., 2021). Yuksekdag et al. (2021) evaluated the influence of waste particle size, pointing to the effect of grinding and particle size on leaching. Moreover, the Authors assessed several solid-liquid ratios and leaching agents (hydrochloric acid, nitric acid, and aqua regia), determining the use of hydrochloric acid and a 12.5 g.L^{-1} solid-liquid ratio as the best option. Under these conditions, they recovered the highest concentrations of neodymium (105 ppm), yttrium (40 ppm), and dysprosium (30 ppm).

Investigating the effect of pre-treatment, Deng et al. (2022) used an electrothermal process (flash Joule heating) to recover REE from PCB, leaching 156% more REE than without it. The Authors emphasize that the increase is due to the greater exposure of REE species since the electrothermal process breaks the matrices encapsulating this material. The study aimed to show that pre-treatment influences recovery. However, despite the expressive increase, leaching yields failed to reach 80% recovery, requiring evaluating other leaching conditions.

Among the leaching agents applied to this residue, nitric acid and hydrochloric acid are found, alone or combined in the aqua regia formation. Unlike other residues, studies assessing PCB did not use sulfuric acid.

Deng et al. (2022) also used a 1 mol.L^{-1} hydrochloric acid concentration and a 5 g.L^{-1} solid-liquid ratio at 85°C for 4 hours for processes with and without electrothermal activation, leaching between 33 and 67% of REE. Once again, the use of small solid-liquid ratios occurs, which can implicate barriers to the scale-up of the processes and can elevate the operation costs.

Focusing on the processes after leaching, Yuksekdag et al. (2022) evaluated one to enhance REE leached concentration prior to solvent extraction. The crushed and sieved solid waste underwent leaching with nitric acid (0.7 mol.L^{-1}) at 25 g.L^{-1} and 60°C for 24 hours. As they did not evaluate optimal leaching conditions, they deemed the long reaction time as an attempt to guarantee maximum yield with lower acid consumption. They concentrated REE by nanofiltration, obtaining thrice as much REE. Furthermore, they extracted REE by a supported liquid membrane process, followed by ceramic membrane distillation. The Authors conclude that this concentration by nanofiltration increases the selectivity of REE separation, further recognizing the need to evaluate its effects on a larger scale.

Examining the use of aqua regia (3:1 HCl: HNO_3) on PCB, Kim, Seo and Roh (2018) leached 70% and 50% of neodymium and praseodymium, respectively. The Authors used a 100 g.L^{-1} solid-liquid ratio for 48 hours at 25°C. They used the highest solid-liquid ratio and the lowest temperature among the studies with PCB. However, they had the highest reaction time, requiring an economic analysis to assess whether it would be preferable to maintain a long reaction and low temperature or whether increasing the temperature would economically make up for a reduction in time. Beyond that, aqua regia is corrosive and would difficult the scale-up process. The Authors also evaluated a three-step precipitation (iron, copper, and REE). Then, they analyzed a biomineralization process to recover manganese and calcium.

As with other residues, studies also assessed bioleaching. Priya and Hait (2020) only leached 27% of lanthanum and cerium, showing the need for better biological leaching processes. As stated before, PCB is commercially recycled to recover base metals. Thus, it is expected that these elements are leached. Priya and Hait (2020) bioleached 96% of copper, 94.5% of zinc, 75% of nickel, and 74.5% of lead. The Authors used fractional chemical precipitation as a recovery step, resulting in 99% of base metals recovered.

2.3.2.7 LED residue

The LED waste comes from different forms and types of lighting containing LEDs (light-emitting diodes). They generally consist of a support called an LED module, in which LED chips are positioned and may be encapsulated by a transparent material. Most studies focused on LED chips already separated from the rest of the waste.

As with other residues, hydrometallurgical processes predominated. However, these studies most often used hydrochloric acid as their leaching agent, unlike others. Research mainly focused on gallium and indium, recovering between 73 and 99% of these materials. Regarding temperature, the investigated processes used 25°C (Chen; Chung; Tien, 2020; Gupta; Mudhar; Singh, 2007), 90 to 100°C (Maarefvand; Sheibani; Rashchi, 2020; Swain et al., 2015; Zhou et al., 2019), and 200°C (Chen; Hsu; Wang, 2018), associating lower temperatures with longer reactions (Gupta; Mudhar; Singh, 2007) or pre-treatments, such as alkaline roasting (Chen, Chung e Tien, 2020).

Alkaline roasting leached 96.9% and 96.6% of gallium and indium with 2 $mol.L^{-1}$ of hydrochloric acid and a 33 $g.L^{-1}$ solid-liquid ratio for only 32 minutes (Chen, Chung e Tien, 2020). With the same acid concentration and a 250 $g.L^{-1}$ solid-liquid ratio, Gupta, Mudhar and Singh (2007) achieved a final recovery of 90.8% of gallium after 24 hours. Finding the balance between energy expenditure and reaction time is essential for scaling up these processes.

Employing a higher temperature (93°C), Maarefvand, Sheibani and Rashchi (2020) developed a process capable of leaching 91.4% of gallium with 4 $mol.L^{-1}$ hydrochloric acid and 2 hours of reaction. Nevertheless, besides the higher temperature, the Authors propose a sequence of pre-treatments containing incineration, acetone application, and oxidation. Thus, research must assess if the effort before leaching is justified or if it would be possible to use milder leaching conditions after such pre-treatments.

An example of these analyses is Chen, Hsu and Wang (2018), who assessed pressurized leaching and leaching after alkaline roasting. The Authors concluded that pressurized leaching, with 15 atm of pressure at 200°C and 0.25 $mol.L^{-1}$ of hydrochloric acid, yielded 98.5% of gallium, more than twice as much as other treatments, highlighting the need to include the energetic expenses of the process.

Swain et al. (2015) also evaluated two possibilities of gallium leaching, with and without oxidative roasting pre-treatment. Adding Na_2CO_3, pre-milling, annealing, and leaching with hydrochloric acid (4 mol.L^{-1}) at 100°C obtained 73.7% of gallium, the lowest result among studies with hydrometallurgy. However, this result is 15 times higher than those with processes without Na_2CO_3 before leaching.

Unlike other studies, Zhou et al. (2019) developed a process with oxalic acid (0.7 mol.L $^{-1}$) which leached 90.4% of gallium. The Authors also used a 10 g.L^{-1} solid-liquid ratio at 90°C for one hour after pyrolysis and milling, combining pyrometallurgy and hydrometallurgy. Its advantages include an organic acid in low concentrations, being less harmful to the environment. On the other hand, a low solid-liquid ratio excessively spends acid, and pyrometallurgical processes can increase costs. Thus, an economic evaluation could assess the feasibility of this association.

Only one study in our portfolio evaluated the application of ionic liquid. Van Den Bossche et al. (2019) developed a process applying tribromide ionic liquids to a 100 g.L^{-1} solid-liquid ratio at 60°C. Then, the first stripping removed arsenic; the second, gallium; and the third, indium, recovering 96% and 99% of the latter two, respectively.

Direct (Pourhossein; Mousavi, 2018) and indirect (Pourhossein; Mousavi, 2019) bioleaching recovered 60 and 84% of gallium, respectively. Studies also explored subcritical and supercritical states to recover gallium. The use of supercritical water recovered 80.5% (Zhang; Zhan; Xu, 2021), whereas the one with anhydrous ethanol and an ethanol-water mixture in sub and supercritical states, 93.1% (Zhan *et al.*, 2020).

Dealing with the residue more generally, Cenci et al. (2021) evaluated a form of mechanically concentrating REE in LED lamps. The Authors used manual separation, grinding, sieving, and electrostatic separation, concentrating cerium, yttrium, and gallium in non-conducting fractions, which can facilitate the recovery of these elements. Table 10 summarizes the processes in each study assessing LED waste as a secondary REE source.

Other metals that constitute the residues are also leached and separated along with the REE. Not all research presented these results since it was not their focus. Some of the highlighted elements also extracted in the processes were gold, silver, copper, and tin. Cenci et al. (2021) conducted the separation of these metals into conductive fractions. However, indirect bioleaching extracted 83% of copper and almost all nickel within the waste (Pourhossein; Mousavi, 2019).

Additional possible recoveries include utilizing the residue as a whole, not only the chip, to recover other critical materials such as yttrium and cerium.

Table 10 - Processes flow to recover rare earth elements from LED residue.

Process flow and unit operations	**Leaching or final recovery yields***		**References**
	Metal	**Recovery (%)**	
Manual separation → mechanical treatment → electrostatic separation	Ce, Y, and Ga concentrated in a non-conducting fraction		(Cenci et al., 2021)
Hydrothermal treatment → transparent encapsulation → hydrothermal treatment → solvent extraction	Ga	80.5	(Zhang; Zhan; Xu, 2021)
Mechanical treatment → alkaline roasting → leaching	Ga	96.88	(Chen; Chung; Tien, 2020)
	In	96.61	
Supercritical anhydrous ethanol → transparent encapsulation → anhydrous ethanol + supercritical water	*Ga	93.10	(Zhan et al., 2020)
	*In	85.72	
Incineration → mechanical treatment → transparent encapsulation → acetone → LED chip → oxidation → leaching	Ga	91.4	(Maarefvand; Sheibani; Rashchi, 2020)
Disassembly → mechanical treatment → direct and indirect bioleaching	Ga	84	(Pourhossein; Mousavi, 2019)
Pyrolysis → mechanical treatment → leaching	Ga	90.36	(Zhou et al., 2019)
Mechanical treatment → leaching → 3 stripping sequences	*Ga	96	(Van Den Bossche et al., 2019)
	*In	99	
Mechanical treatment → adaptation of bacteria → bioleaching	Ga	60	(Pourhossein; Mousavi, 2018)
Grinding → drying → pressurized leaching	Ga	98.46	(Chen; Hsu; Wang, 2018)
Pyrolysis → mechanical treatment → vacuum metallurgical separation	*Ga	93.48	(Zhan *et al.*, 2015)
	*In	95.67	
Addition of Na_2CO_3 → mechanical treatment → annealing → leaching	Ga	73.68	(Swain et al., 2015)
Leaching → solvent extraction	*Ga	90.8	(Gupta, Mudhar e Singh, 2007)

NI = percentage not informed. * Final recovery yields
Source: Authors

2.3.2.8 Other residues

A few studies assessed other residues and mixtures. Thus, Table 11 shows the process flows applied in three different secondary materials in the evaluated literature.

Table 11 - Processes flow to recover rare earth elements from waste from several batteries, cell phones, and LCD.

Process flow and unit operations	**Leaching or final recovery yields***		**Residue/ References**
	Metal	**Recovery (%)**	
Mechanical treatment → reduction in an inert atmosphere → magnetic separation → acid leaching → solvent extraction	*Ce	90	Various batteries/ (Provazi *et al.*, 2011)
	*La	80	
Leaching → precipitation → transformation into oxides → thermal decomposition	Nd	14.1 → *91.7	Cell phones/ (Sronsri *et al.*, 2021)
	Ce	3.4 → *86.7	
Mechanical treatment → leaching → (solid) magnetic separation	Leach Liquor - Gd	12	Liquid crystal displays (LCD)/(Toache -Pérez *et al.*, 2020)
	Leach Liquor - Pr	0	
	Solid – Gd	85	
	Solid – Pr	87	

NI = percentage not informed. * Final recovery yields
Source: Authors

Using a mixed residue from several batteries, Provazi et al. (2011) evaluated leaching with sulfuric acid and two final recovery routes, chemical precipitation and solvent extraction. The leaching conditions were 1 mol.L^{-1} of acid at 25°C for 24 hours with a 100 g.L^{-1} solid-liquid ratio. Such conditions are interesting for their low acid concentration and temperature. However, its reaction time can make it commercially impractical. As the Authors focused on the recovery processes, we can assume that the long reaction aims to increase the amount of REE leached for subsequent analyses. The Authors concluded that solvent extraction was more selective in separation, recovering 90% and 80% of cerium and lanthanum, respectively.

Evaluating discarded cell phones, Sronsri et al. (2021) studied the recovery of gold, industrial metals, cerium, and neodymium. To recover REE, the Authors leached the waste in an inert atmosphere with sulfuric acid (1.6 mol.L^{-1}) at 25°C for 16 hours, reaching 14.1% and 3.4% of neodymium and cerium leached, respectively. These results are lower than for other residues. However, after precipitation, oxidation, and thermal decomposition, they recovered 91.7% and 86.7% of neodymium and cerium. Thus, there is a need to improve this leaching step since the next steps obtained high yields. Further studies should focus on applying higher temperatures, higher acid concentrations, and lower reaction times.

Unlike most studies, Toache-Pérez et al. (2020) collected LCD waste from various electronic equipment to concentrate gadolinium and praseodymium in a solid phase. The Authors combined acid leaching and an ultrasonic process in a medium containing pyrophosphate at 25°C and a 20 $g.L^{-1}$ solid concentration.

They were able to leach only 12% of gadolinium and no praseodymium in a liquid medium. The Authors expected this outcome because, unlike other Authors, their primary focus was not on REE in the leach but on the post-leaching solid material. They subjected the remaining residue to magnetic separation, concentrating gadolinium and praseodymium in a magnetic fraction and recovering 85% and 87% of each element, respectively. The Authors describe this process as satisfactory to concentrate REE and point out that the ultrasonic process aimed to rupture particles and increase the penetration rate of the leachate into the solid by cavitation, thus improving its exposure to the leachate (Toache-Pérez et al., 2020).

As the residues brought in this section are widely different, there is almost no similarity in the processes applied, except for the application of sulfuric acid in the first two research in Table 11.

2.3.3 Other remarks

In addition to the explored residues and recovered rare earth elements (REE) mentioned previously, there is untapped potential for further exploration. The prevalence of devices with screens in our daily lives is evident, with personal devices alone accounting for up to half of the waste electrical and electronic equipment (WEEE) generated (World Economic Forum, 2019).

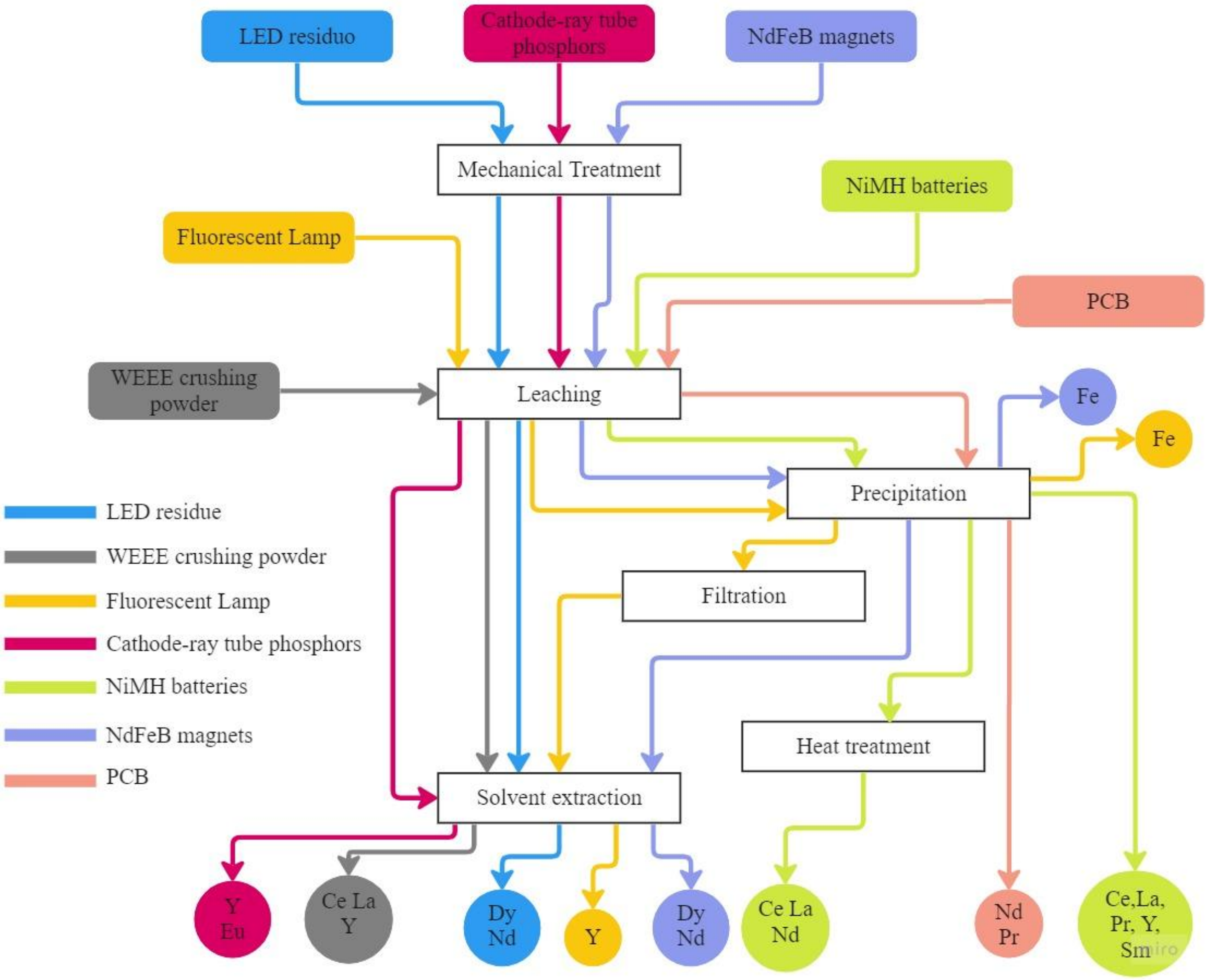
The LCD screens, for example, offer a potential source of valuable REE such as yttrium, cerium, europium, and terbium (Binnemans *et al.*, 2018). However, it is worth noting that limited research has been conducted thus far on the effective recovery of these elements from waste streams associated with LCD screens. Regarding processes, electrochemical associations and use of ionic liquids could be more explored, focusing on resolving issues such as chemical stability, and reuse of the solvent (Binnemans; Jones, 2023).

Moreover, some of the REE present in the residues were poorly explored, mainly due to the small concentration compared to others. Some elements that can be further researched include indium, scandium, ytterbium, dysprosium, and gadolinium.

Figure 2 was assembled by combining some of the high-yield processes' flowcharts from different residues as a way of supplementing this review. The WEEE presented in subsection 2.3.2.8 were not included in the image since they were diverse and poorly explored. The different color lines represent the process for each residue.

It is possible to note similarities between the most efficient methods among different residues. One of these similarities is that they all applied hydrometallurgical processes, varying the recovery step by using precipitation, solvent extraction, or both. Variation on the operational parameters occur depending on WEEE and REE of interest, despite following a similar flow.

Figure 2 - Process flowchart combining those used in different waste sources.

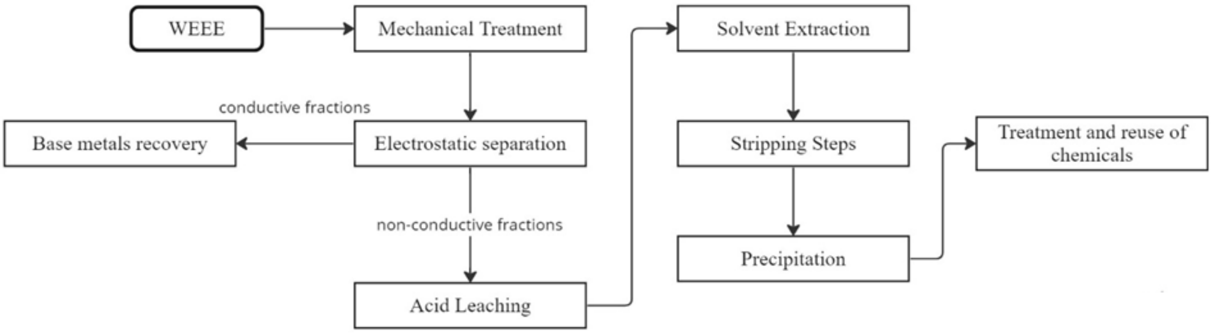


Source: Adapted, modified, and reproduced from (Ahn et al., 2020; Van Den Bossche et al., 2019; Erust et al., 2019; Kim; Seo; Roh, 2018; Porvali et al., 2020; Porvali; Wilson; Lundström, 2018; Saratale, G. et al., 2020; Talebi et al., 2018; Tian et al., 2018)

Aligned with the exposed so far and considering the most used processes presented in this review, Figure 3 shows a proposed processes flow for a general recovery of REE from WEEE. As other alternatives with less harmful products must still be consolidated, we suggest applying hydrometallurgy.

The processes focus only on the REE recovery, not addressing other metals or waste treatment processes. Mechanical treatment refers to shredding/milling. Since sulfuric acid (at 2 mol.L^{-1} concentration) is the most used leaching agent, we suggest beginning the investigation with it. However, operational details, such as temperature and solid-liquid ratio, must be tested for the specific residue of interest. The same goes for the conditions of the following steps. It is important to note that the suggestions were not based on environmental and economic studies.

Figure 3 - Suggested process' flowchart.(Prodius et al., 2020a; Takano; Asano; Goto, 2022).



Undoubtedly, the hydrometallurgical process generates a significant amount of waste streams, which, if not treated properly, can have a detrimental impact on the environment (Prodius et al., 2020a; Takano; Asano; Goto, 2022). Nevertheless, the issue of waste generation is also present in primary metal production but, unlike that process, recycling rare earth elements (REEs) from secondary materials does not deplete natural resources.

A life cycle assessment of NdFeB magnets revealed that producing magnets using recycled neodymium was superior in terms of both economic and environmental factors (Karal *et al.*, 2021). Despite being a better alternative when compared with natural resource mining, the development of new processes must consider ways to reduce these environmental impacts.

Throughout this review, it is evident that researchers have made substantial efforts to mitigate the environmental impact associated with these processes. These include the implementation of auxiliary mechanisms to minimize acid concentration, the exploration of organic acids as alternatives to inorganic acids, and the advancement of bioleaching routes. Furthermore, another possibility is the reuse of acid from different industries, such as the etching and cleaning processes of semiconductor manufacturing, also reducing operational costs (Lie; Liu, 2021a). In addition, alternative wastewater treatment methods, including biological, oxidative, and ultrafiltration treatments, have been developed (Takano; Asano; Goto, 2022).

Before scaling up the mentioned process improvements, further research on economic and environmental assessments should be conducted. From a cost standpoint, hydrometallurgy is considered more economically favorable than pyrometallurgy due to its lower energy demands. However, it is essential to consider the cost of chemicals when developing a process. Thus, it is important to highlight that sulfuric acid, the most utilized leaching agent discussed in this review, is favored for its ability to achieve effective metal recoveries and its cost-effectiveness compared to other chemical alternatives (Erust *et al.*, 2019).

2.3.4 Research challenges and gaps

Based on the literature review, the main challenge highlighted is the integration of already established processes for the recovery of base and precious metals with those specifically designed for rare earth elements (REEs). In general, all residues shown require, after verifying the recovery range in processes aiming only to recover REE, assessing them as an integrating part of a broader process, whether before or after the recovery of other materials. The study of integrating the recovery of rare earth elements (REEs) with the recovery of other metals is crucial for the commercial-scale application of this process.

Still, to commercially apply the processes, we stress the need for the technical, environmental, and economic viability of scaling-up previously validated processes in laboratory scale.

The assessment of alternatives to inorganic acids as leaching agents is more prominent in studies involving NdFeB magnet residues. Thus, we emphasize the need for this investigation for other residues. Moreover, it is essential to assess lower temperatures, pressures, and acid concentrations in all these processes.

Regarding residues, it is worth noting that the processes proposed for recovering REE from PCBs generally result in yields below 70%, emphasizing the need of further research to investigate different process conditions and enhance yield optimization.

The need for evaluating multiple waste types in a streamlined process with fewer mechanical separation steps before leaching can be addressed by investigating LED waste more broadly and assessing all electronic components alongside the LED chip.

Only cathode-ray tubes and fluorescent lamps underwent simultaneous assessments to recover REE. Thus, studies must also assess the recovery of REE from different secondary materials (mixed residues) to unify and make it more attractive to the market. However, the requirement for a more comprehensive process that recycles different secondary materials as primary materials requires investigating residues both individually and combined, being the latter commonly found in recycling companies.

Thus, further studies should focus on the use of innovative and environmentally friendly leaching agents, along with the advancement of milder operational conditions. Furthermore, time required for bioleaching should be reduced to make it a more appealing option. Additionally, we emphasize the necessity of developing a unified process capable of recovering rare earth elements (REE) from various types of WEEE.

2.4 CONCLUSION

Recovering REE by hydrometallurgical processes stands out among the studies with WEEE as a secondary material. Its cost-effectiveness, lower energy consumption, and gaseous emissions compared to pyrometallurgical processes make it an attractive option. Researchers most often used sulfuric acid as a leaching agent, especially when interested in cerium, yttrium, lanthanum, neodymium, praseodymium, and europium, followed by hydrochloric acid, mainly to recover gallium, gadolinium, and samarium.

Note that even in residues with a highly variable composition, such as e-scrap, sulfuric acid obtains satisfactory yields, a good alternative for studies with mixed wastes of several electronics in more unified processes.

Studies on LED waste mainly focused on chips already separated from the residue, such as LED lamps and pins. This mechanical separation, despite concentrating REE, demands greater effort in the pre-processes. Moreover, all studies assessed gallium recovery. The literature must investigate processes that include recovering other REE in this residue (such as cerium and yttrium). Further research should also assess all electronic components in these residues in addition to LED chips.

Several other metals of interest, including base metals, such as copper, iron, nickel, cobalt, and zinc, were leached and recovered using different proposed processes. Despite the reviewed papers primarily emphasizing REE by recognizing the importance of extracting these metals, it is crucial to consider and factor in the significance of these supplementary metals when making process choices.

We found a strong trend toward biohydrometallurgy, especially with fluorescent lamps, e-scrap, LED, and printed circuit boards. Alternatives to acid leaching were found mainly on NdFeB magnets researches. Studies mainly used pyrometallurgy as a step before hydrometallurgy. Moreover, the assessed literature most often investigated the recovery from NdFeB magnets, followed by NiMH batteries and fluorescent lamps. As for the REE, yttrium was the primarily investigated one.

CHAPTER 3

EXTRACTION OF RARE EARTH ELEMENTS FROM WASTE LED LAMPS USING ACID LEACHING

Resumo

O uso de lâmpadas de LED como fonte secundária de elementos terras raras (ETR) ainda é um tópico pouco explorado na literatura, não existindo ainda um processo consolidado para a recuperação de ETR a partir desse resíduo, ocorrendo o mesmo para outros resíduos eletroeletrônicos (REEE). Assim, este estudo teve como objetivo estudar a lixiviação ácida para extração de elementos terras raras de placas de circuito impresso (PCB) e componentes eletrônicos a partir de lâmpadas LED inservíveis. A influência da temperatura, concentração de ácidos e relação sólido-líquido foi estudada utilizando um delineamento experimental Box-Behnken, analisando três níveis em cada fator. Nas condições ótimas (55°C e 100 g.L^{-1}, as extrações obtidas foram 78,82% e 41,19% de cério e ítrio, respectivamente, tendo como agente lixiviante a combinação de ácido sulfúrico 2,5 mol.L^{-1} e peróxido de hidrogênio. Utilizando tais parâmetros a temperatura e a relação solido-líquido apresentaram influência no resultado de extração. O aumento da temperatura de 25 para 55°C resultou em uma extração 93% e 90% maior para cério e ítrio respectivamente. Já a variação de 25 g.L^{-1} para 100 g.L^{-1} resultou em aumento de 84% na extração de cério e de 86,8% na do ítrio. Contudo, analisando estatisticamente as variações dentro do range estudado, nenhuma das variáveis apresentou influencia estatisticamente significativa na extração quando ácido sulfúrico e peroxido de hidrogênio foram utilizados. Sugere-se estudar a combinação com outros processos para aumentar a concentração de ETR na amostra ou extrair em fase preliminar outros metais contaminantes.

Palavras Chaves: Elementos Terras Raras, Cério, Ítrio, Lâmpadas de LED, RE, Lixiviação.

Abstract

The use of LED lamps as a secondary material of REE is still a topic little explored in the literature, and there is still no consolidated process for recovering REE from this waste, the same occurring for other electrical and electronic waste (WEEE). Thus, this study aimed to develop a leaching process for extracting rare earth elements from printed circuit boards (PCB) and electronic components of end-of-life LED lamps. The influence of temperature, acid concentration, and solid-liquid ratio was studied using a Box-Behnken Design, analyzing three levels in each factor. Under optimal conditions (55°C and 100 g.L^{-1}), the extractions obtained were 78.82% and 41.19% of cerium and yttrium, respectively, using the combination of sulfuric acid 2.5 mol.L^{-1} and hydrogen peroxide as a leaching agent. Using these parameters, temperature and the solid-liquid ratio influenced the extraction result. Increasing the temperature from 25 to 55°C resulted in a 93% and 90% increase in cerium and yttrium extractions, respectively. The variation from 25 g.L^{-1} to 100 g.L^{-1} resulted in an increase of 84% in the extraction of cerium and 86.8% in that of yttrium. However, statistically analyzing the variations within the studied range, none of the variables showed a statistically significant influence in extraction when sulfuric acid and hydrogen peroxide were used. It is suggested to study the combination with other processes to increase the ETR concentration in the sample or extract other contaminating metals in a preliminary phase.

Keywords: Rare Earth Elements, Cerium, Yttrium, LED Lamps, Leaching.

3.1 INTRODUCTION

Light-emitting diodes (LEDs) are solid-state semiconductor lighting device that transforms electrical energy into visible light. As a result of significant technological advancements, LED lamps outperform conventional technologies in terms of energy efficiency, longevity, adaptability, and color quality (Morgan Pattison; Hansen; Tsao, 2018; U.S. Department of Energy, 2019). Due to this energy efficiency, the Energy Savings Forecast of Solid-State Lighting in General Illumination Applications anticipates that by 2035, this category of lamps will constitute 84% of the lighting market (U.S. Department of Energy, 2019).

Thus, it is relevant to describe that LED lamps consist of polymeric and metallic fractions, printed circuit boards (PCB), electronic components, batteries, and cables. In the metallic fraction and the PCB, metals such as gold, silver, aluminum, copper, and rare earth elements (REE) are found (Martins; Tanabe; Bertuol, 2020; Rebello et al., 2020). Within the composition, yttrium is used as a color converter material, and cerium is a color converter doping material (Franz and Wenzl, 2017), often present as $Ce:Y_3Al_5O_{12}$. Consequently, primarily attributed to the inclusion of valuable metals and rare earth elements in their composition, recycling procedures for LED lamps have garnered considerable research attention.

Rare earth elements are essential for future technologies and have mineral reserves concentrated in specific countries, such as China, which hold 97% of their production (Lie; Liu, 2021a). According to Mishra, Devi, and Sukla (2020), REEs are the most critical resources in traditional and high-tech industries due to their unique physical and electrochemical characteristics, which is why they are considered critical metals.

Identifying alternative secondary materials becomes essential for furthering the sustainable use of these elements (Annoni *et al.*, 2020). Gaustad et al. (2019) report that the rare earth elements contained in secondary materials could meet world demand. However, the recycling processes related to obtaining these metals from WEEE are still being developed and improved. Even so, studies involving secondary materials, such as WEEE, are more focused on the recovery of gold and silver (Caldas et al., 2021; Zhan et al., 2020; Zhang; Zhan; Xu, 2021), with a gap in studies focusing on the recovery of rare earth elements.

The hydrometallurgical method is preferred when extracting rare earth metals from WEEE in general, as reported by Pimassoni et al. (2023). Within this process, after the variety of mechanical and chemical pre-treatments available such as the ones shown by De Oliveira (2022), there is the step consisting of the leaching elements into liquid media. To that end, mineral acids, such as hydrochloric acid, nitric acid, and sulfuric acid, are the most used in the leaching of rare earth elements from secondary and primary sources (Marra; Cesaro; Belgiorno, 2019), with sulfuric acid being the most exploited for WEEE. Specifically for LED residues, there is a gap in the assessment of REE extraction, with gallium and indium being the most investigated critical metals and hydrochloric acid being the most used leaching agent (Pimassoni *et al.*, 2023). Nonetheless, the selection of the leaching agent represents the initial phase in the investigation of hydrometallurgical process development. Altering the composition of the waste's initial matrix can yield diverse outcomes, emphasizing the significance of this step.

The association of the leaching agent with other processes is investigated to develop processes at lower concentrations of acids, temperatures, and time (Yin *et al.*, 2018). Among the investigated associations is applying an oxidizing agent in the reaction medium that, associated with sulfuric acid, returns satisfactory results in the extraction of REE (Innocenzi et al., 2013a; Innocenzi et al., 2013b; Marra; Cesaro; Belgiorno, 2019; Talebi et al., 2018).

Beyond the type of leaching agent, temperature, acid concentration, and solid-liquid ratio are also reported to affect the metals extraction (Lie, Lin e Liu, 2021) . As the investigation of the recovery of cerium and yttrium from LED lamps is scarce, identifying the effects and optimal conditions among these variables is essential.

Hydrometallurgy is reported as the most common method to recover rare earth elements from secondary materials (Marra; Cesaro; Belgiorno, 2019). As advantages, these methods apply lower temperature, consuming less energy when compared with pyrometallurgical ones. In addition, it also has lower greenhouse gas emissions (Lisińska *et al.*, 2018).

The method is composed, generally, of extraction, separation/purification, and final recovery steps. Acid leaching is the focus of this research, and it was evaluated as the first step of the hydrometallurgical method.

Various factors influence leaching outcomes, such as the leaching agent, solid-liquid ratio, temperature, and reaction time (Lie; Lin; Liu, 2021). Leaching agents varied with the waste matrix and the metal of interest. For the extraction of rare earth elements, inorganic acids such as nitric, hydrochloric, hydrofluoric, and sulfuric acids were the most used, with a preference for the latter (Jha *et al.*, 2016; Pimassoni *et al.*, 2023; Sethurajan *et al.*, 2019; Tunsu *et al.*, 2015; Zhang *et al.*, 2019). Besides having satisfactory leaching results, Liu et al. (2019) point out that sulfuric acid is also economically advantageous, and preferred in larger scale processes.

Nevertheless, multiple studies asses the most suitable leaching agent for the specific waste (Choi; Iyas; Kim, 2022; Erust et al., 2019; Michelis et al., 2011; Pavón et al., 2019; Peelman; Sietsma; Yang, 2018; Saratale, R. et al., 2020; Sobianowska-Turek, 2018). Hydrochloric acid is primarily applied when gallium is the critical metal of interest, resulting in 20 to 30% less cerium and yttrium leached than sulfuric acid (Sobianowska-Turek, 2018; Tunsu; Ekberg; Retegan, 2014). Thus, nitric and sulfuric acid were evaluated.

Beyond the mentioned acids, the use of oxidizing agents substantially improves the dissolution of metals. Among the available ones, hydrogen peroxide is preferred due to being cost-effective, not harmful to the environment, and not affecting downstream processes or adding contaminants to the process (Zhang *et al.*, 2021). The combination of sulfuric acid and hydrogen peroxide resulted in high extractions. According to Yin et al. (2018), this association also reduces the generation of the toxic gas H_2S.

The concentration of the leaching agent is a factor that influences the extraction. De Michelis et al. (2011), Zhang et al. (2019) and Song et al. (2017) shown that this factor alone and combined with the solid-liquid ratio have a statistically significant influence on the REE extraction from fluorescent lamps, spent asymmetric-capacitance power batteries, and waste trichromatic phosphors. Concentrations ranged from 0.5 and 12 $mol.L^{-1}$, with the most commonly evaluated range being 1 to 4 $mol.L^{-1}$.

Solid-liquid ratio or solid concentration is another contributing factor. Generally, small solid-liquid ratios result in higher leaching results (Ciro *et al.*, 2019) due to higher acid availability. However, this condition generates high acid costs, high amounts of wastewater and may not be attractive even if returning higher extractions (Alkan *et al.*, 2018).

The bibliometric analysis revealed that sulfuric acid reactions encompass a range of 25 to 200 g.L^{-1}, while reactions involving nitric acid span from 10 g.L^{-1} to 500 g.L^{-1}. The prevailing concentration was 100 g.L^{-1}. Consequently, it was established the study interval as 25 to 100 g.L^{-1}.

The temperature analysis is present in most research, in an interval from 20 to 200°C. Yin et al. (2018) showed that the increase in temperature results in an increase in REE extraction from cathode-ray tube phosphorus. However, Zhang et al. (2019) did not observe any changes with this parameter variation. When determining the temperature, it is essential to consider the presence of hydrogen peroxide, as its decomposition becomes more pronounced at temperatures exceeding 60°C (Hidalgo *et al.*, 2022; Zhang *et al.*, 2021). With that in mind and aiming to develop a process in milder conditions, it was determined that the temperature would be varied from 25 to 55°C. The same range was assessed for all leaching agents to enable a comparison among the acids tested.

Thus, in this chapter, it is proposed to develop the leaching step of the hydrometallurgical process for recovering rare earth elements from LED lamps, identifying the optimal leaching agent and process parameters. Three different leaching agents were tested, studying the influence of temperature, acid concentration, and solid-liquid ratio for each one on the cerium and yttrium extractions.

3.2 METHODOLOGY

3.2.1 Waste samples and characterization

The end-of-life LED lamps used in this research were collected, mechanically processed, and characterized in previous research. The samples were composed of printed circuit boards (PCB) and electronic components (such as capacitors, chips, and resistors) from a variety of LED lamps, as described in Rebello et al. (2020).

In the article, Rabello et al. (2020) performed three main steps: collection, gravimetric composition, and characterization of PCB and electronic components. The last step was mechanical processing, acid digestion, and loss-on-ignition.

For the mechanical treatment step, Rabello et al. (2020) reduced the size of samples to approximately 1 cm2 using a manual guillotine. The Authors then comminuted the samples using a ring mill until the passing size of 1.29mm of a vibrating sieve. The material was then directed to the metal characterization through acid leaching using nitric acid (2 mol.L^{-1}, 40°C, 25 g.L^{-1}) and aqua regia (25°C, 50 g.L^{-1}) (Rabello et al., 2020). The characterization results obtained were used as a starting point in the leaching outcome determination. The results for the metals that were quantified by Rabello et al. (2020) and investigated in the present research are shown in Table 12.

Table 12 - Concentration in mg.kg^{-1} in the PCB and electronic components of end-of-life LED lamps

Element	Silver	Gold	Cerium	Gallium	Yttrium	Copper
Concentration (mg.kg^{-1})	384	348,5	16,29	ND	20,8	94492

Source: Adapted from Rabello et al. (2020)

The powder resulting from the mechanical processing is the starting material in this research, and the values in Table 12 were used to determine the percentage of extraction.

The characterization method did not quantify all the elements identified in the leach. As it was not possible to calculate the leaching (%) regarding these elements, the absolute values (mg.kg^{-1}) were utilized.

3.2.2 Materials

All the glassware used underwent a cleaning process to minimize possible contaminations and errors during the analytical procedures. Firstly, the glassware was washed with detergent, then kept in a nitric acid solution (15% v/v) for twenty-four hours. Finally, the acid solution was rinsed with ultrapure water.

With the same intent of minimizing contamination, the nitric acid used (65-67%, Sigma-Aldrich) as a leaching agent was distilled. Other reagents used as leaching agents were sulfuric acid (95-98%, Sigma-Aldrich) and hydrogen peroxide (35% PA, Neon).

An analytical scale model Q-500L2010C (Quimis) was used to weigh the powder samples. The leaching tests were carried out in 1000 milliliters Erlenmeyer flasks in a shaker model TE-4200 (Tecnal) under constant 200 ± 2 rpm agitation. Volumetric pipets were used to prepare the leaching solutions and to add them to the Erlenmeyer flasks. The leaching samples were filtered under vacuum using quantitative rapid filtration paper filters (C41 – Unifil).

3.2.3 Acid leaching

Acid leaching was performed using three leaching agents: nitric acid, sulfuric acid, and a combination of sulfuric acid and 10% of hydrogen peroxide (30%). It was assessed the influence of acid concentration, solid-liquid ratio, and temperature. Furthermore, samples were taken in 10, 20, 30, 60, 120, and 180 minutes to evaluate the reaction behavior throughout time.

A Box-Behnken experimental design was employed to evaluate the impacts of the factors. Equation 1 for three independent variables (k) and three additions in the center point (cp) results in 15 experiments for each leaching agent (Box; Behnken, 1960).

$$Number\ of\ experiments = 2.k.(k-1) + cp \qquad \text{Equation 1}$$

Table 13 shows the conditions of each factor and Table 14 shows the experimental parameter for each experiment. The experiments were executed in a randomized order.

Table 13 - Real and coded values for each variable.

Factors (Unit)			
Coded	-1	0	+1
Temperature (°C)	25	40	55
Acid Concentration (mol.L^{-1})	1	2.5	4
Solid-liquid ratio (g.L^{-1})	25	62.5	100

Source: Author

Table 14 - Box-Bhenken planning matrix.

Experiment	**Temperature**	**Acid Concentration**	**Solid-liquid ratio**
1 (A)	25	1	62,5
2 (B)	55	1	62,5
3 (C)	25	4	62,5
4 (D)	55	4	62,5
5 (E)	25	2,5	25
6 (F)	55	2,5	25
7 (G)	25	2,5	100

Experiment	Temperature	Acid Concentration	Solid-liquid ratio
8 (H)	55	2,5	100
9 (I)	40	1	25
10 (J)	40	4	25
11 (K)	40	1	100
12 (L)	40	4	100
13 (M)	40	2,5	62,5
14 (N)	40	2,5	62,5
15 (O)	40	2,5	62,5

Source: Author

The leaching experiments used an Erlenmeyer of 1000 milliliters due to foam formation in some experiments. In absolute values, the volume of reaction was fixated in 150 milliliters and the residue mass added varied in accordance with the solid-liquid ratio used. For 25 g.L^{-1} the corresponding mass was 3.75 grams, for 62.5 g.L^{-1} it was 9.375 grams and for 100 g.L^{-1} it was 15 grams.

3.2.4 REEs extraction analysis

The behavior throughout time was accessed by creating curves using the average extraction of each variable in its respective levels, thus each variable was individually analyzed. These curves also enable the identification of the influence each variable has on the response. The optimal extraction time for each element was identified by assessing the time point that yielded the highest extraction percentage and evaluating the percentage difference compared to the previous and next time interval. A difference lower than 5% resulted in the shorter reaction time as the best option.

Results of the leaching experiments, planned by the Box-Behnken experiment design, were used to determine the effect of each factor in the response variable (leaching results). Statistically significant factors were determined through Pareto charts of standardized effects and analysis of variance (ANOVA), with a 5% significance level. At a confidence level of 95% ($\alpha = 0.05$), the factors holding a $p - value \leq \alpha$ resulted in significance for the process response. The empirical models were not determined due to low leaching results or the lack of significant factors.

Additionally, the results of the experiment that resulted in higher extractions were analyzed descriptively by plotting the behavior through time of this experiment compared to experiments that differ only in one variable. These graphs made it possible to analyze if, in those particular conditions, the variables had any influence.

To assess the extraction's selectivity, a selectivity index (SI) was calculated, as outlined in Equation 2. SI was determined by dividing the extracted amounts (in mg.kg^{-1}) of cerium, yttrium, and gallium by the quantities of iron, copper, tin, and lead. A higher SI value indicates more favorable extraction conditions.

$$SI = \frac{cerium + yttrium + gallium}{copper + iron + tin + lead} \qquad \text{Equation 2}$$

3.2.5 Analytical procedures for determining REE concentration

The determination of REEs concentration were carried out by the Laboratório de Espectrometria Atômica (LEA/LabPetro). The analysis of rare earth elements, gallium, silver, and gold in the solution after leaching was performed using Inductively Coupled Plasma Mass Spectrometry (ICP - MS) (Nexlon 300D; brand Perkin Elmer). Other metals were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) (Optima 7000-DV; brand Perkin Elmer). Table 15 and Source: LEA/LabPetro.

Table 16 show the parameters used for ICP-MS and ICP OES, respectively.

Table 15 – Parameters used in the quantitative analysis of metals leached by ICP OES.

Nebulization chamber	Cyclonic
Nebulizer	Concentric
Radio Frequency Power	1300 W
Plasma gas flow	15 L min^{-1}
Nebulization gas flow	0,8 L min^{-1}
Auxiliary gas flow	0,2 L min^{-1}
Sample aspiration rate	1,5 mL min^{-1}
Torch configuration	Pb - 220,353 nm axial, Cu - 327,393 nm axial, Sn – 189,927 nm axial, Fe – 238,204 nm radial.

Source: LEA/LabPetro.

Table 16 - Parameters used in the quantitative analysis of metals leached by ICP-MS.

Nebulization chamber	Baffled cyclonic
Nebulizer	Concentric Seaspray
Radio Frequency Power	1350 W
Plasma gas flow	16 L min^{-1}
Nebulization gas flow	1,2 L min^{-1}

Auxiliary gas flow	1,1 L min^{-1}
Sample aspiration rate	1,5 mL min^{-1}
Torch	Quartz
Cones	Nickel
Isotopes	^{107}Ag, ^{197}Au, ^{140}Ce, ^{69}Ga*, ^{89}Y, ^{103}Rh (Internal Standard)

Source: LEA/LabPetro.

3.3 RESULTS AND DISCUSSION

This section presents the metal extraction results using each leaching agent and the analysis of the optimal condition for the extraction of rare earth elements. The combination of sulfuric acid and hydrogen peroxide proved to be the most efficient leaching agent for extracting rare earth elements from end-of-life LED lamps.

Yttrium and cerium are present in the $Ce:Y_3Al_5O_{12}$ structure and the oxidizing effect of the hydrogen peroxide enabled a better extraction than the use of isolated acids. The optimal condition to extract cerium, yttrium, and gallium was applying sulfuric acid 2.5 $mol.L^{-1}$ and 10% of hydrogen peroxide at 55°C at a solid-liquid ratio of 100 $g.L^{-1}$. At these conditions, 78.82% of cerium and 41.19% of yttrium were extracted after 120 minutes, and 157.93 $mg.kg^{-1}$ of gallium after 180 minutes. Gallium was not identified in the characterization of the residue, probably due to the focus of the characterization being REE. Thus, the results were expressed in absolute values and not in extraction percentage.

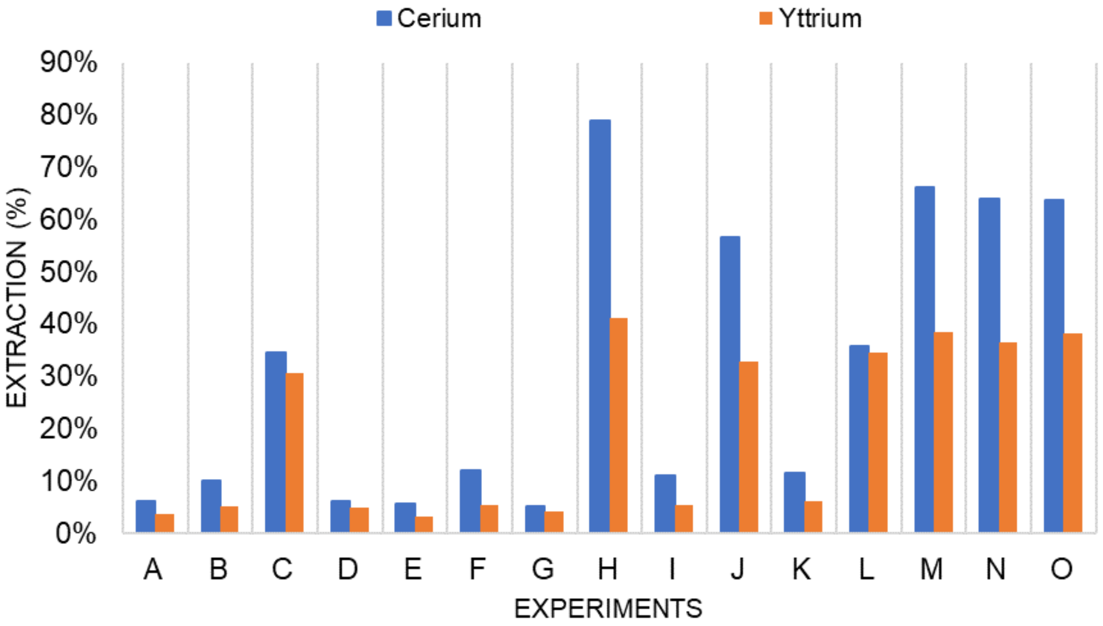
Sulfuric acid had lower extractions compared to nitric acid due to its lower oxidizing power. This also explains why the best leaching conditions to extract REE using sulfuric acid were in higher temperatures, as an increase in the temperature can improve the oxidizing power of the acid (Vogel, 1981). Additionally, this behavior shows that a highly oxidizing environment is necessary to leach REE from more complex structures, such as yttrium aluminate garnet (Choi, Ilyas e Kim, 2022; Song *et al.*, 2017). Thus, it is reasonable that the using of hydrogen peroxide extracted higher amounts of REE, as it has a higher oxidizing power compared to nitric acid.

The kinetics of the extraction can differ with the change in leaching agent, for instance, Innocenzi et al. (2017) show that for the recovery of yttrium from fluorescent lamps, the leaching process with sulfuric acid was controlled by the chemical regime, and with the addition of hydrogen peroxide the reaction followed the kinetic model controlled by diffusion through the product layer. This difference in kinetics can also account for the lower extraction using sulfuric acid when compared to the reaction using the combination of sulfuric acid and hydrogen peroxide in the present research, with the addition of hydrogen peroxide reducing the activation energy.

Thus, one of the factors influencing the extraction of REE from fluorescent powders is the crystal structures of the phosphorus, which generally varies from borate, silicate, phosphate, and aluminate systems (Hua *et al.*, 2019), the latter being the case in the present research. As the crystal structure varies, the acid resistance also changes, for instance, rare earth oxides are more easily dissolved than REE phosphates (Ippolito *et al.*, 2017).

The extraction behavior throughout the experiments was very similar for yttrium and cerium due to being present in the same structure. For the extraction using sulfuric acid and hydrogen peroxide, this similarity can be seen in Figure 4. Tunsu et al. (2016) observed a distinct behavior among these extractions justified by the different chemical forms these elements were in the fluorescent lamp waste. It is worth noting that, in other waste streams, yttrium is more present as less complex oxides, unlike cerium, which is generally doped into aluminates, for example, in green phosphorus. Congruent to the observed in the present research, Innocenzi et al. (2017) observed a similar behavior of europium and yttrium extraction as they were both in the red phosphorus structure.

Figure 4 - Comparison of cerium and yttrium extraction throughout the experiments after 120 minutes using sulfuric acid and hydrogen peroxide.



Source: Author

The behavior seen in Figure 4 indicates that cerium and yttrium are in similar chemical forms in the residue. As shown by Cenci et al. (2020a) characterization, and mentioned above, cerium and yttrium are inserted as $Ce:Y_3Al_5O_{12}$ (yellow phosphorus) in the LED chips.

All the acids tested extracted less yttrium than cerium despite the similar behavior throughout the experiments. This differs from other residues that contain yttrium as less complex oxides, such as red phosphorus, and cerium dopped into more complex structures, such as green phosphorus. A possible explanation for this behavior is that, within the cerium-doped yttrium garnet structure, cerium is a larger ion than yttrium, and it is, therefore, more difficult for it to fit into the YAG (yttrium aluminate garnet) crystal structure (Singh *et al.*, 2017).

Additionally, the chains yttrium bonded to aluminum oxides (- Y- AlO_4 - Y- AlO_4 -) are particularly compact in the YAG structure (Muñoz-García; Seijo, 2011). Moreover, cerium has a higher oxidation state than yttrium, which makes it more likely to be attracted to the negatively charged oxygen ions, weakening the bond between cerium and the aluminum ions in the YAG crystal structure (Kosyanov et al., 2021; Muñoz-

García; Seijo, 2011). It is worth mentioning that these characteristics vary with the percentage of cerium present in the structure and the form of the Ce:YAG production (Singh *et al.*, 2017).

It is worth mentioning that the mechanical treatment of the samples used transformed the residue into powder. The phosphorus powder might have been fully released from the encapsulant in this configuration; nevertheless, an evaluation of the impact of sample size distribution was not conducted. Therefore, it is not possible to state whether the distribution of REE in the residue (inside or outside the encapsulant) and how this distribution would distribute the leaching results.

Another possibility to justify the lower extraction is the formation of silica gel, presented as a drawback of using acid leaching of materials that have silicon in the composition (Botelho Junior; Espinosa; Tenório, 2021b; Voßenkaul et al., 2017).

De Oliveira (2022) observed this formation when extracting yttrium from LED lamps, stating that higher temperatures contributed to reducing this formation. Botelho Junior, Espinosa, and Tenório (2021b) point out that adding hydrogen peroxide reduces silica gel formation, which is a possibility as to why the combination of hydrogen peroxide and sulfuric acid had higher extractions.

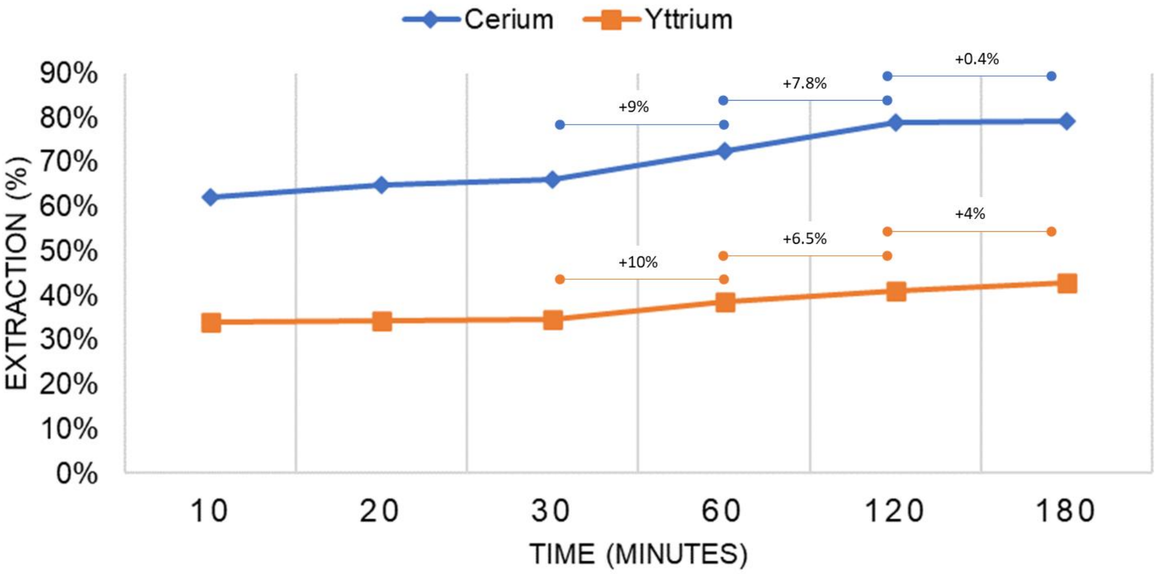
The order of most suitable leaching agents for the other metals accessed differs from the REE order. For iron, copper, lead, and tin leaching, nitric acid had better extraction results, followed by the combination of sulfuric acid and hydrogen peroxide and then sulfuric acid alone. This might be due to the higher spontaneity of the reactions of these metals with nitric acid. With nitric acid being consumed by these reactions (Botelho Junior; Espinosa; Tenório, 2021a; Ferdowsi; Yoozbashizadeh, 2017), another possible explanation for the low REE extraction would be that the remaining acid was not strong enough to leach cerium and yttrium from the yttrium aluminate garnet.

The leaching results also depend on the presence of other ions in the solution (Qian *et al.*, 2014), for instance, the presence of iron in the residue influences the extraction of copper, as shown by Vogel (1981).

The optimal leaching time for cerium and yttrium was established as 120 minutes. The behavior in time of cerium and yttrium extraction in the experiment with higher extraction is shown in Figure 5.

The determination considered the differences in cerium and yttrium extraction between 120 and 180 minutes and also examined the amount of base metals extracted at these times. As detailed before, the extraction of cerium and yttrium stabilized after 120 minutes, and beyond that, the extraction of copper and iron increased with the addition of an extra hour (Cu: from 12.5 to 25.45 mg.kg^{-1}; Fe: 48591 to 59820 mg.kg^{-1}) which it is not favorable for the refining stages.

Figure 5 - Behavior throughout time of cerium and yttrium extractions at the experiment with higher extraction results using sulfuric acid and hydrogen peroxide.



Source: Author

The detailed influence of each variable in these elements extraction for each leaching agent is explored in the following topics.

3.3.1 Cerium

The results obtained for cerium extraction for each leaching agent are presented in Table 17, as well as the most favorable leaching time.

Table 17 - Extraction results for cerium in mg.kg^{-1} and %.

Experiments	**HNO_3**		**H_2SO_4**		**$H_2SO_4 + H_2O_2$**	
	120 minutes		120 minutes		120 minutes	
A	0.891	5.47%	0.647	3.97%	0.998	6.13%
B	1.060	6.51%	1.720	10.56%	1.623	9.96%
C	1.356	8.33%	ND	ND	5.618	34.49%
D	2.283	14.01%	0.780	4.79%	1.008	6.19%
E	0.890	5.46%	0.851	5.22%	0.924	5.67%
F	2.051	12.59%	1.995	12.24%	1.957	12.01%
G	1.458	8.95%	0.388	2.38%	0.854	5.24%
H	1.434	8.81%	ND	ND	12.839	78.82%
I	4.176	25.64%	ND	ND	1.813	11.13%

Experiments	**HNO_3**		**H_2SO_4**		**$H_2SO_4 + H_2O_2$**	
	120 minutes		120 minutes		120 minutes	
J	1.518	9.32%	0.919	5.64%	9.223	56.61%
K	0.823	5.05%	0.000	0.00%	1.864	11.44%
L	2.423	14.87%	0.446	2.74%	5.846	35.89%
Central Point (M, N, O)	1.186 ±0.25	11.27±2%	0.346±0.599	2,12±4%	10.527±0,207	64.62±1%

ND= not detected
Source: Author

78.82% of cerium was extracted in experiment H using sulfuric acid and hydrogen peroxide. As seen in Table 17, nitric acid and sulfuric acid had low extractions, not having significant differences between the results. To ensure the success of the hydrometallurgical process, the complete dissolution of the REE is essential, and it strongly depends on the crystal structures of the phosphors (Hua *et al.*, 2019).

The results indicate resistance of the cerium-containing material to dissolution in an acidic environment, requiring a more oxidizing media to leach due to the aluminate structure in which cerium is inserted (Choi; Ilyas; Kim, 2022).

Comparing the leaching conditions among the experiments that resulted in the higher extractions using sulfuric acid (55°C, 2.5 mol.L^{-1} and 25 g.L^{-1}) and sulfuric acid with hydrogen peroxide (55°C, 2.5 mol.L^{-1} and 100 g.L^{-1}) it is possible to note that the temperature and the acid concentration were the same, however, the addition of hydrogen peroxide enabled the higher extraction to be at the higher level of solid-liquid ratio (100 g.L^{-1}).

Moreover, the optimal result when applying sulfuric acid and hydrogen peroxide was 84% higher than when using only sulfuric acid. As said before, this is likely due to the oxidizing medium provided by the addition of hydrogen peroxide enabling the removal of cerium ions from the cerium-doped yttrium aluminum garnet structure.

Nitric Acid

Nitric acid is not the most common inorganic acid adopted to extract cerium from WEEE, as reported by Pimassoni et al. (2023). Nevertheless, it was tested due to its application in mining operations and for industrial and mining residues (Marra; Cesaro; Belgiorno, 2019). The results showed that the maximum cerium extraction from PCB and electronic components from LED lamps was 25,64%. This lower extraction can be related, as stated before, to the aluminate garnet structure, the formation of silica gel, and the acid consumption on the leaching of base metals such as copper and iron.

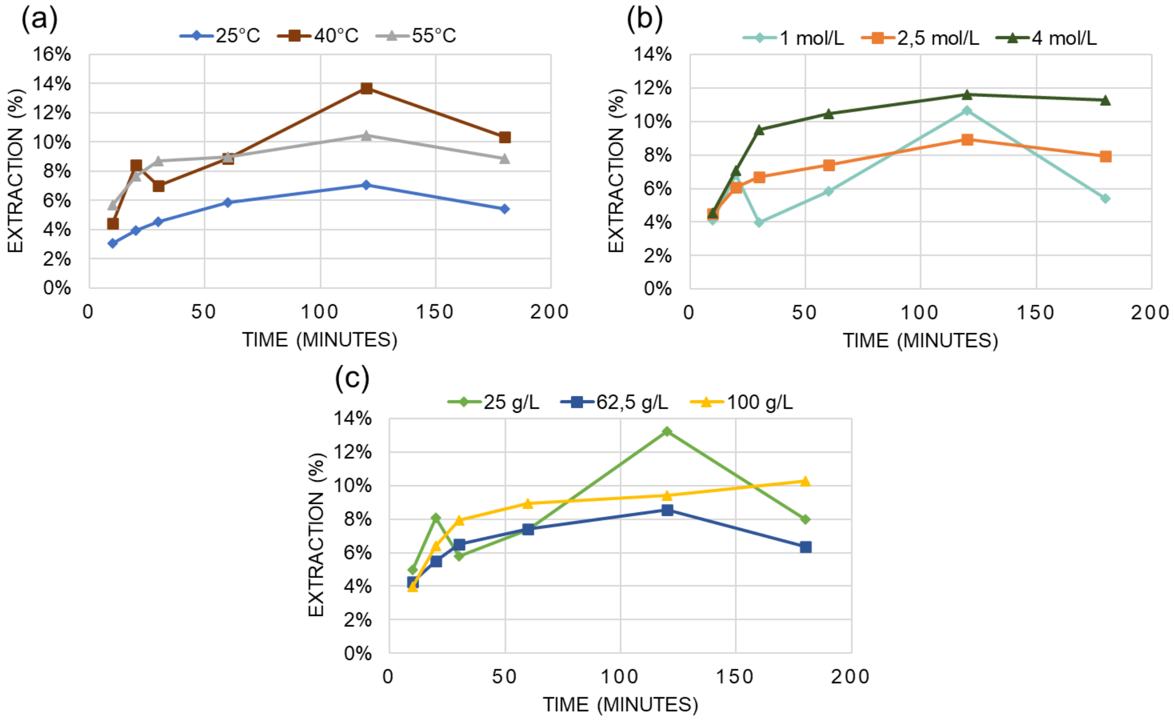
Despite being able to extract cerium using nitric acid, the range tested for the variables did not reach satisfactory results compared to other residues in the literature. Mining residues have less variety of metals influencing the extraction, suggesting that this discrepancy in the extraction results is due to the influence of the composition of the starting material.

Still, the material containing the REE in mining differs from the fluorescent materials present in LED lamps. Even in waste from mining industries, the acid-leaching extraction would probably be lower if the structure containing cerium is acid-resistant, such as perovskite (Deng *et al.*, 2019).

Additionally, nitric acid has a high affinity to copper and iron, and these elements were highly extracted using this acid (Vogel, 1981). As the structure containing cerium is less susceptible to acid attack (Jowitt et al., 2018; Van Loy; Binnemans; Van Gerven, 2017), a possible explanation for the lower extraction is that the acid consumed by the leaching of the contaminant metals such as copper, iron, lead and tin and the remaining acid available were insufficient to leach the cerium from the YAG structure (Botelho Junior; Espinosa; Tenório, 2021a).

In most experiments, including the higher extraction, 120 minutes was the optimal leaching time. The temporal behavior can be analyzed through the mean values at each time. Figure 6 shows the comparison of average results at each level of temperature (Figure 6(a)), acid concentration (Figure 6(b)), and solid-liquid ratio (Figure 6(c)) over time. As described before, the Figure was assembled with the mean extraction values, thus, no parameter is fixated at a certain value in this analysis.

Figure 6 - Comparison of average cerium extraction (%) at each level of (a) temperature, (b) acid concentration and (c) solid-liquid ratio over time, using nitric acid.



Source: Author

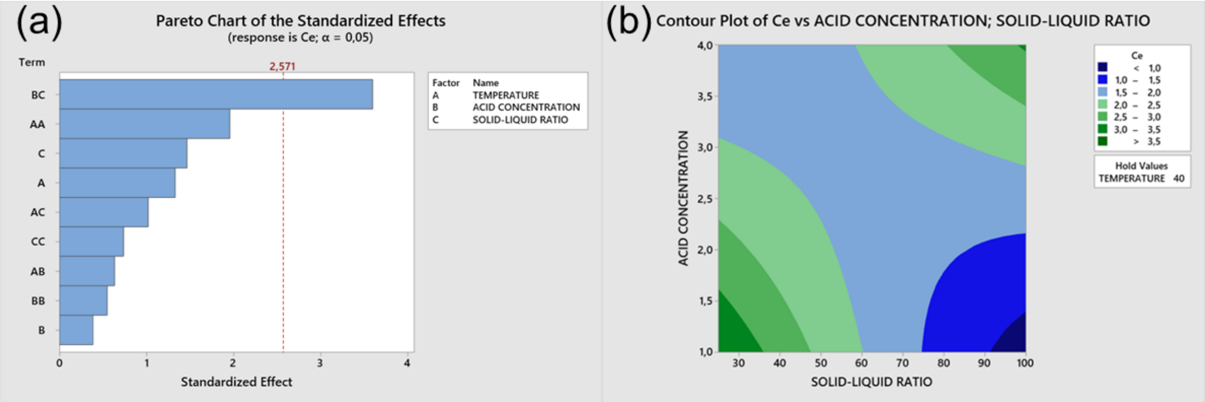
As can be seen in Figure 6, the increase in extraction is more pronounced in the early stages of the extraction in almost all the mean results curves. A probable explanation is the leaching kinetics of cerium. Ferdowsi and Yoozbashizadeh (2017) show that cerium extraction became slower in time, with two mechanisms being limitans in individual extraction stages. This change was explained by the authors as a result of the consumption of acid and decreasing the acid concentration in the solution.

An extraction decrease occurred after 20 minutes at the mean extraction values of 40°C (Figure 6(a)), 1 mol.L^{-1} (Figure 6(b)), and 25 g.L^{-1} (Figure 6(c)), the variation in pH or the reaction potential could account for the precipitation of cerium compounds (Botelho Junior, Espinosa e Tenório, 2021a; Bouchaud *et al.*, 2012). The origin of this variation is unclear as the composition of the leach liquor is complex, and many metal ions can participate in diverse redox interactions, affecting the state of oxidation of cerium. Additionally, the assessment of pH and Eh would have been necessary to corroborate this hypothesis. Thus, compared to the other curves, the increase was more accentuated until 120 minutes, indicating a different kinetic behavior.

Additionally, the formation of silica gel could have trapped some of the cerium extracted, causing a reduction of cerium present in the solution (Botelho Junior; Espinosa; Tenório, 2021b; Oliveira, 2022; Voßenkaul et al., 2017). The fact that this behavior happened at lower temperatures supports this possibility in the higher extraction experiment, and the fact that it happened at specific times could be related to the concentration of silicon in the leach solution. It would be necessary to further investigate the composition of the solid portion of the leaching processes to confirm this hypothesis.

The main effects had a limited impact on the response, as only minor differences in extractions were discernible across each level. To assess the interaction factors and the statistical significance of each effect, Figure 7 depicts the statistical analysis of the results, showing the Pareto chat of standardized effects (Figure 7(a)) and the contour plot (Figure 7(b)).

Figure 7 - (a)Pareto chart of standardized effects for cerium (HNO3); (b) Contour plot for cerium extraction using nitric acid with the temperature fixed at 40°C.



Source: Author

In the studied intervals, the higher and lower extraction percentages were in the two extremes of acid concentration and solid-liquid ratio. The Pareto chart of standardized effects for cerium (Figure 7(a)), shows that only the interaction factor between acid concentration and solid-liquid ratio was statistically significant for the response.

Thus, the relation between the response variable and acid concentration depends on the solid-liquid ratio level. Given the significance of the interaction factor, by combining a high concentration with a high solid-liquid ratio, the extraction will be increased. The same will happen with the opposed conditions. This interaction was also observed by Ferdowsi and Yoozbashizadeh (2017) when leaching cerium from apatite minerals.

The contour plot (Figure 7(b)) illustrates this interaction. The temperature was fixated at 40°C as the two higher experimental results were at this value. Higher solid-liquid ratios need to be combined with high acid concentrations, likely due to the need for a sufficient amount of acid to react with the metals.

A similar behavior was observed for the leaching of REE from NiMH batteries using sulfuric acid. The increase in the solid-liquid ratio improves the extraction as the acid concentration rises (Ahn *et al.*, 2020). As observed in the present research, Hassankhani-Majd and Anbia (2021) did not observe the influence of the temperature when assessing the leaching of phosphorus slag and asymmetric-capacitance nickel-metal hydride power batteries.

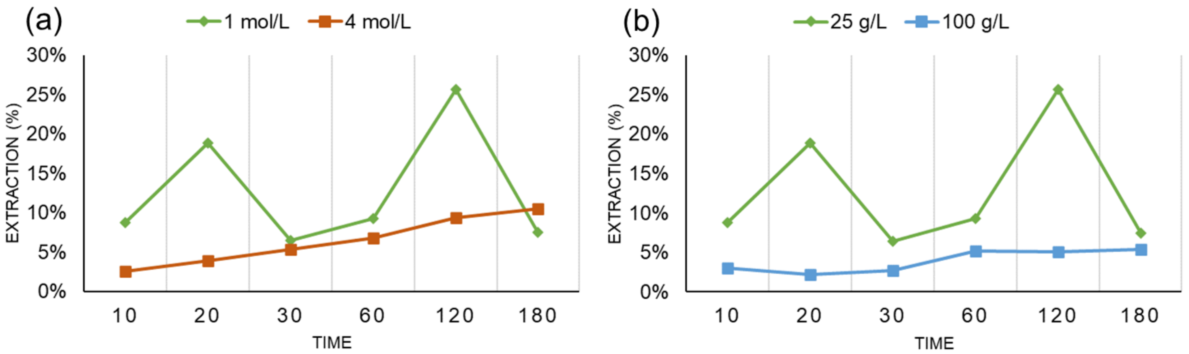
Soukeur et al. (2021) suggest a beneficial impact of raising the acid concentration, a phenomenon not observed within the outcomes attained in this study. Nevertheless, Deng et al. (2019) did not observe the acid concentration effect in the results. It is crucial to state that most studies did not assess the influence of the variables through statistical analysis, making unvaried observations. This type of study makes it difficult to observe the interaction factors and how they impact the response.

Analyzing the behavior of the experiment that resulted in the highest extraction can help determine changes needed for future investigations of cerium extractions from aluminate structures.

Experiment I behaved differently than the ones changing only the acid concentration and the solid-liquid ratio (

Figure 8). As stated before, the variation in the reaction’s pH and the electronic interaction with other metals in ionic form could have led to this distinct behavior. Another possibility was the formation of silica gel compounds, as mentioned previously. Despite having points with distinctive results, an overall difference between the levels cannot be affirmed.

Figure 8 - Effect of (a) the acid concentration at 40°C and 25 g.L^{-1} and (b) solid-liquid ratio at 40°C and 1 mol.L^{-1} on cerium extraction at experiment I (40°C, 1 mol.L^{-1}, 25 g.L^{-1}), using nitric acid.



Source: Author

Nguyen et al. (2018) achieved results similar to the maximum extraction obtained in the present study, extracting 25% of cerium from residues of fluid catalytic cracking catalysts (FCCCs). In contrast to experiment I, the Authors employed more aggressive conditions, with a concentration of 2 mol.L^{-1} at 80°C for a one-hour reaction. Besides needing half the time to reach 25%, acid concentration and temperature were twice the necessary to achieve this result for PCBs and electronic components from LED lamps. The composition of the FCCCs is closely related to the LED lamps as it has a high concentration of aluminum and the presence of iron. The Authors do not elucidate why the low extraction of cerium occurred.

Soukeur et al. (2021) achieved 60% of cerium extraction from phosphate mining industry waste using nitric acid at a concentration of 3 mol.L^{-1}, 25°C and solid-liquid ratio of 80 g.L^{-1} for 3 hours, reaching 100% after 24 hours of reaction. Even using concentrations and solid-liquid ratios lower than the most extreme conditions of these factors in the present research, the Authors achieved an extraction over twice as high. The difference in residue composition could account for this discrepancy in extraction results. The phosphate mining industry waste is mainly composed of carbonate-fluorapatite, with the main composition being calcium, phosphorus, oxygen, and fluorine (Soukeur *et al.*, 2021). Thus, unlike the LED residue used in the present research, the samples did not contain possible competing metals like copper, iron, and lead.

Also evaluating a residue matrix containing fewer competing metals, Choi, Ilyas, and Kim (2022) reported that cerium was not extracted in quantifiable amounts from fluorescent lamps using nitric acid (0.5 and 2 mol.L^{-1}) at 55°C and one-hour duration. This residue also varies from the composition of the LED lamp waste, with a higher percentage of REE and the major contaminants being calcium and aluminum. However, the Author states that the low extraction is due to the refractoriness of the green phosphorus material ($LaPO_4$:Ce^{3+},Tb^{3+} and (Ce, Tb)$MgAl_{11}O_{19}$.

Similar to the LED lamp residue used in this research, it is worth mentioning that the residue studied by Choi, Ilyas, and Kim (2022) has cerium as an aluminate compound. These results might indicate that the form in which cerium is present in the residue has a higher effect on the extraction results than the competing metals of the overall residue composition.

Sulfuric Acid

Sulfuric acid had the lowest extraction results among the three leaching agents. These outcomes were unexpected, considering this inorganic acid has been consistently utilized for cerium leaching from other WEEE, as demonstrated by Pimassoni et al. (2023). A possible reason for this behavior is the formation of insoluble components, as mentioned by Ahn et al. (2020).

As the initial matrix changed, the extraction differed from the literature. Therefore, the REE form and the contaminants in the initial powder seem to influence the extraction. As stated before, cerium is present within the structure of the yttrium aluminate garnet, which has some resistance to acid attack. Thus, as few researchers target cerium extraction from LED lamps, the range studied was selected based on other residues. The difference in the extraction results reiterates the need to investigate isolated residues before integrating them into recycling processes.

A leaching time of 120 minutes resulted in the higher extraction in most experiments, including the higher leaching achieved, 12.24% (experiment F – 55°C, 2.5 $mol.L^{-1}$, and 25 $g.L^{-1}$). The lower extraction obtained can also be related to the lower oxidizing power sulfuric acid has. As mentioned before, the leaching of Ce:YAG seems to require a more oxidizing environment. The behavior over time can be observed in

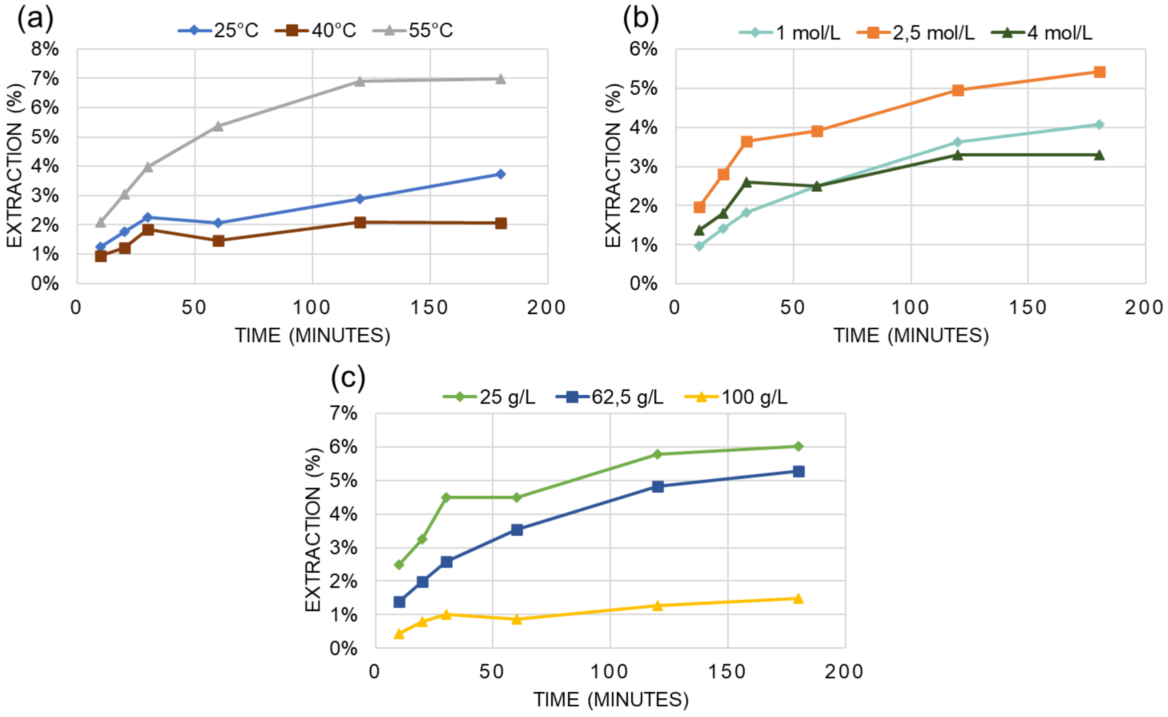
Figure 9, which shows the comparison of average results at each level of temperature (

Figure 9(a)), acid concentration (

Figure 9(b)), and solid-liquid ratio (

Figure 9(c)).

Figure 9 - Comparison of average cerium extraction at each level of (a) temperature, (b) acid concentration and (c) solid-liquid ratio over time, using sulfuric acid.



Source: Author

The behavior was similar despite the level of the variables, indicating that none of the variables influenced the reaction time. The increase in extraction occurs more significantly at the beginning of the reaction. At 55 and 40°C, the extraction reached a plateau after 120 minutes. This behavior indicates that, similarly to nitric acid, the kinetics of the beginning of the extraction differs from the rest of the time (Takano, Asano e Goto, 2022).

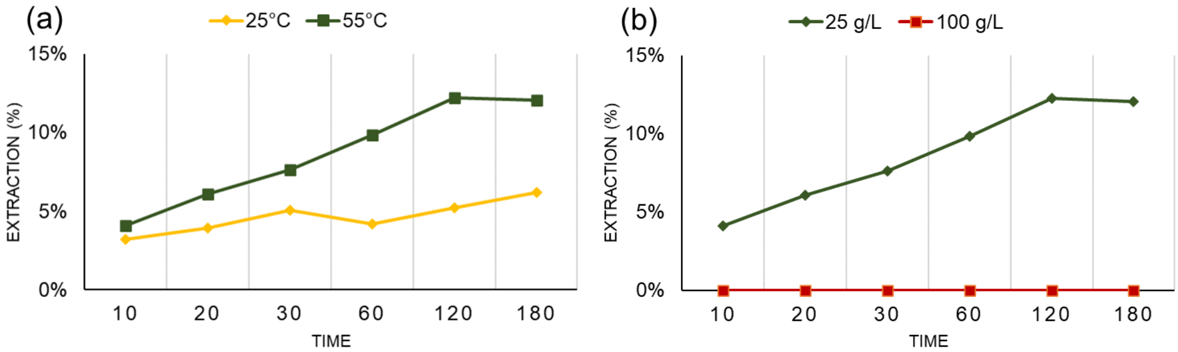
As described before, the molecule in which cerium is inserted affects the extraction, with oxides more susceptible to acid attack. Similar to the observed in the present research, Botelho Junior, Espinosa, and Tenório (2021) reached only 10% of cerium extraction from fluorescent lamps at 35°C using 2 mol.L^{-1}, stating that the presence of cerium as phosphates impacted the recovery.

Even though the difference between the mean values appears significant for temperature and solid-liquid ratio, analyzing the statistical significance of the variables, none of the factors had, in the evaluated range, a statistically significant effect on the response. This result contradicts the expected, once these factors significantly affected the extraction when used for other residues (Ahn *et al.*, 2020; Ciro *et al.*, 2019; Song *et al.*, 2017; Zhang *et al.*, 2019).

Takano, Asano, and Goto (2022) reported no significant influence of temperature and solid-liquid ratio in the range from 50 to 100 g.L^{-1} n cerium extraction, similar to the observed in the present research. However, the Authors observed adverse effects beyond 150 g.L^{-1}, being closely related to the availability of acid.

Still, it is possible to analyze descriptively the behavior of the experimental results. Figure 10 shows the behavior through time of experiment F compared to experiments that differ only in the temperature (Figure 10(a)) and solid-liquid ratio (Figure 10(b)).

Figure 10 - Effect of (a) the temperature at 2.5 mol.L^{-1} and 25 g.L^{-1} and (b) the solid-liquid ratio 55°C, 2.5 mol.L^{-1} on cerium extraction at experiment F (55°C, 2.5 mol.L^{-1}, 25 g.L^{-1}), using sulfuric acid



Source: Author

It is possible to note that both these variables seem to impact the extraction results in these specific conditions. The extraction process had a positive correlation with the temperature under the conditions returning the higher extraction results (experiment F), as depicted in Figure 10(a), in which 55°C leached over twice as much cerium than 25°C.

This difference could be related to the increase in oxidation and dissociation brought by the increase in temperature (Vogel, 1981). Moreover, as for using nitric acid, the increase in temperature can decrease the formation of silica gel (Botelho Junior, Espinosa e Tenório, 2021b; Oliveira, 2022).

On the contrary, at 2.5 mol.L^{-1} and 100 g.L^{-1}, the results showed a negative effect of the temperature. None of the cerium was extracted at 55°C, contradicting the present in the literature since this condition is at a higher level of solid-liquid ratio, it was expected that a higher temperature would result in higher extractions (Song *et al.*, 2017).

It is possible that at higher solid-liquid ratios the acid was consumed in the dissolution of other metals present in the residue not leaving enough strength to leach cerium, even at higher temperatures (Botelho Junior, Espinosa e Tenório, 2021a).

Moreover, at lower temperatures, the reaction did not reach a plateau, indicating that lower temperatures could demand a longer time to stabilize, possibly due to the lower oxidizing media, lower diffusion, or higher viscosity related to the temperature (Song *et al.*, 2017; Takano, Asano e Goto, 2022).

The solid-liquid ratio negatively affects the extraction, with lower levels resulting in higher extractions, showing that for this leaching agent, without aggressive conditions of temperature and acid concentration, it would not be possible to elevate this parameter at more economically favorable conditions. For instance, at 2.5 mol.L^{-1} and 55°C (Figure 10(b)), 100 g.L^{-1} did not extract cerium, suggesting that, at this concentration and temperature, the solid-liquid ratio cannot be elevated.

However, using slightly milder conditions (2 mol.L^{-1}, 50°C, and 113 g.L^{-1}), Porvali et al. (2020) extracted almost 90% of cerium from NiMH batteries. This difference is most likely related to the difference in residue composition, with NiMH batteries having a less complex matrix, with the main competing metal being nickel and the cerium present mainly as a Co/Ni alloy compound.

The conditions in the experimental plan were established using research done with other residues and were performed as a whole to enable the statistical analysis. Based on the above-mentioned observed conditions, it is coherent that under lower conditions of acid concentration and temperature, at 1 mol.L^{-1} and 40°C, cerium was not extracted in quantifiable amounts regardless of solid-liquid levels, indicating that the solid-liquid factor did not have an effect under these conditions.

Cerium is strongly recovered from NiMH batteries using sulfuric acid as a leaching agent. The cerium final extractions varied from 88% to 100% (Alonso et al., 2015; Lie; Liu, 2021a; Meshram; Pandey; Mankhand, 2016; Porvali et al., 2020; Porvali; Wilson; Lundström, 2018; Takano; Asano; Goto, 2022; Zhang et al., 2019) surpassing the values obtained for LED lamps within the scope of the current research.

For fluorescent lamp waste, the range goes from 77 to 85% of extraction (He *et al.*, 2018; Song *et al.*, 2017; Tunsu *et al.*, 2016). or both residues, the initial matrix was composed of fewer metals, had contaminant metals in lower concentrations, and/or received pre-treatments to make the crystalline structures containing REE more susceptible to acid attack.

Song et al. (2017) extracted 77.3% of cerium present in the waste trichromatic phosphors by applying 2 mol.L^{-1} of sulfuric acid, a reaction time of one hour, 70°C, and 12.5 g L^{-1} of solid-liquid ratio after mechanical activation. Although the acid concentrations were comparable, a reduced solid-liquid ratio, alongside an elevated temperature, could account for the superior extraction. This outcome is attributed to the temperature elevation promoting acid oxidation and concurrently diminishing the reaction's viscosity, as noted by Song et al. (2017). Additionally, the mechanical activation processes increased the vulnerability of the green phosphorus to the acid attack. Without this process, only 25% of cerium was extracted from the aluminate structure.

Using conditions similar to the ones studied in this research (100 g.L^{-1}, 3 mol.L^{-1} sulfuric acid), Sobianowska-Turek (2018) leached 97.7% of cerium present in NiMH waste at a temperature of 25°C.

Also at lower temperatures, Tunsu et al. (2016) extracted 78% of cerium at only 20°C for a longer period. As mentioned above, the extractions at lower temperatures did not reach a plateau, a possibility that the leaching kinetics of cerium are slower for being in a more complex structure than reported by Tunsu et al. (2016). For the LED residue used in the present research, however, the effect of solid-liquid ratio, acid concentration, and time were not enough to compensate for the lower temperature, compared to the literature, not returning satisfactory results.

Previous studies employed elevated temperatures, ranging from 70 to 90°C, as observed by Ahn et al. (2020), He et al. (2018), Meshram, Pandey, and Mankhand (2016), Takano, Asano, and Goto (2022). At the present state, it remains uncertain whether a higher temperature would have enhanced the extractions. Even with results much lower than expected, the optimal leaching condition was consistent with the literature in acid concentration, as the general reported in most studies was 2 mol.L^{-1}, and, in the present research, it was 2.5 mol.L^{-1}.

Sulfuric acid and hydrogen peroxide

It’s reported in studies (Marra; Cesaro; Belgiorno, 2019; Talebi et al., 2018) that the incorporation of hydrogen peroxide increased the cerium extraction due to the intensification of materials “opening” provided by the oxidizing properties this reagent has, with the interaction of oxygen atoms with surface metal cations (Choi; Ilyas; Kim, 2022). So, as expected, the addition of hydrogen peroxide resulted in a final extraction nearly six times higher than the maximum extraction achieved using only sulfuric acid.

The higher extraction of cerium, 79.17%, occurred in experiment H after 180 minutes. At 55°C, 2.5 mol.L^{-1}, and 100 g.L^{-1}, the extraction increased with time, reaching 78.82% at 120 minutes. As the percentage difference between the extraction at 120 and 180 minutes was less than 1%, it was considered that the reaction stabilized after two hours.

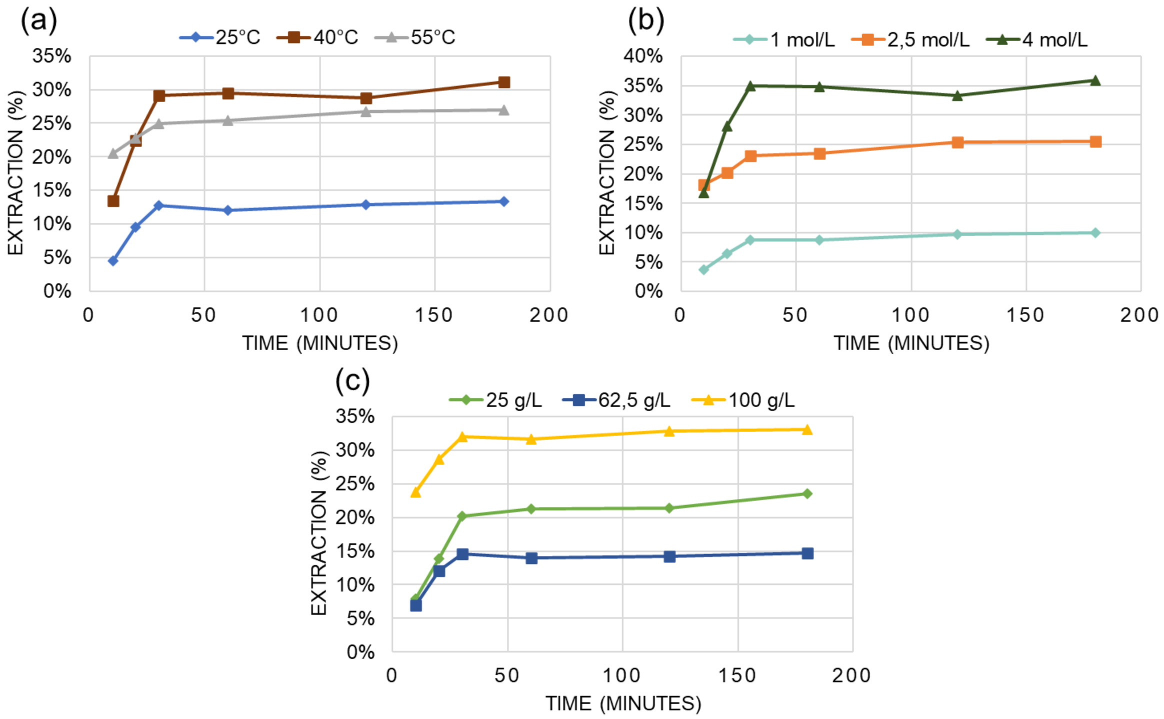
Figure 11 shows the comparison of average results at each level of temperature (

Figure 11(a)), acid concentration (

Figure 11(b)), and solid-liquid ratio (

Figure 11(c)) over time.

Figure 11 - Comparison of average cerium extraction at each level of (a) temperature, (b) acid concentration, and (c) solid-liquid ratio over time, using sulfuric acid and hydrogen peroxide.



Source: Author

The analysis of the mean values at each variable suggests that the stabilization occurred at 30 minutes in most experiments. However, in the leaching experiment with higher results, the extraction at 120 minutes was sixteen percent higher than the one at 30 minutes, not being considered a stabilization. Thus, adding hydrogen peroxide did not reduce the extraction time but elevated the results, as said before, due to the oxidizing power.

The curves demonstrate that none of the variables had a notable influence on time, exhibiting a similar pattern. As for sulfuric acid alone, the increase at the beginning of the extraction is more pronounced (Takano; Asano; Goto, 2022), with a more inclined line. It is possible to note in

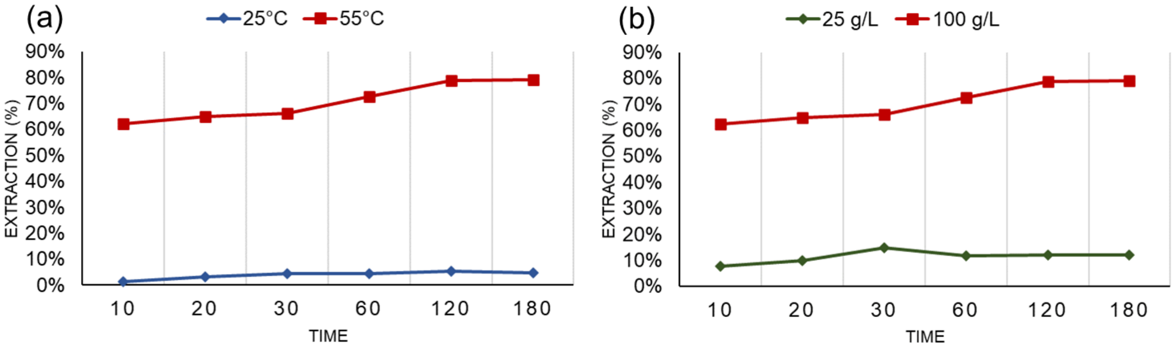
Figure 11(a) hat the average extraction obtained at 40 and 55°C do not differ significantly. Nonetheless, at 25°C, the results were half the ones of the other levels. A possibility is that the increase in the temperature reduces the viscosity and improves the diffusion of the leaching agent in the solution (Song *et al.*, 2017). Moreover, the reduced temperature might lead to a higher silica gel formation, as stated before.

It is interesting to note that the mean values using 4 mol.L^{-1} were higher than 2.5 mol.L^{-1}. However, the central level resulted in the higher extraction achieved in the experimental plan. Nevertheless, the central level led to the highest extraction, likely attributed to the significant increase observed when only combining the central concentration level with the higher levels of the other two variables—a distinction not evident in the mean extraction results.

Similar to what occurred for the extraction using only sulfuric acid, none of the effects evaluated in the proposed range had statistical significance in the response variable. That happened even with the high discrepancy in some experiments once the difference in the mean extraction results in each condition was low and intersected when analyzed with the standard deviation.

To individually analyze the influence on the condition that better extracted cerium, Figure 12 shows the behavior throughout the time of experiment H compared to experiments that differ only in temperature (Figure 12(a)) and solid-liquid ratio (Figure 12(b)).

Figure 12 - Effect of (a)the temperature at 2.5 mol.L^{-1} and 100 g.L^{-1} and (b)the solid-liquid ratio at 55°C and 2.5 mol.L^{-1} on cerium extraction at experiment H (55°C, 2.5 mol.L^{-1}, 100 g.L^{-1}), using sulfuric acid and hydrogen peroxide.



Source: Author

It was possible to note that, at 2.5 mol.L^{-1} and 100 g.L^{-1}, the temperature positively affected cerium extraction (Figure 12(a)), extracting 93% more at 55°C compared to 25°C extraction. As said before, the increase in temperature can increase the diffusion and reduce the viscosity of the leaching agent, being more effective in the acid attack (Song *et al.*, 2017).

Zhang et al. (2019) did not observe this effect of temperature when varying the condition from 60 to 90°C in the extraction of cerium from NiMH batteries using 2 mol.L^{-1} sulfuric acid and 0.4% hydrogen peroxide. The Authors point out that the reason for this effect is that the solubility of the rare earth metals decreases with the temperature, and, to overcome this problem, suggested a stepwise leaching. Considering this effect, raising the extraction temperature would not be advantageous.

Focusing on the solid-liquid ratio, maintaining the concentration at 2.5 mol.L^{-1} and the temperature of 55°C (Figure 12(b)), it is possible to note that the solid-liquid ratio appears to affect the extraction, extracting 84% more at 100 g.L^{-1} if compared to 25 g.L^{-1}. This behavior shows that it might be possible to elevate this parameter even further without reducing the extractions.

Given that the optimal experiment's concentration is at the central level, no other experiment within the experimental plan varied solely in acid concentration. Hence, a direct comparison with experiment H is not feasible. Nonetheless, in most cases, a higher concentration led to increased cerium extraction. Unlike the other variables, and consistently with the literature (Zhang *et al.*, 2019), the acid concentration appeared to influence outcomes in most conditions.

The higher leaching results are comparable to the ones achieved in the literature. Using the same solid-liquid ratio (100 g.L^{-1}) and a 2 mol.L^{-1} acid concentration with 20%v/v of hydrogen peroxide (30%v/v), Marra, Cesaro, and Belgiorno (2019) achieved, after a three-hour leaching, around 89% of cerium from WEEE shredding dust (e-scrap). The composition of the solid matrix resembles the one used in the present research in the presence of high amounts of copper, aluminum, iron, and lead. The difference remains in the form in which the REE is present in the residue, and in the e-scrap, cerium and yttrium are in the form of oxides. This difference is probably the reason that, in milder conditions, similar results were obtained by the Authors.

Comparing the conditions with experiment H, Marra, Cesaro, and Belgiorno (2019) used a lower temperature and acid concentration but a higher proportion of hydrogen peroxide. It remains uncertain whether the percentage of hydrogen peroxide in the leaching agent would have significance within the scope of this research, given that this variable was not assessed.

When comparing the results of Marra, Cesaro, and Belgiorno (2019) with the ones from experiment G (25°C, 100 g.L^{-1}, 2.5 mol.L^{-1}), 5.24% of cerium extracted, it is possible to state that the temperature had more influence when leaching cerium from end-of-life LED lamps then it did on e-scraps leaching, probably due to the resistance of the Ce:YAG.

3.3.2 Yttrium

The results of yttrium extraction and the optimal reaction time for each leaching agent are presented in Table 18. As observed at cerium extraction, the combination of sulfuric acid and hydrogen peroxide stands out as the optimal leaching agent to extract yttrium from PCB and electronic components of LED lamps, reaching 41.19% of yttrium extracted. The optimal conditions were at experiment H (55°C, 2.5 mol.L^{-1} and 100 g.L^{-1}) after 120 minutes.

Hydrogen peroxide addition increased 84% of the extraction of yttrium if compared to the experiment that resulted in the higher extraction using only sulfuric acid. As reported by De Oliveira (2022), these low extractions using nitric and sulfuric acid could be related to the structure of the yttrium aluminate garnet, and the addition of the hydrogen peroxide enables a more oxidative ambient (Marra, Cesaro e Belgiorno, 2019), resulting in better extractions.

Additionally, lower extractions of yttrium from CTR phosphorus using sulfuric acid were attributed to the mass percentage yttrium represents in the residue, with research using more purified residues (with higher percenteges of REE) resulting in higher extractions (Botelho Junior, Espinosa e Tenório, 2021a; Miskufova *et al.*, 2018).

Another possibility for the lower extraction using nitric and sulfuric acid is silica gel formation that encapsulates the extracted metals, as observed by De Oliveira (2022) and in other residues that contain silicon in the composition. Botelho Junior, Espinosa, and Tenório (2021b) point out that adding hydrogen peroxide could reduce this formation, accounting for the higher extraction using the combination of sulfuric acid and hydrogen peroxide.

Table 18 - Extraction results for yttrium in mg.kg^{-1} and %.

Experiments	**HNO_3**		**H_2SO_4**		**H_2SO_4 + H_2O_2**	
	180 minutes		120 minutes		120 minutes	
A	0.5393	2.59%	0.6733	3.24%	0.7793	3.75%
B	0.7101	3.41%	1.3234	6.36%	1.0699	5.14%
C	1.7074	8.21%	0.3311	1.59%	6.3691	30.62%
D	1.8750	9.01%	0.9887	4.75%	1.0005	4.81%
E	1.0454	5.03%	0.6510	3.13%	0.6876	3.31%
F	1.0117	4.86%	1.3682	6.58%	1.1237	5.40%
G	1.1452	5.51%	0.6388	3.07%	0.8563	4.12%
H	1.0221	4.91%	0.8821	4.24%	8.5676	41.19%
I	0.8940	4.30%	0.6790	3.26%	1.1194	5.38%
J	1.5900	7.64%	0.7776	3.74%	6.8295	32.83%
K	0.8467	4.07%	0.7555	3.63%	1.2673	6.09%
L	2.2927	11.02%	0.7202	3.46%	7.1755	34.50%
Central Point (M, N, O)	1.7418±0.22	8.37±1%	0.700±0.273	3.37±1%	7.8643±0,215	37.81±1%

Source: Author

Nitric Acid

For the extraction of yttrium using nitric acid, the most favorable leaching time was 180 minutes, as the highest extraction was after this time, and the difference between the obtained in the time before (120 minutes) was higher than 5%. The highest extraction was 11.02% obtained at experiment L (40°C, 4 mol.L^{-1}, and 100 g.L^{-1}). This low extraction is closely related to the dense crystalline structure of the yttrium aluminum garnet.

The recovery results achieved in the present research were similar to those obtained by De Oliveira (2022). The Author showed that, after grinding and without additional pretreatment, less than 20% of yttrium was extracted from LED devices using nitric acid 4 mol.L^{-1} at 45°C. The Author attributes the low extractions to the structure in which the yttrium is inserted.

It is possible to analyze the behavior throughout time for each variable by creating a curve using the mean extraction at each time. Thus,

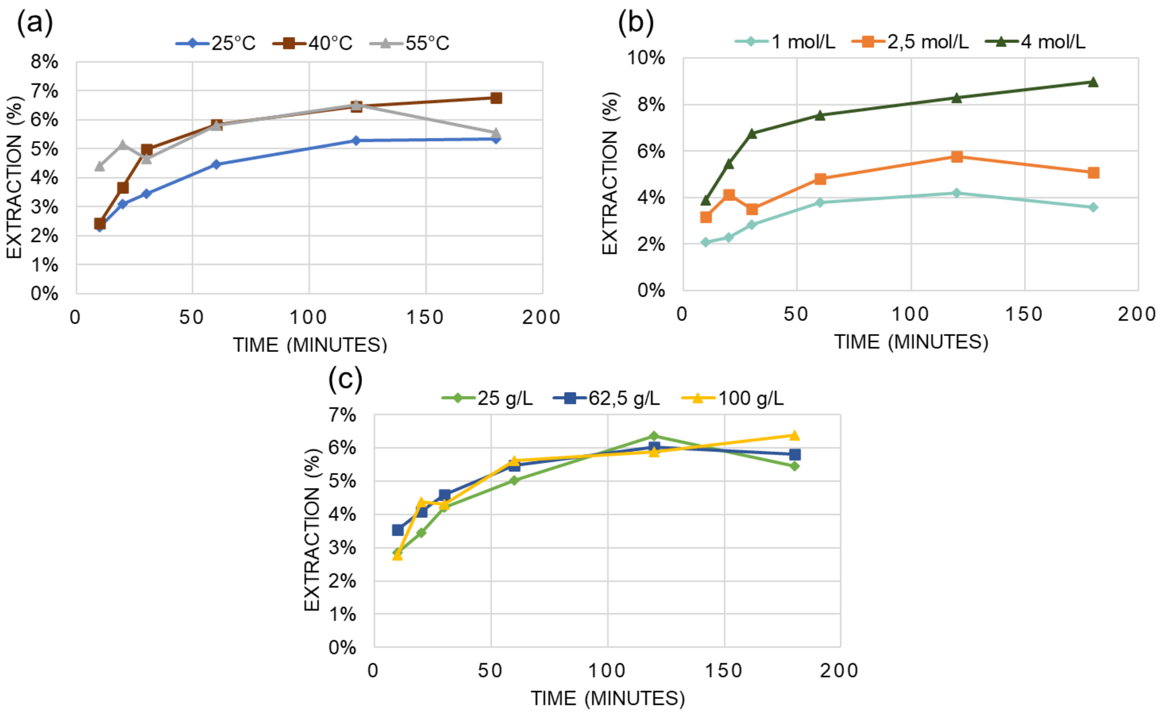
Figure 13 shows the comparison of average results at each level of temperature (

Figure 13(a)), acid concentration (

Figure 13(b)), and solid-liquid ratio (

Figure 13(c)) over time.

Figure 13 - Comparison of average yttrium extraction at each level of (a) temperature, (b) acid concentration, and (c) solid-liquid ratio over time, using nitric acid.



Source: Author

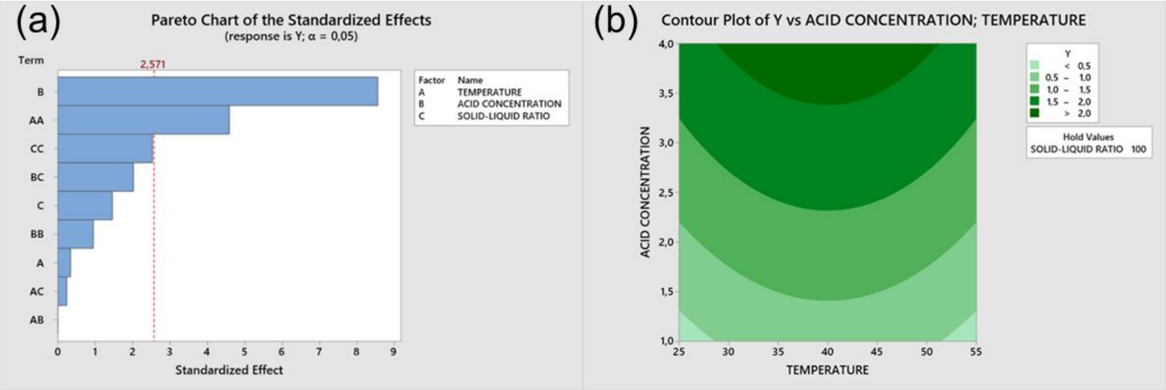
It is worth mentioning that none of the variables impacted the behavior over time, as their curves remained relatively similar. The extraction increases significantly at the first thirty minutes, reaching some stability after 120 minutes. Similarly to cerium extraction, the kinetics could be controlled by two different mechanisms, slowing with time (Ferdowsi; Yoozbashizadeh, 2017).

The analysis of these curves shows that the mean extraction was different when varying the acid concentration and slightly different when changing the temperature. Still, it is possible to see that the temperature influenced more in the early stages of the reaction at 55°C, differing from the other two levels. After 20 minutes, the mean extraction of 55 and 40°C are almost identical. These results could also indicate that the reaction had different controlling mechanisms at different stages (Ferdowsi; Yoozbashizadeh, 2017).

The acid concentration had a pronounced influence on the response variable. Thus, extraction increased with this factor, and the mean result using 4 $mol.L^{-1}$ was 60% higher than 1 $mol.L^{-1}$. A possibility for this behavior is that the higher concentration had more strength to leach yttrium from the YAG structure, compared to the other extraction with this leaching agent. Moreover, another possible explanation would be that the amount of acid remaining after leaching the other metals in the residue was higher at the elevated concentration. A similar behavior was also observed by Lee et al. (2017).

The solid-liquid ratio did not have significant differences between the levels, as seen in Figure 13(c). However, it is worth noting that 100 g.L^{-1} was the level with the higher extraction. That is an advantage once it is economically favorable to use higher solid-liquid ratios. Thus, the statistical analysis of the results is presented in Figure 14.

Figure 14 – (a)Pareto chart of standardized effects for yttrium (HNO_3); (b) Contour plot for yttrium extraction using nitric acid with the solid-liquid ratio fixed at 100 g.L^{-1}.



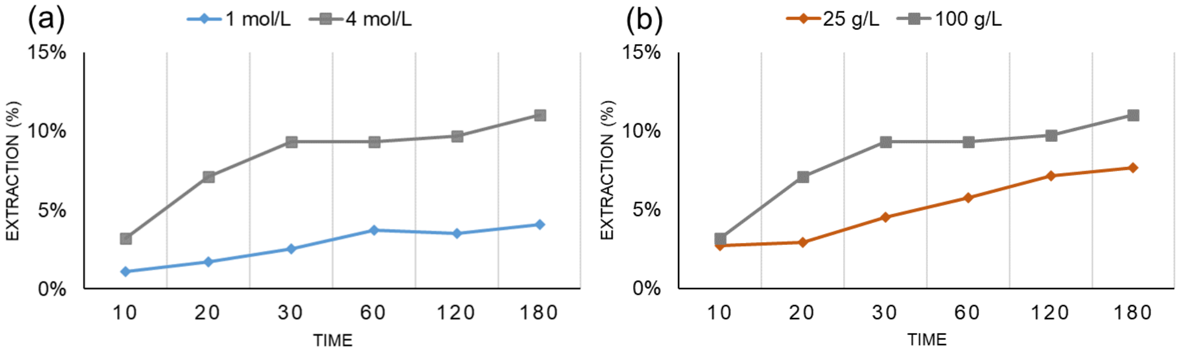
Source: Author

As can be seen in the Pareto chart of the standardized effects (Figure 14(a)), the factor with more significance in the response is the acid concentration, followed by the quadratic effect of the temperature, as expected. Unlike the observed, Tunsu et al. (2016) did not observe an influence of the nitric acid concentration in the extraction of yttrium from fluorescent lamp waste.

The contour blot shown in Figure 14(b) illustrates the optimal conditions and the direction to dislocate the experimental design in future research. The solid-liquid ratio was set at 100 g.L^{-1}, as it was the condition yielding the most favorable outcomes. It is possible to say that higher acid concentrations combined with intermediate temperatures would be the ideal option.

It is worth analyzing the behavior of the leaching experiment with the highest extraction once this could indicate future investigation ranges. Figure 15 shows the behavior through time of experiment L compared to experiments that differ only in the solid-liquid ratio (Figure 15(a)) and acid concentration (Figure 15(b)). As the higher leaching results occurred at the temperature's central level, there were no experiments differing only in this parameter that allowed this comparison for the temperature.

Figure 15 - Effect of (a) the acid concentration at 40°C and 100 g.L^{-1} and (b) the solid-liquid ratio at 40°C and 4 mol.L^{-1} on yttrium extraction at experiment L (40°C, 4 mol.L^{-1}, 100 g.L^{-1}), using nitric acid.



Source: Author

At 40°C and 100 g.L^{-1} (Figure 15(b)), the acid concentration exhibited the most pronounced impact, resulting in the highest leaching among all variations for this particular leaching agent. The increase in the acid concentration might have compensated for the lower temperature and higher solid-liquid ratio, thus, the combination of effects was beneficial to the attack of the YAG structure.

It was possible to see in Figure 15(a) some difference between the results at 25 and 100 g.L^{-1}, despite not having statistical significance within a 95% confidence interval. However, it is not possible to state that, within the standard deviation, these results would be different.

Nitric acid was not the preferred acid for recovering yttrium from WEEE. Nonetheless, the literature presents results of up to 100% of yttrium extracted for other residues.

Tunsu et al. (2016) tested nitric acid along with other acids and achieved around 97% of yttrium from end-of-life fluorescent lamps using from 0.5 to 4 mol.L^{-1} of acid, 100 g.L^{-1} at 20°C. However, the reaction lasted for 168 hours, being unpractical in a large-scale process. Beyond that, the Authors did not observe a difference in extraction between the acids applied.

Also extracting yttrium from end-of-life fluorescent lamps, Choi, Ilyas, and Kim (2022) achieved 84% of extraction by applying 2 mol.L^{-1} of nitric acid at 55°C, for one hour and with a solid-liquid ratio of 50 g.L^{-1}. Pavón et al. (2019) leached 99% of yttrium using a much longer time, 48 hours of reaction using the same 2 mol.L^{-1} acid concentration, a solid-liquid ratio of 100 g.L^{-1}, and a temperature of 20°C. Both reached higher extraction with milder conditions than the ones applied in the present research, probably related to the fact that yttrium is in the form of oxides in the residue used, being more susceptible to acid attack.

Closer to the obtained in the present work, Lee et al. (2017) extracted only 13.68% of yttrium from fluorescent powder residue using 1 mol.L^{-1} of nitric acid at 70°C, 20 g.L^{-1} of solid-liquid ratio and 4 hours of reaction, the Authors did not provide a probable cause for this reduced extraction. Still, this supports the fact that even using similar residues, in this case fluorescent lamps, the final extraction may vary.

Individually analyzing the influence on the condition that better-extracted yttrium and the statistical analysis, it is possible to conclude that the acid concentration played a critical role in the extraction. As expressed above, milder conditions had higher extractions when applied to fluorescent lamps. However, when applied to bauxite and fluorescent powder waste, the extractions were similarly low to those obtained for end-of-life LED lamps.

Sulfuric Acid

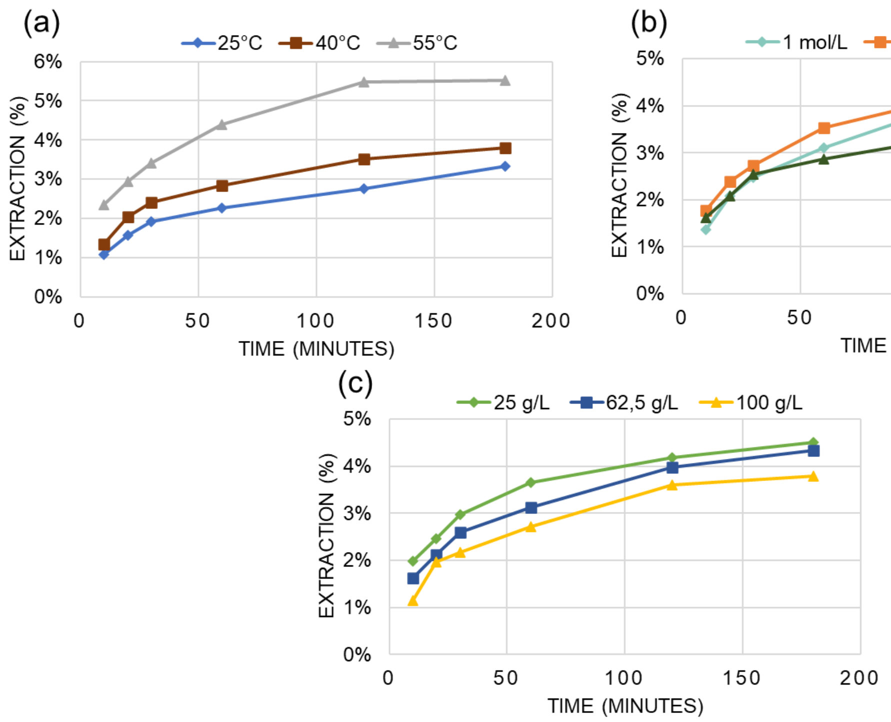
For sulfuric acid, the highest extraction was 6.66%, obtained at 180 minutes in experiment B. When compared to the results obtained at 120 minutes in this same experiment, the difference is less than 5%, and if compared to the result obtained at 120 minutes in experiment F, the difference is close to one percent. Hence, a 120-minute duration at experiment F was determined as the optimal condition for the extraction of yttrium using sulfuric acid.

Leaching results were even lower than the ones with nitric acid, as seen in Table 18. A possible explanation is, as stated before, the lower oxidizing power of sulfuric acid compared to nitric acid (Vogel, 1981). The higher extraction after 120 minutes was 6.58%, at 55°C, 2.5 mol.L^{-1}, and 25 g.L^{-1} (experiment F). The lower one was in experiment 3 (25°C, 4 mol.L^{-1}, and 62.5 g.L^{-1}). The temperature can increase the oxidizing power of the acid, thus, explaining why the higher extractions were in the higher level of temperature.

This result is congruent with the obtained by De Oliveira (2022). The Author reports no yttrium extraction by applying sulfuric acid (2 and 8 mol.L^{-1}) at 45°C to LED devices after calcination, stating that the aluminate structure is the probable cause of this result. Moreover, the form of the REE present in the residue was appointed as the reason for the low extraction of yttrium from fluorescent lamp powder (Botelho Junior; Espinosa; Tenório, 2021). Similarly, lower results were obtained by Innocenzi et al. (2017) that leached around 7% of the yttrium present in fluorescent powder using sulfuric acid 2.5 mol.L^{-1} and 40°C. The authors do not clearly state what caused the lower extraction but highlight that the activation energy for the extraction was higher than the one adding sulfuric acid.

Creating a curve using the mean extraction at each time and each level makes it possible to analyze the behavior throughout time for each variable. Thus, Figure 16 shows the comparison of average results at each level of temperature (Figure 16(a)), acid concentration (Figure 16(b)), and solid-liquid ratio (Figure 16(c)) over time.

Figure 16 - Comparison of average yttrium extraction at each level of (a) temperature, (b) acid concentration, and (c) solid-liquid ratio over time, using sulfuric acid.



Source: Author

None of the variables influenced the behavior, having relatively similar curves. The evolution of the extraction is similar to the one using nitric acid, with the extraction increasing significantly at the first thirty minutes and, at the higher levels, reaching some stability after 120 minutes, as observed by Innocenzi et al. (2017).

It is noteworthy that, across all conditions, higher temperatures resulted in greater extraction, probably due to oxidizing power increase with the temperature. Behavior that can also be seen by analyzing the mean extraction for each temperature level (Figure 16(a)). Lie and Liu (2021b) observed that an increase in temperature improved yttrium extraction from CRT phosphorus powder due to the increase in movement, diffusivity, and mass transfers that occur in higher temperatures.

The effect of acid concentration in the extraction was not noticeable, as seen in Figure 16(b). The difference between the extraction results is lower than 1% in most conditions.

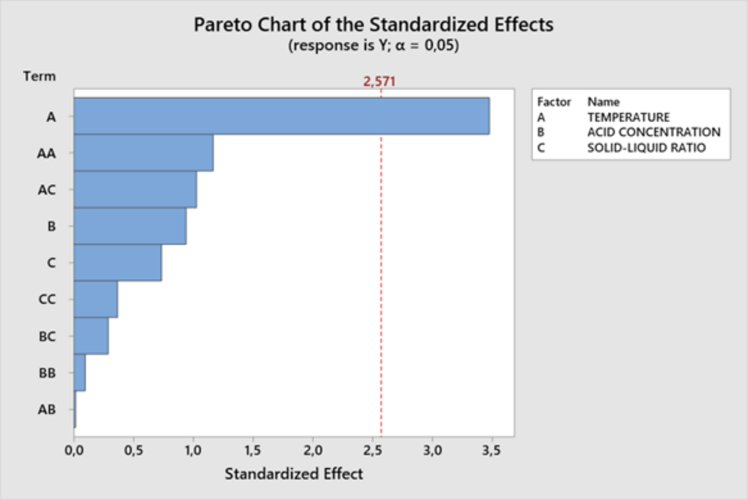
Similarly, Song et al. (2017) observed that increasing the acid concentration from 2 to 4 mol.L^{-1} did not impact the extraction of yttrium from fluorescent lamp waste. For CTR phosphorus waste, on the other hand, Lie and Liu (2021b) found that the increase in acid concentration is beneficial for the extraction.

However, according to Saratale, R. et al. (2020), a high acid concentration may reduce the extraction efficiency due to an insoluble yttrium complex formation ($Y_2(SO_4)_3$). This formation could be a possible explanation for the lower extraction in the present research, as the lower extraction was at the higher concentration tested.

It is possible to note that, as expected based on the literature, a lower solid-liquid ratio returns higher extractions. Nonetheless, the difference is minimal, as seen in Figure 16(c). Even though it weakly influences the extraction, Saratale, R. et al. (2020) highlight that this factor cannot be neglected, as the proportion can affect the interaction between metal and acid in the solution.

All these low differences show a weak influence of these factors in the response, confirmed by the statistical analysis. Figure 17 shows the Pareto chart of the standardized effects of the yttrium extraction using sulfuric acid.

Figure 17 - Pareto chart of standardized effects for yttrium (H_2SO_4)

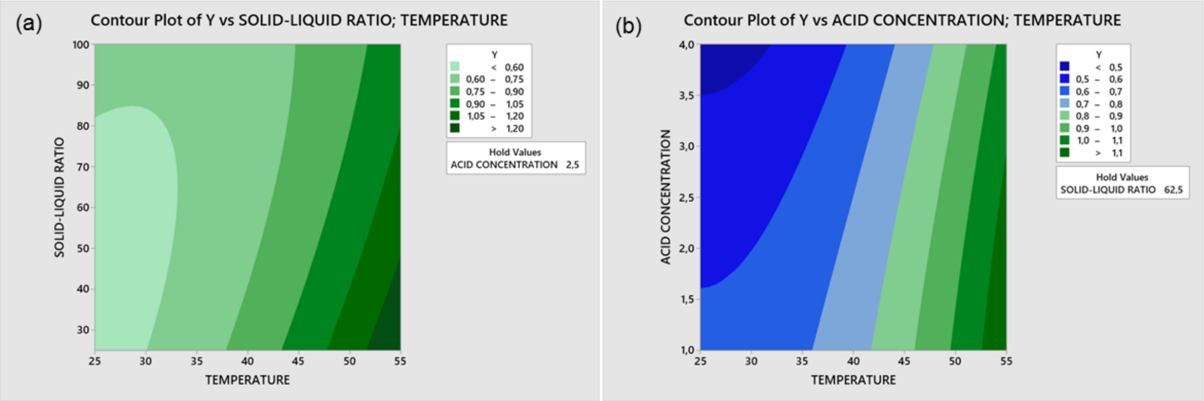


Source: Author

In alignment with the earlier observation, it is evident that only the temperature had a statistically significant influence on the response within the examined range. This influence opposes the observed by De Michelis et al. (2011), who noticed a negative effect of the temperature when extracting yttrium from fluorescent lamps.

Figure 18(a) shows the contour plot at a concentration of 2.5 mol.L^{-1}. The contour plot presented in Figure 18(b) shows the relation between acid concentration and temperature, fixating the solid-liquid ratio at 62.5 g.L^{-1}.

Figure 18 - Contour plot for yttrium extraction using sulfuric acid with (a) the acid concentration fixed at 2.5 mol.L^{-1} (b) solid-liquid ratio fixed at 62.5 g.L^{-1}



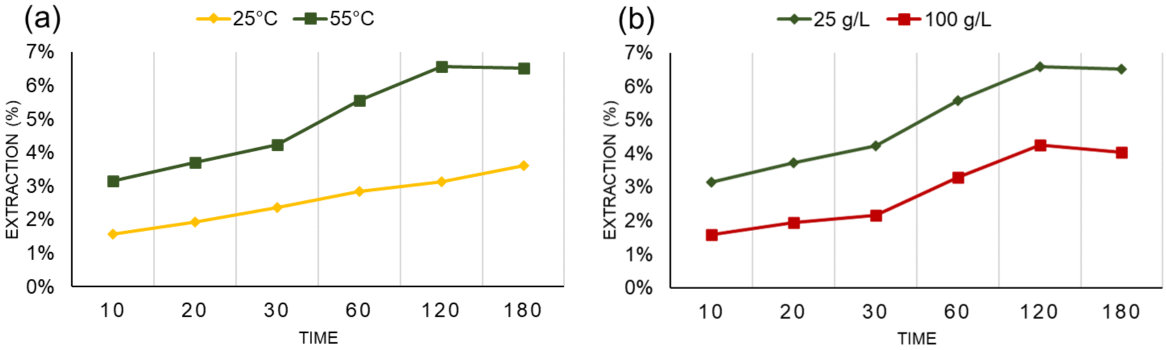
Source: Author

Higher temperatures returned better results, especially if paired with lower solid-liquid ratios (Figure 18(a)). The contour plot also shows that, possibly, in lower solid-liquid ratios, the influence of this factor would be more significant. Dislocating the experimental plan in this direction could be a possibility. However, it would be necessary to evaluate it economically once lower solid-liquid extractions require more acid volume consumption.

It is evident that (Figure 18(b)), as said before, higher temperatures increase the extraction and that the acid concentration has almost no influence on the response. Also, it is possible to note that, at higher temperatures, lower acid concentrations had better results. Dislocating the experimental plan in this direction has attractive operational conditions once milder conditions of acid concentration are both economically and environmentally advantageous.

Figure 19 shows the behavior through time of experiment F compared to experiments that differ only in the temperature (Figure 19(a)) and solid-liquid ratio (Figure 19(b)).

Figure 19 - Effect of (a) the temperature at 2.5 mol.L^{-1} and 25 g.L^{-1} and (b) the solid-liquid ratio at 55°C and 2.5 mol.L^{-1} on yttrium extraction at experiment F (55°C, 2.5 mol.L^{-1}, 25 g.L^{-1}), using sulfuric acid



Source: Author

It is possible to note that, at the leaching experiment that returned higher extraction, the difference in the results at both temperature levels increased over time. After 30 minutes, the reaction at 55°C had a more significant increase than at 25°C. This behavior might occur due to the reaction being controlled by the chemical regime, with higher temperatures being necessary to increase extraction (Innocenzi *et al.*, 2017).

A study of the reaction's kinetic could show the reason for this occurrence. It is also worth noting that at 25°C, there were no signs of stabilization, indicating that, at that temperature, more time would be necessary to attain a plateau. The behavior of the results at both solid-liquid ratio levels was identical in time, and despite not having a statistically significant effect on the response, this variable had an effect that doubled the extraction in experiment F.

The extraction results were lower than expected based on the literature review. Studies with fluorescent lamps reached extractions over 85% using sulfuric acid (Botelho Junior; Espinosa; Tenório, 2021; De Michelis et al., 2011; Song et al., 2017; Tunsu et al., 2016).

The effect of temperature was evident in individually analyzing the most favorable leaching condition and the statistical analysis in the whole range studied. However, Botelho Junior, Espinosa, and Tenório (2021) extracted 95% of yttrium from fluorescent lamps at 45°C, and Porvali et al. (2020) extracted 97% of the yttrium present in the NiMH residue at 50°C. Thus, to develop a process in milder conditions, and based on these previous results, the range of the temperature was determined.

Song et al. (2017) extracted 96.3% of yttrium from fluorescent lamps using sulfuric acid at2 mol.L^{-1} after mechanical activation. The Authors used a higher temperature (70°C) and half the solid-liquid ratio (12.5 g.L^{-1}). When contrasted with the results for the samples without the pretreatment, the extraction of yttrium drops to around 40%, still much higher than obtained for the LED lamp waste. The Authors highlight that the mechanical activation increased the crystal structure disorder, favoring the leaching of REE.

Evaluating the recovery from cathode ray tube (CRT) phosphor, Lie, Ismadji, and Liu (2019) leached 79.6% of yttrium using 2 mol.L^{-1} for 2 hours. The Authors also employed a higher temperature (100°C) and a lower solid-liquid ratio (10 g.L^{-1}) compared to the present research; both factors were identified by the Authors as influential in the response. With similar conditions but assisted by microwave, Lie and Liu (2021b) leached 86.67% in 30 minutes.

Sulfuric acid and hydrogen peroxide

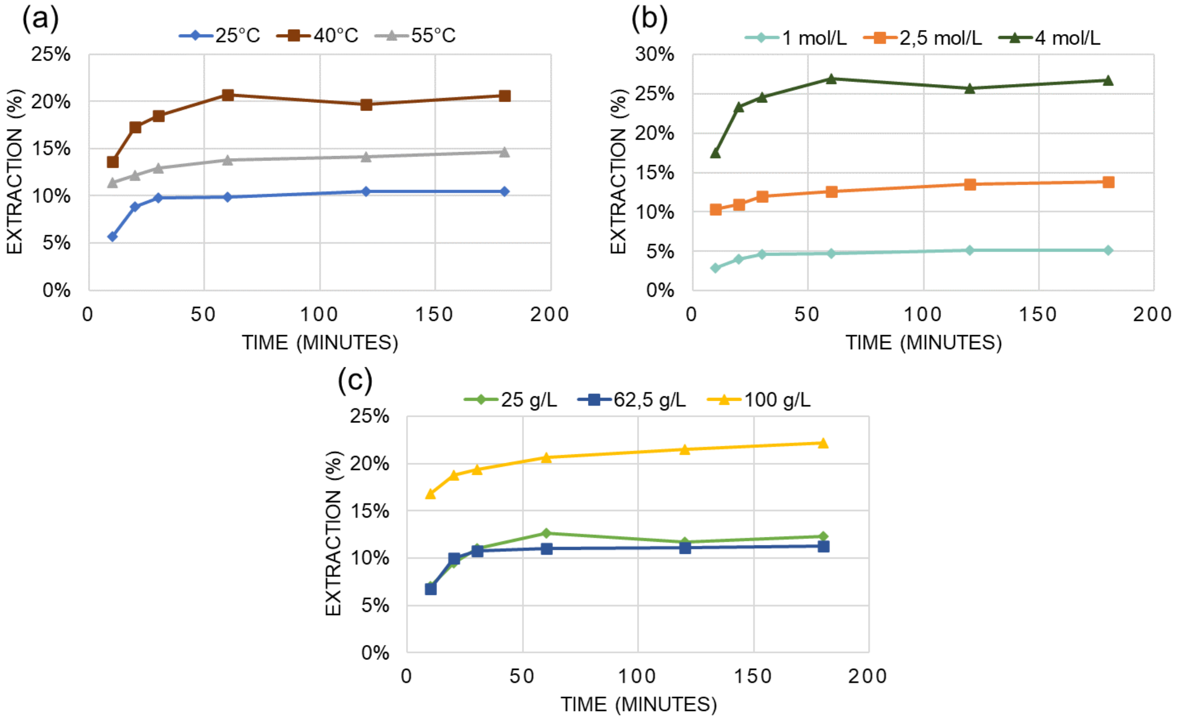
The addition of hydrogen peroxide led to a noteworthy enhancement in yttrium extraction. The enhancement was attributed to the oxidizing power of the hydrogen peroxide, the same as for cerium. In contrast to the outcomes achieved using sulfuric acid alone, this condition leached around 84% more yttrium. The highest extraction (42.91%) was reached at 180 minutes in experiment H. However, after 120 minutes, in this same experiment, 41.19% of yttrium was already extracted. As the difference is lower than 5%, it was established that 120 minutes was the optimal leaching time for yttrium using the combination of sulfuric acid and hydrogen peroxide.

Despite achieving the higher extractions among the leaching acid tested, the results were still below desirable, probably due to the refractoriness of the material and the tightness of the (- Y- AlO4 - Y- AlO4 -) structure, as mentioned above.

The behavior throughout time can be observed through the curves of the mean extraction presented in Figure 20. Similar to the observed for the other acids, none of the variables impacted the reaction time as the curves are all similar. However, differing from nitric and sulfuric acid, the variation through time was less noticeable for sulfuric acid and hydrogen peroxide after 30 minutes, as it is possible to note by the average extraction curves.

This behavior might indicate a different reaction kinetics as the activation energy needed to extract yttrium using sulfuric acid and hydrogen peroxide is lower than using only the acid (Innocenzi *et al.*, 2017). The difference in extraction from 30 to 120 minutes is in the majority of experiments over 5%. Thus, 120 minutes was determined as the optimal one.

Figure 20 - Comparison of average yttrium extraction at each level of (a) temperature, (b) acid concentration, and (c) solid-liquid ratio over time, using sulfuric acid and hydrogen peroxide.



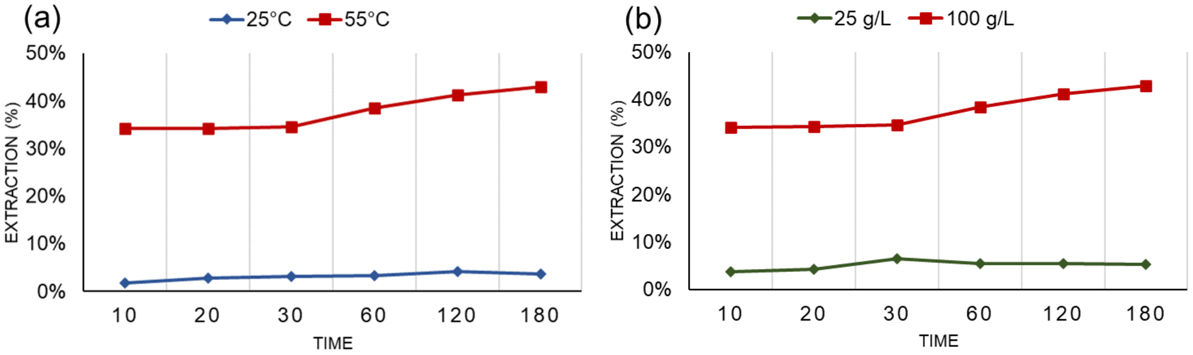
Source: Author

It is possible to see by analyzing Figure 20(a) that increasing the temperature from 25 to 40°C increased the mean extraction, however, elevating it to 55°C did not. Despite that, the higher leaching result was using 55°C. These results could be due to the reduction in viscosity and improvement in the diffusion brought by the increase in the temperature. Botelho Junior, Espinosa, and Tenório (2021) obtained similar results when applying only sulfuric acid to fluorescent lamp waste.

For the acid concentration, increasing the levels rose the extraction average. However, at the conditions of the higher extraction experiments, the acid concentration was 2.5 mol.L^{-1}. A possibility is that, at those values, the increase in acid concentration would have caused the formation of insoluble sulfates (Ahn *et al.*, 2020).

Although it seems to have an influence, the statistical analyses show that none of the factors analyzed had statistically significant effects on the response, since their p-value was higher than 0,05. Regardless, it is worth descriptively analyzing the conditions that resulted in the higher extraction. Thus, Figure 21 shows the results for experiment H compared with experiments that varied only temperature (Figure 21(a)) and solid-liquid ratio (Figure 21 (b)).

Figure 21 - Effect of (a) the temperature at 2.5 mol.L^{-1} and 100 g.L^{-1} and (b) the solid-liquid ratio at 55°C and 2.5 mol.L^{-1} on yttrium extraction at experiment H (55°C, 2.5 mol.L^{-1}, 100 g.L^{-1}), using sulfuric acid and hydrogen peroxide.



Source: Author

At experiment H’s condition, the temperature and the solid-liquid ratio influenced the extraction. It is worth mentioning that increasing the temperature raised the extraction by over 90%, as shown in Figure 21(a). The same was observed by Yin et al. (2018), which pointed out that the temperature had the most influence on the extraction of yttrium from CTR waste phosphorus. The Authors also determined 55°C as the optimal temperature for the extraction.

The solid-liquid ratio also had a similar effect in the conditions that resulted in the higher extraction (Figure 21(a)), suggesting that this variable can be elevated without resulting in a decrease in extraction. These results are both environmentally and economically advantageous. As the acid concentration for the experiment with higher results was at the central point value, no experiment differed only in the acid concentration level. Therefore, it was not feasible to directly assess its impact in the higher extraction experiment.

The association of sulfuric acid and hydrogen peroxide was used to extract yttrium from fluorescent lamps, CRT phosphor, and e-scraps, resulting in extractions higher than 92% (Innocenzi et al., 2013a; Innocenzi et al., 2013b; Marra; Cesaro; Belgiorno, 2019; Talebi et al., 2018; Yin et al., 2018).

Marra, Cesaro, and Belgiorno (2019) leached e-scraps twice using 2 mol.L^{-1} at 25°C and a solid-liquid ratio of 100 g.L^{-1} reaching 92% of extraction. The conditions applied differ in temperature from the higher extraction experiment in the present research. As was observed for cerium, the temperature exerted a higher impact when leaching LED lamp residue. The Authors highlighted that the high extractions at room temperature are closely related to the form of the REE in the residue (as oxides).

Innocenzi et al. (2013a) extracted all yttrium in the CRT phosphor residue by combining sulfuric acid (2 $mol.L^{-1}$) with 10% v/v of hydrogen peroxide (30% v/v) at 70°C. The authors analyzed the influence of acid and hydrogen peroxide concentration, pointing out that only the latter had a statistically significant effect on the response variable. Thus, as observed in this research, the acid concentration did not affect the extraction with statistical significance. Another discrepancy between the research is the percentage of yttrium in the residue and the presence of this element in the form of oxides.

3.3.3 Gallium

Gallium was the most recovered critical metal from LED lamps in the literature. As for the rare earth elements, gallium is considered a critical element (Elshkaki *et al.*, 2018). Thus, despite not being identified by the residue characterization, the results were presented and expressed in absolute values ($mg.kg^{-1}$) in Table 19.

Table 19 - Extraction results for gallium in $mg.kg^{-1}$.

Experiments	**HNO_3**	**H_2SO_4**	**$H_2SO_4 + H_2O_2$**
	180 minutes	180 minutes	180 minutes
A	11.1630	1.7802	7.124
B	9.4826	5.5049	13.455
C	28.8985	1.9375	122.143
D	47.5439	7.1664	17.396
E	21.5576	2.2322	8.716
F	25.0395	7.8141	16.005
G	21.4522	1.8633	11.436
H	12.9489	5.1730	157.934
I	51.7794	4.0490	12.861
J	42.5609	3.7888	131.658
K	6.3672	3.0939	9.302
L	43.8033	2.8120	156.320
Central Point (M, N, O)	27.4832±6.481	3.8146±0.531	146.457±12.927

Source: Author

As for the other two elements presented, sulfuric acid combined with hydrogen peroxide was the most suitable leaching agent, extracting 157.93 mg.kg^{-1} of gallium at experiment H (see Table 19). If compared to the characterizations provided in the literature review, this would be equivalent to 22.6% of the gallium present in LED lamps.

Hydrometallurgy is recommended to extract gallium. Nevertheless, De Oliveira, Benvenuti and Espinosa (2021) highlight that a preceding pyrometallurgical process is advisable before the hydrometallurgical one. Most gallium recovery research applied hydrochloric acid as a leaching agent, however almost no data was published on the recovery of this element from WEEE using other inorganic acids, as reported by Pimassoni et al. (2023).

The lower extractions could be related to gallium being present as gallium nitrate (GaN) in the LED residue. GaN is a high-bond energy crystal with high hardness and high melting point, making it difficult to leach (Chen; Hsu; Wang, 2018; Nagy et al., 2017). Moreover, the surface packaging materials pose difficulties in gallium extraction from LED materials (Zhan *et al.*, 2015).

As few research use these acids for gallium extraction from WEEE, the results were presented in this topic to demonstrate the achieved and be used as a starting point when the main goal is this element. Gallium was not the goal of the extraction processes tested in this research, however, it is possible to conclude that none of the conditions tested were suitable to leach gallium from the residue.

Unlike the other elements, the extraction of gallium did not show stabilization after 120 minutes. It is not possible to state that 3 hours is the optimal leaching time once there is no plateau, however, results achieved after 180 minutes were used for the analysis.

Nitric Acid

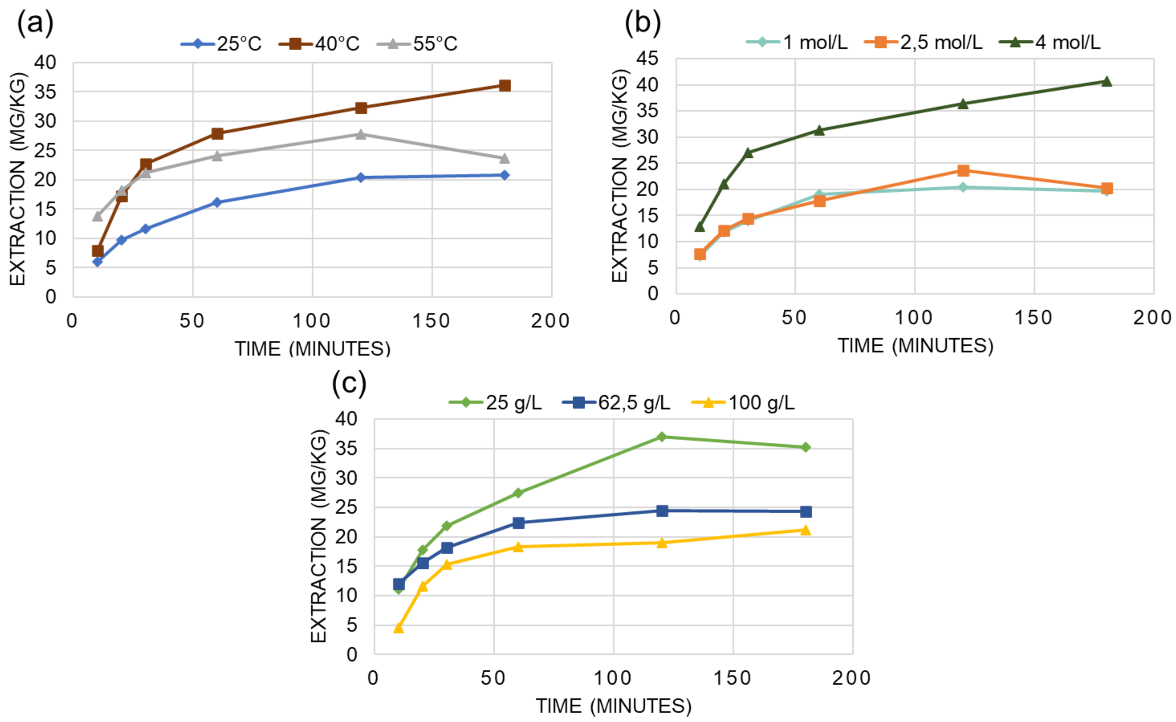
The highest extraction using nitric acid occurred in experiment I conditions after 180 minutes, where 51.77 mg.kg^{-1} of gallium was extracted at 40°C, 1 mol.L^{-1}, and 25 g.L^{-1}. The worst extraction result was in experiment K, at 40°C, 1 mol.L^{-1}, and 100 g.L^{-1}, extracting only 6.37 mg.kg^{-1} of gallium. he only difference between the highest and lowest extraction rates is the solid-liquid ratio, suggesting that this factor likely influences the response.

Most research that applied acid leaching to extract gallium used hydrochloric acid. Chen, Hsu, and Wang (2018) tested nitric acid in multiple conditions and, using acid at a concentration of 10 mol.L^{-1}, a solid-liquid ratio of 20 g.L^{-1} at 90°C, the Authors leached only 1.36% of the gallium present in the residue. At 25°C and the same conditions above, only 0.17% was extracted. To compare the results, using the data from Table 2 to calculate the percentage of leaching, the conditions of the present research leached 7.40% of gallium using milder conditions (1 mol.L^{-1}, 40°C, and 25 g.L^{-1}). As stated before, the properties of the gallium compound present in the LED waste make it less susceptible to leaching.

Li et al. (2023) achieved 99% of extraction by using nitric acid 3 mol.L^{-1} at 40°C to leach gallium from gallium-based liquid metal waste. Also starting from a more purified material (GaAs), Hu et al. (2015) leached 100% of the gallium from the residue applying nitric acid 1.5 mol.L^{-1} at 40°C for 90 minutes. However, the starting material was composed of its majority of gallium, which is a possibility for the difference in extraction.

The evolution of the reaction throughout time can be evaluated by analyzing curves generated using the mean extraction value at each time and each factor. Hence, Figure 22 shows the comparison of average results at each level of temperature (Figure 22(a)), acid concentration (Figure 22(b)), and solid-liquid ratio (Figure 22(c)) over time.

Figure 22 - Comparison of average gallium extraction (mg.kg^{-1}) at each level of (a) temperature, (b) acid concentration, and (c) solid-liquid ratio over time, using nitric acid.



Source: Author

Similar behaviors occurred at all levels, resulting in similar curves. It is possible to note in Figure 22(a) that the mean extraction at 40°C had a pronounced increase until 30 minutes compared to the other levels, indicating the leaching rate was higher at this temperature (Chen, Hsu e Wang, 2018). Additionally, in the first 30 minutes, the difference in extraction results between 40 and 55°C is almost nonexistent.

Examining Figure 22(b), it becomes evident that there was no significant difference in the extraction when using 1 or 2.5 mol.L^{-1}, but a notable distinction when using 4 mol.L^{-1}, probably due to insufficient acid up to 2.5 mol.L^{-1} (Zhang; Zhan; Xu, 2021). At the last level, the extraction did not reach a plateau, the same observed in the 40°C curve, not being possible to affirm if the reaction would have better results in longer times.

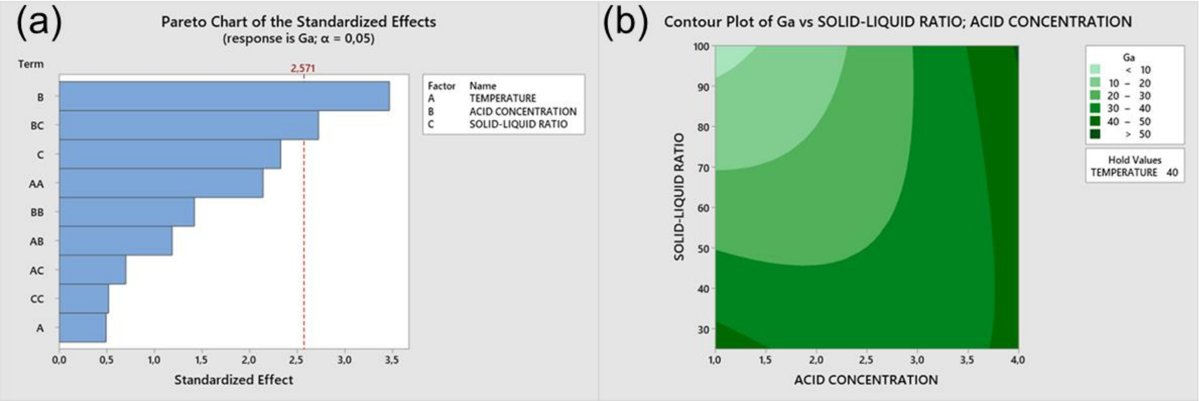
The solid-liquid ratio behavior follows the same pattern, and the difference in extraction appears to grow over time. The distinction between the results at 25 g.L^{-1} stands out from the other two levels assessed. These results were expected, as the literature showed that lower solid-liquid ratios had better results in other residues. At the other solid-liquid ratios, the acid was insufficient to leach the gallium present in the residue

(Chen, Hsu e Wang, 2018). Among the three variables depicted in Figure 22, acid concentration and solid-liquid ratio seem to impact the response.

The statistical analysis confirms that the main effect of acid concentration had statistical significance, positively influencing the extraction, as seen in the Pareto chart of standardized effects in Figure 23(a). Thus, higher acid concentrations result in higher leaching. The interaction between acid concentration and solid-liquid ratio also had statistical significance. When low solid-liquid ratios are combined with low acid concentrations, or when high solid-liquid ratios are coupled with high acid concentrations, the outcome is an increase in extraction, as seen in the contour plot (Figure 23(b)).

The experiment that combined 100 g.L^{-1} and 4 mol.L^{-1} also had high extractions (43.80 mg.kg^{-1}). Hence, an economic and environmental evaluation would be necessary to ascertain whether employing a lower solid-liquid ratio in conjunction with reduced acid concentration would be more advantageous than the reverse conditions. The contour plot suggests that higher and lower solid-liquid ratios and acid concentrations than the limits tested in this study would return better leaching results. Unlike those found by Chen, Hsu, and Wang (2018), the temperature did not influence with statistical significance the response.

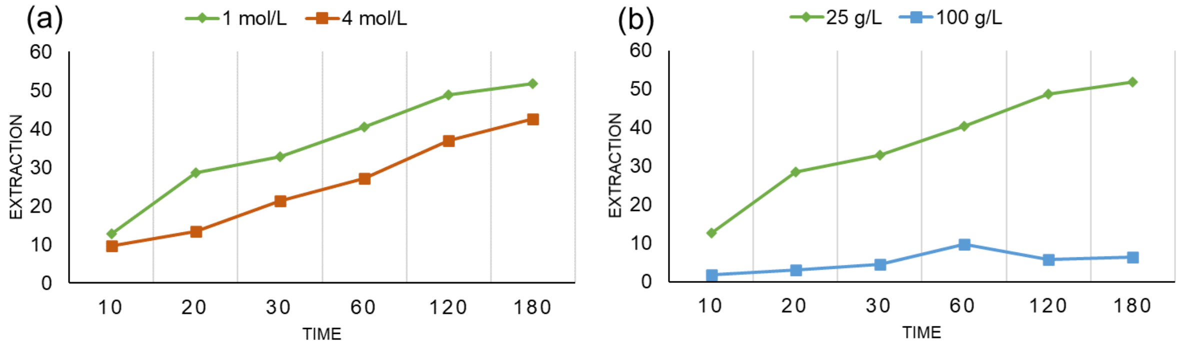
Figure 23 - (a)Pareto chart of standardized effects for gallium (HNO_3); (b) Contour plot for gallium extraction using nitric acid with the temperature fixed at 40°C.



Source: Author

It is worth qualitatively assessing the behavior of the higher extraction experiment contrasted with the ones that changed solely acid concentration (Figure 24(a)) and solid-liquid ratio (Figure 24(b)). As the temperature was at the central level, there was no experiment to compare directly.

Figure 24 - Effect of (a) the acid concentration at 40°C and 25 g.L^{-1} and (b) the solid-liquid ratio at 40°C, 1 mol.L^{-1} on gallium extraction (mg.kg^{-1}) at experiment I (40°C, 1 mol.L^{-1}, 25 g.L^{-1}), using nitric acid.



Source: Author

The graphics show in Figure 24 do not allow the visualization of the interaction between the variables. However, it makes it possible to see that, despite not having statistical significance in the overall response, in the experiment resulting in higher extraction, the lower level of solid-liquid ratio extracted 87% more gallium than the higher level, indicating influence.

A possible reason is that the amount of acid in the reaction with a higher solid-liquid ratio was insufficient to leach gallium in higher amounts. This difference is lower when analyzing the acid concentration, where applying the lower level resulted in 17% more gallium extracted than the higher level.

Sulfuric Acid

Gallium was better extracted after 180 minutes, and, as for the other critical metals analyzed, the lower extraction of gallium occurred using sulfuric acid as a leaching agent, possibly due to the lower oxidizing power of the acid compared to the other leaching agents, as said before.

The higher extraction was 7.81 mg.kg^{-1} obtained at experiment F (55°C, 2.5 mol.L^{-1}, and 25 g.L^{-1}), combining higher temperature and lower solid-liquid ratio. These conditions resulted in higher extraction likely due to favoring the contact between the acid solution and the solid matrix.

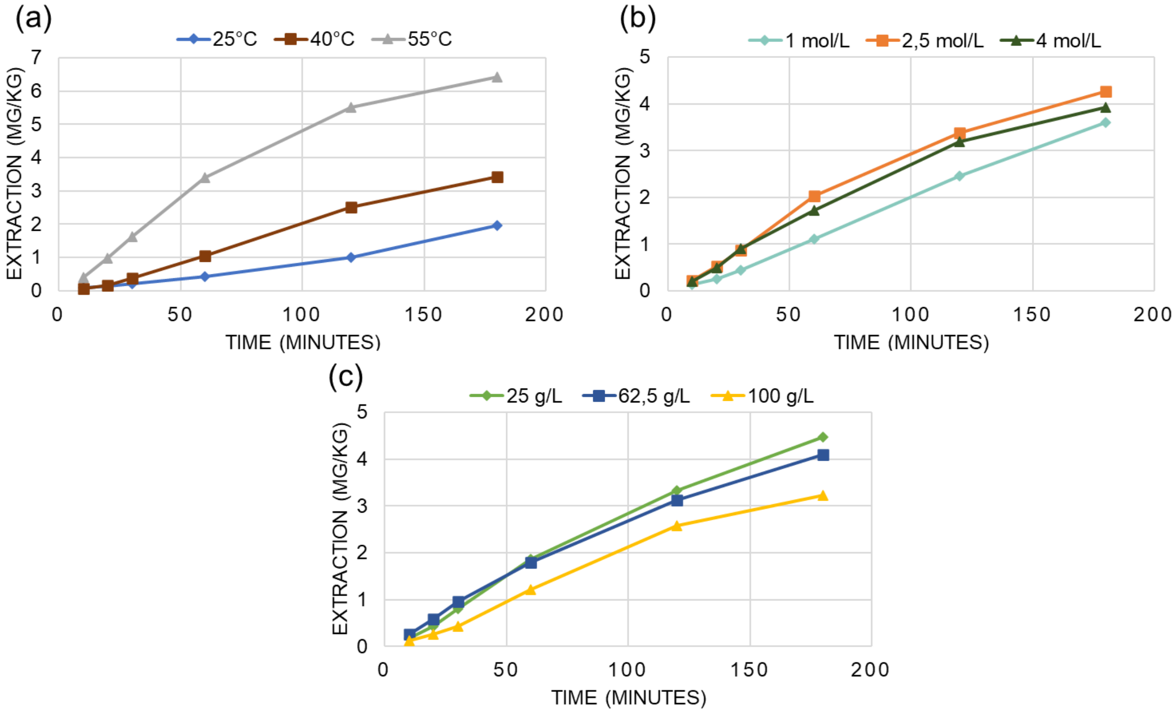
Appling sulfuric acid at a concentration of 6 mol.L^{-1}, 50 g.L^{-1} at 90°C for 4 hours, Pourrahim, Rezai and Gharabaghi (2017) leached 86.7% of gallium from zinc oxide concentrate. The Authors demonstrate that increasing the acid concentration from 2 to

6 mol.L^{-1} enhances the extraction process, but this trend diminishes at concentrations beyond that range.

Additionally, they concluded that the temperature positively affected the response, similar to the present research. However, contrary to the present study, the solid-liquid ratio barely influenced the response. Also having higher results, Zhang et al. (2023) leached 93% of the gallium in brown corundum dust. As for nitric acid, both residues presented a less complex matrix compared to the samples used in the present research.

The temporal behavior can be analyzed through the mean values at each time. Figure 25 shows the comparison of average results at each level of temperature (Figure 25(a)), acid concentration (Figure 25(b)), and solid-liquid ratio (Figure 25(c)) over time.

Figure 25 - Comparison of average gallium extraction (mg.kg^{-1}) at each level of (a) temperature, (b) acid concentration, and (c) solid-liquid ratio over time, using sulfuric acid.



Source: Author

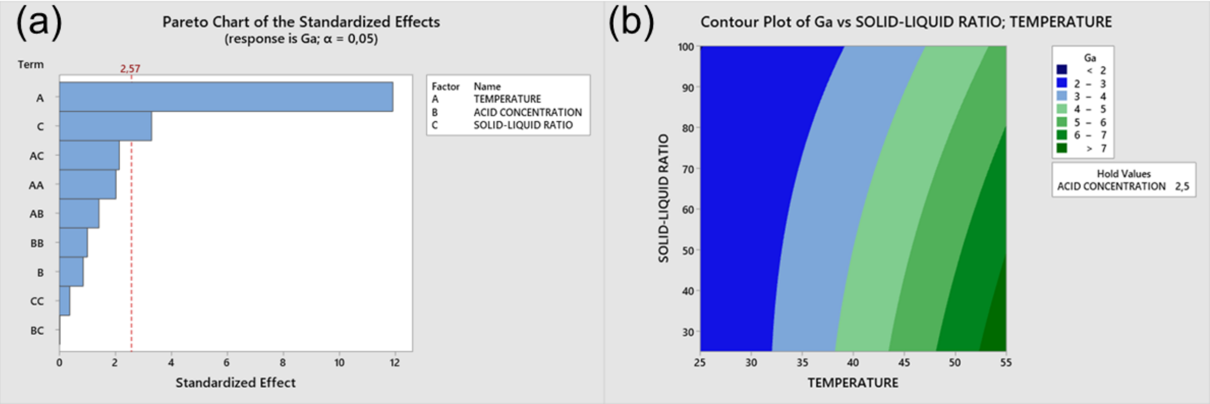
Among the variables, the temperature positively impacted the extraction process as can be seen in Figure 25(a). Consequently, higher extractions were observed at elevated temperatures, with this difference increasing over time. Again, higher temperatures could improve the oxidizing media and diffusion, and diminish the viscosity, increasing the extraction (Song *et al.*, 2017; Takano, Asano e Goto, 2022).

According to Wu et al. (2012), at lower temperatures, gallium extraction is reduced. Increasing the acid concentration up to 2.5 mol.L^{-1} increased extraction, however, elevating it to 4 mol.L^{-1} did not show significant differences. This same behavior was observed by Wu et al. (2012), leaching gallium from zinc residue.

Varying acid concentration and solid-liquid ratio, the extractions had little to no difference (see Figure 25(b) and (c)), suggesting that these factors did not affect the response variable. Still, none of the mean extraction curves reached a plateau, suggesting that more extended reactions could improve the extraction (Xu *et al.*, 2007).

However, the statistical analysis shows that the temperature and the solid-liquid ratio influenced the response variable with statistical significance, as can be seen in the Pareto chart of standardized effects in Figure 26(a).

Figure 26 - (a)Pareto chart of standardized effects for gallium (H_2SO_4); (b) Contour plot for gallium extraction using sulfuric acid with the acid concentration fixed at 2.5 mol.L^{-1}.



Source: Author

The temperature positively influenced the response, as observed by Xu et al. (2007). However, the solid-liquid ratio negatively affects the extraction. Hence, when higher temperatures were combined with lower solid-liquid ratios, the result was an increased extraction, as visually depicted in the contour plot in Figure 26(b).

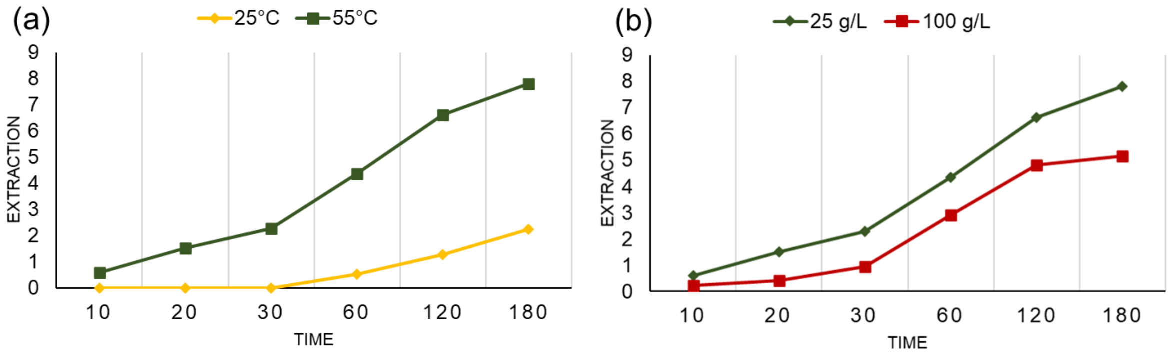
Chen, Hsu, and Wang (2018) show that when using sulfuric acid, the temperature employed often exceeds 80°C. Nonetheless, even at 90°C, 10 mol.L^{-1}, and 20 g.L^{-1}, the Authors only extracted 3.28% of gallium from GaN waste, indicating that the composition of the material is also a factor to be considered.

Xu et al. (2007) recovered over 80% of gallium from phosphorus flue dust using sulfuric acid 2 mol.L^{-1}, 125 g.L^{-1} at 80°C. Compared to experiment F, the authors used higher temperatures, which is a possibility for the increased extraction. The Authors also highlight that temperature, acid concentration, and solid-liquid ratio positively affected the extraction.

It is possible to observe how the variables influenced specific conditions when individually assessing the performance of the optimal experiment and contrast it with those that solely varied temperature and solid-liquid ratio.

Thus, Figure 27 shows the behavior through time of experiment L compared to experiments that differ only in the temperature (Figure 27(a)) and solid-liquid ratio (Figure 27(b)). The acid concentration of the experiment with higher results was at the central level, so it was impossible to make a direct comparison. It is noteworthy that, compared to the solid-liquid ratio, the temperature had a higher impact on the extraction.

Figure 27 - Effect of (a) the temperature at 2.5 mol.L^{-1} and 25 g.L^{-1} and (b) the solid-liquid ratio at 55°C and 2.5 mol.L^{-1} on gallium extraction (mg.kg^{-1}) at experiment F (55°C, 2.5 mol.L^{-1}, 25 g.L^{-1}), using sulfuric acid



Source: Author

The extraction at 55°C was 71% higher than at 25°C, and, similarly observed for nitric acid, the solid-liquid ratio negatively impacted the results. It is possible to note that at 25°C the extraction begins after 30 minutes, indicating a slower reaction kinetics, not being possible to discard the possibility that in a longer reaction, the extraction would improve. The difference was, however, lower than for nitric acid, with the extraction at 25 g.L^{-1} being 33% higher than 100 g.L^{-1}. Figure 27 illustrates that the extraction did not reach a plateau under the conditions of experiment F, implying that extending the reaction times should be explored for further investigation.

Sulfuric Acid and Hydrogen Peroxide

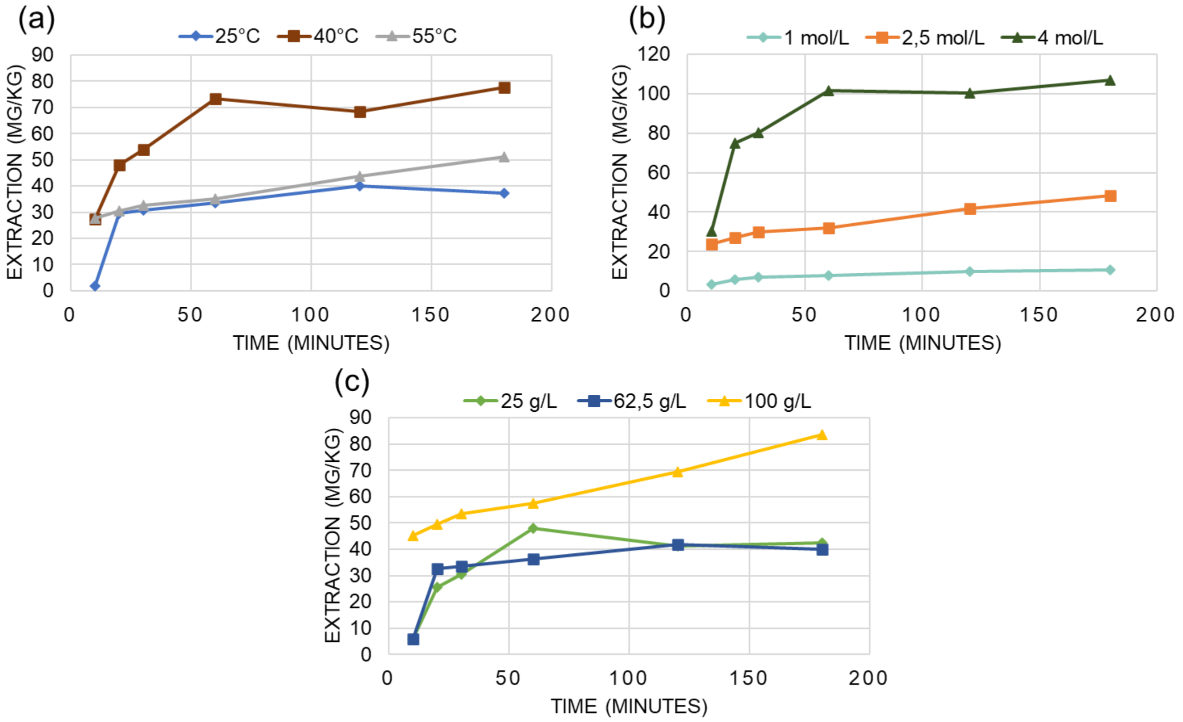
The association of hydrogen peroxide and sulfuric acid increased the extraction, reaching 157.93 mg.kg^{-1} of gallium extracted at experiment H (55°C, 2.5 mol.L^{-1}, and 100 g.L^{-1}). Similar extractions were obtained at 40°C, 4 mol.L^{-1}, and 100 g.L^{-1} (156.32 mg.kg^{-1}), possibly indicating that the increase in the acid concentration compensated the reduction in the temperature. Research applying sulfuric acid and hydrogen peroxide to extract gallium is almost inexistant, both on WEEE and other residues.

However, adding hydrogen peroxide positively affected the extraction of gallium from zinc powder replacement residue when associated with oxalic acid. Liu et al. (2017) attribute this effect to the fact that hydrogen peroxide oxidized the elemental gallium, while a gallium complex formation was promoted by oxalic acid.

Hydrogen peroxide was also applied to increase the dissolution of the polymeric material containing the gallium material. This use could also account for the better extraction using this leaching agent (Zhang; Zhan; Xu, 2021).

As for the other two leaching agents, higher results were obtained at 180 minutes. The behavior over time can be observed in Figure 28, which shows the comparison of average results at each level of temperature (Figure 28(a)), acid concentration (Figure 28(b)), and solid-liquid ratio (Figure 28(c)).

Figure 28 - Comparison of average gallium extraction (mg.kg^{-1}) at each level of (a) temperature, (b) acid concentration, and (c) solid-liquid ratio over time, using sulfuric acid and hydrogen peroxide.



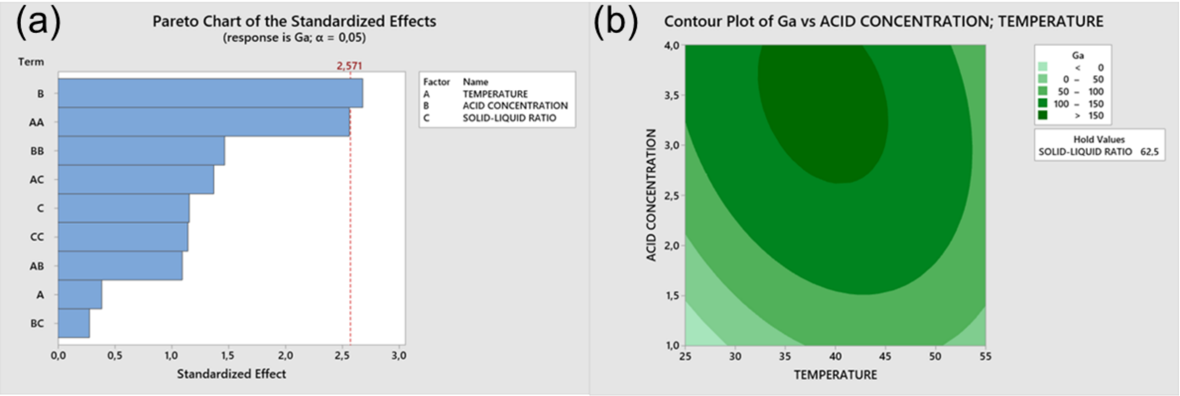
Source: Author

The difference in the extraction obtained using 25 and 55°C was nearly nonexistent, with only the results of 40°C standing out. This behavior may suggest that the main effect of the temperature did not significantly influence the response. Unlike the observed, Zhou et al. (2019) observed a clear increase in extraction with the increase in temperature.

The same linear behavior was observed at the curves for 1 and 2.5 mol.L^{-1}, contrasting with 4 mol.L^{-1}. The disparity of results among the three levels shows an influence of the acid concentration's main effect on the response.

A performance similar to the temperature was observed when examining the solid-liquid ratio. The results for 25 g.L^{-1} and 62.5 g.L^{-1} had no significant differences, being surpassed by the 100 g.L^{-1} extractions. However, unlike the temperature, the higher level had the higher extraction. Additionally, the extraction using 100 g.L^{-1} did not reach a plateau, suggesting a more extended reaction. Figure 29 shows the statistical analysis of the extraction using this leaching agent.

Figure 29 - (a) Pareto chart of standardized effects for gallium (H_2SO_4 + H_2O_2); (b) Contour plot for gallium extraction using sulfuric acid and hydrogen peroxide at solid-liquid ratio of 62.5 g.L^{-1}.

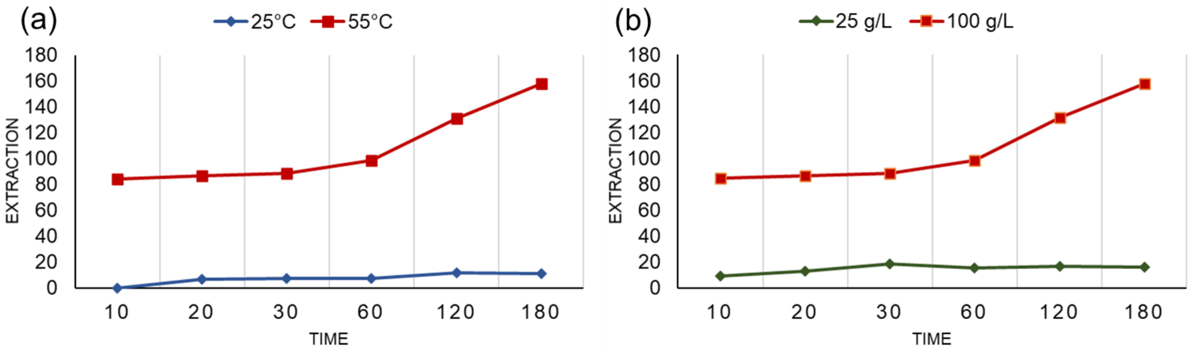


Source: Author

The acid concentration stood as the sole factor exerting a statistically significant impact on the response for this particular leaching agent (Figure 29(a)). Thus, increasing the range of investigation on this variable could return higher extractions. In the contour plot depicted in Figure 29(b), it becomes evident that the influence of temperature is not linear, as higher extractions were observed at intermediate temperature values (between 35 and 45°C) and higher acid concentrations.

It is worth analyzing descriptively the conditions that resulted in the higher extraction. Thus, Figure 30 shows the results for experiment H compared with experiments that varied only temperature (Figure 30(a)) and solid-liquid ratio (Figure 30(b)).

Figure 30 - Effect of (a) the temperature at 2.5 mol.L^{-1} and 100 g.L^{-1} and (b) the solid-liquid ratio at 55°C and 2.5 mol.L^{-1} on gallium extraction (mg.kg^{-1}) at experiment H (55°C, 2.5 mol.L^{-1}, 100 g.L^{-1}), using sulfuric acid and hydrogen peroxide.



Source: Author

It is noticeable that, for this condition, the temperature and solid-liquid ratio influenced the response despite not having statistically significant effects in the whole experimental plan. At 55°C, the extraction was 93% higher than at 25°C, and the difference between the high and low levels of solid-liquid ratio was 90%. As for the other two leaching agents, the plateau was not reached, thus indicating a possible need for more time, as the kinetics are possibly slower, as the extraction starts to increase after 60 minutes.

The use of sulfuric acid and hydrogen peroxide did not appear in the recovery of gallium from the WEEE presented in Chapter 2, however it was used to recover gallium from solar cells. Hsiang et al. (2016) used the combination (sulfuric acid and hydrogen peroxide) to recover gallium from spent copper—indium—gallium—diselenide (CIGS) solar cells, obtaining complete dissolution using sulfuric acid at 3 mol.L^{-1} and 5 g.L^{-1} of solid-liquid ratio at 140°C for four hours. Since the experimental plan does not encompass higher temperatures, it is impossible to definitively state that elevated temperatures would result in significant extraction increases. Yet, if a similar trend were to persist at higher temperature levels, this displacement might not give notable improvements.

3.3.4 Other metals and extraction selectivity

In addition to examining the rare earth elements, other metals were quantified in the leach. These specific metals were selected due to their comparatively higher concentrations within LED residues, as indicated in Table 2 (Chapter 2).

Some of the chosen metals were not analyzed or not identified in the residue characterization done by Rebello et al. (2020). Consequently, the extractions for these metals were reported in absolute values (mg.kg^{-1}). The time employed in analyzing these metals was the same as the one established for cerium and yttrium for each leaching agent, as the objective was to extract rare earth elements (REE). It's worth highlighting that the aim was to achieve a selective extraction of REE, thus emphasizing a preference for lower extraction of other metals as optimal results.

Nitric acid was the leaching agent that most extracted lead probably due to the formation of insoluble sulfates when sulfuric acid was used (Lie; Ismadji; Liu, 2019). This presents as a disadvantage of using nitric acid in residues containing this hazardous metal.

Copper was also most extracted by nitric acid, this was expected as the use of inorganic acids is broadly used to recover this metal. The low extraction when using sulfuric acid and its combination with hydrogen peroxide was also reported by other authors, suggesting that one step using these leaching agents was inefficient to leach copper in residues that contained other metals such as iron and aluminum (Marra; Cesaro; Belgiorno, 2019).

Silver and gold were poorly extracted in all conditions tested, as expected, once these metals require stronger leaching agents such as cyanide (Cerecedo-Sáenz *et al.*, 2021; Diaz *et al.*, 2016; Pourhossein *et al.*, 2021).

The results of all the metals analyzed and the selectivity index (SI) in the time and experiments with higher extraction results for cerium and yttrium are shown in Table 20.

Table 20 - Extraction results in mg.kg^{-1} for all metals analyzed in the experiments with higher extraction results for cerium and yttrium.

Element	**HNO_3 (Experiment L)**	**HNO_3 (Experiment I)**	**H_2SO_4 (Experiment F)**	**H_2SO_4 + H_2O_2 (Experiment H)**
	180 minutes	120 minutes	120 minutes	120 minutes
Cerium	2.93	4.18	1.99	12.84
Yttrium	2.29	1.14	1.37	8.57
Gallium	43.80	48.80	6.62	131.33
Silver	3.31	10.95	ND	0.40
Gold	4.46	0.38	ND	ND
Lead	25251.38	24375.39	80.05	19.44
Tin	5785.25	4025.19	4396.50	7986.79
Iron	37481.38	45682.83	24416.76	48591.59
Copper	101563.13	88856.00	ND	12.50
SI	0.00033	0.00033	0.00034	0.0027

ND = not detected
Source: Author

The results for nitric acid and sulfuric acid were lower than 30% for both cerium and yttrium, and a high amount of other metals were extracted, such as copper, lead, and iron. A possibility would be to optimize the results to minimize the extraction of REE and maximize the extraction of base metals, using these processes to purify the residue and concentrate REE in the solid matrix.

A combination of multiple leaching steps could result in better extractions, with a first step using nitric acid at conditions that leached high amounts of copper, iron, lead, and tin but did not leach REE. Followed by an oxidating leaching step using sulfuric acid combined with hydrogen peroxide. Another possibility could be to apply an electrostatic separation to concentrate REE in the non-conducting fraction, as Cenci et al. (2021) suggests, to concentrate the REE and remove base metals.

All the leaching agents used simultaneously extracted some contaminants because the complexity of the original solid matrix has an impact on the selectivity of the extraction. Thus, the greater the number of different metals in the residue, the lower the selectivity tends to be (Marra; Cesaro; Belgiorno, 2019).

It is possible to make this comparison by calculating a selectivity index (SI), as shown in Equation 2 (Section 3.2.4). The results of de SI using nitric acid for experiment I after 120 minutes (higher extraction of cerium) and for experiment L after 180 minutes (higher extraction of yttrium) was 0.00033.

Using sulfuric acid, the SI for experiment F was 0.00034, and using sulfuric acid with hydrogen peroxide, the SI for experiment H was 0.0027. Thus, it is even clear that using sulfuric acid with hydrogen peroxide is the most favorable option, with 10 times more selectivity than the other acids tested.

It is possible to note that the optimal leaching condition among the experiments (experiment H using sulfuric acid and hydrogen peroxide) has a satisfactory selectivity of REE over copper, having more cerium than copper in the leach. It is possible to highlight that varying only in temperature, Marra, Cesaro, and Belgiorno (2019) extracted higher amounts of copper from e-scraps at 25°C when compared with the present work. In absolute values (mg.kg^{-1}), the Authors have 300 and 700 times more copper than cerium and yttrium in the solution, respectively.

Nitric Acid

Silver and gold were barely extracted by nitric acid leaching. In the experiments of higher extraction for cerium (experiment I) and yttrium (experiment L), extraction was almost inexistent, with only 2.83 and 0.83% of silver and 0.11 and 0.69% of gold. Nevertheless, in mg.kg^{-1}, the amounts are comparable to the amount of REE in the leached.

The low extraction was expected for the precious metals once they require stronger leaching agents such as cyanide, aqua regia, and thiourea (Cerecedo-Sáenz *et al.*, 2021; Diaz *et al.*, 2016; Pourhossein *et al.*, 2021). Caldas et al. (2021), highlight that silver is soluble in nitrite media up to a pH of 10.5, however, the species formed can be depredated by light, forming insoluble compounds.

Nitric acid leaching proved effective in extracting lead. Under the optimal experimental conditions for cerium and yttrium extraction, 24375 mg.kg^{-1} and 25251 mg.kg^{-1} of lead were obtained, respectively. These amounts are higher than the reported in the literature as the composition of LED lamps, indicating a necessity for a better characterization of lead in these residues.

Tin was also detected in the leachate following nitric acid usage. In experiment I, 4025.20 mg.kg^{-1} of tin was extracted, while in experiment L, the amount of tin leached was even higher at 5668.24 mg.kg^{-1}. In contrast to the composition values of LED waste in the literature, the extraction percentage remained below 5%. Nevertheless, the value is more than three thousand times greater than the amount of cerium and yttrium in the solution.

Compared to the amount of cerium and yttrium extracted in the present research, a high concentration of iron was identified, 45682 and 37044 mg.kg^{-1} in experiments I and F respectively. This is consistent with the observed in the literature. Erust et al. (2019) had over 80% of iron extraction using nitric acid at a concentration of 2 mol.L^{-1}.

At the experimental conditions of runs I and L, copper, one of the primary components of the residue, exhibited extraction efficiencies of 94% and 105%, respectively. These results are also consistent with the literature that points out nitric acid as the most suitable leaching agent for the extraction of copper from waste silica-rich integrated circuits and used printed circuit boards when compared to sulfuric and hydrochloric acid (Ajiboye *et al.*, 2019; Dutta *et al.*, 2018).

Compared to Ajiboye et al. (2019), these results were achieved using lower temperatures (40°C) and higher acid concentrations (1 and 4 mol.L^{-1}). Less than 1% of copper was extracted in experiments that combined a high solid-liquid ratio and low acid concentration. However, the higher extraction achieved in the experiments than most leached cerium and yttrium was a disadvantage once it reduced the selectivity of the leaching process.

Sulfuric Acid

Gold was not extracted in quantifiable amounts using sulfuric acid. Silver was also poorly leached in an overall analysis, reaching less than 1% of extraction. For the experiments with the higher results for cerium and yttrium using sulfuric acid (experiment F), silver was not detected in the chemical analysis.

Sulfuric acid was used as a leaching agent to recover metals from printed circuit boards by Caldas et al. (2021). The Authors did not extract silver using 2 mol.L^{-1} sulfuric acid, 100 g.L^{-1} solid-liquid ratio, and 95°C for 18 hours. The same was observed by Wei et al. (2023) that did not reach 10% of silver leached from LED waste after pyrolysis using lower acid concentration (2.36 mol.L^{-1}) but higher temperature and time if compared to the present research (80°C and 7.76 hours). On the other hand, in both researches, over 90% of iron was extracted.

Erust et al. (2019) also recovered 100% of the iron in the NdFeB residue using sulfuric acid at 2 mol.L^{-1} at 27°C. Similarly, iron was extracted at the experiment with higher extraction of cerium and yttrium determined for this leaching agent, experiment H (55°C, 2.5 mol.L^{-1}, and 100 g.L^{-1}). Despite being the lowest extraction among the three leaching agents, 21982 mg.kg^{-1} of iron was present in the leach liquor. This value is much higher than the REE concentration in the leach, possibly interfering with the following steps of the hydrometallurgical process. This high extraction is coherent with the literature, that states iron can be well recovered using sulfuric acid, however, the conditions applied are, generally, more aggressive.

Tin exhibited extraction levels comparable to nitric acid. In experiment F, the tin leached amounted to 4396.50 mg.kg^{-1}. This value was substantial when compared to the cerium and yttrium content in the solution, yet remains relatively low compared to the composition documented in the literature.

In contrast to tin, lead was extracted in smaller quantities using sulfuric acid. In experiment F, optimal for leaching cerium and yttrium, 80 mg.kg^{-1} of lead was extracted. These results are according to the expressed in the literature since lead sulfate salts have very low solubilities, lead sulfate (Lie, Ismadji e Liu, 2019; Vogel, 1981). That is also an advantage of using sulfuric acid in the process, preventing the dissolution of Pb by generating insoluble sulfates (De Michelis et al., 2011; Mishra; Devi; Sukla, 2020).

Copper was not extracted in quantifiable amounts under the conditions of experiment F (55°C, 2.5 mol.L^{-1}, and 25 g.L^{-1}). Sulfuric acid was tested by Ajiboye et al. (2019) in a study aiming to extract copper from waste silica-rich integrated circuits, having the worst performance compared to nitric and hydrochloric acids. The same was observed by Dutta et al. (2018) even using higher acid concentration (3 mol.L^{-1}). Both studies concluded that the most favorable temperature for leaching was 75°C, a fact also supported by Vogel (1981), who stated that heated sulfuric acid can dissolve copper.

Wei et al. (2023) only leached satisfactory results of copper after adding nitric acid along with the sulfuric acid, extracting over 99% of the copper present in the residue. The addition of nitric acid acted as an oxidizing agent. Thus, a possible explanation for the lower extraction of copper by sulfuric acid is the lack of an oxidizing agent (Dhanunjaya Rao, Shahin e Jha, 2021).

Another possibility to account for the low extraction of copper is the influence of the iron present in the leach, as reported by Caldas et al. (2021), iron in the solution can cause the copper cementation process.

Sulfuric Acid and hydrogen peroxide

Quantifiable extraction of gold did not occur when utilizing the association of sulfuric acid and hydrogen peroxide. For silver, in the experiment that most extracted cerium and yttrium using this leaching agent (experiment H), the extraction was also slim, 0.105%. Similar results were obtained by Marra, Cesaro, and Belgiorno (2019). After two leaching steps using 2 mol.L^{-1} sulfuric acid and 10% hydrogen peroxide (30%) at 25°C, gold was not found in the leach, and only 8% of silver was extracted.

The outcomes of the current study contrast with those reported by Caldas et al. (2021). After a first step using only sulfuric acid, the Authors extracted 100% of silver using the combination of hydrogen peroxide and sulfuric acid (2 mol.L^{-1}) at 95°C and 100 g.L^{-1} of solid-liquid ratio. The Authors also evaluated using these conditions as a single-step leaching, resulting in 94% of silver extracted.

The results also differ in the extraction of tin. Caldas et al. (2021) extracted only 2% of this element using a single leaching step using sulfuric acid and hydrogen peroxide as exposed before. In the present research, using sulfuric acid with hydrogen peroxide extracted higher amounts of tin when compared to the other two leaching agents. 7986 mg.kg^{-1} was removed from the solid matrix into the leach, being one of the contaminants in higher proportions. This is a drawback of employing the combination of sulfuric acid and hydrogen peroxide under the conditions of experiment H.

Similar to the results obtained by Caldas et al. (2021), high amounts of iron were extracted using this combination if compared with the absolute value of cerium and yttrium extracted. 48591 mg.kg^{-1} of iron was present in the leach resulting from experiment H.

Parallel to the outcome with sulfuric acid, lead was not extracted in high amounts. In experiment H only 19 mg.kg^{-1} was leached, a value close to the amount of cerium in the leach solution.

The amount of copper extracted in experiment H was at the same magnitude as cerium in absolute values. However, compared to the initial quantity present in the residue, only 0.01% of copper was extracted. This leaching agent was applied to extract copper from other residues in the literature. Most research used higher temperatures, from 75 to 95°C, periodic additions of hydrogen peroxide, and multiple stages of leaching (De Andrade et al., 2021; Birloaga et al., 2013; Martins et al., 2021).

Marra, Cesaro, and Belgiorno (2019) state that a single step using oxidative leaching is insufficient to extract copper, with aluminum and zinc being preferentially dissolved. These conditions play a fundamental role in developing more selective leaching processes. The low extraction of copper in experiment H is an advantage of the conditions applied (55°C, 2.5 mol.L^{-1}, and 100 g.L^{-1}).

3.4 CONCLUSIONS

This Chapter had a goal of identifying the most suitable leaching agent and the optimal conditions to extract cerium and yttrium from end-of-life LED lamps.

The order from highest to lowest extraction of REE among the leaching agents tested was $H_2SO_4+H_2O_2 > HNO_3 > H_2SO_4$. Thus, the most favorable leaching agent to extract cerium, yttrium and gallium was the association of sulfuric acid and hydrogen peroxide, probably to the higher oxidizing power need to leach the Ce:YAG structure. It was not possible to optimize based on the empirical model as the statistical analysis did not show a significant influence of the variables and ranges used.

The conditions that achieved the higher extractions of REE was 55°C, 2.5 mol.L^{-1}, and 100 g.L^{-1}, resulting in 78.82% and 41,19% of cerium and yttrium extracted, respectively. For cerium and yttrium, the optimal time was 120 minutes and for gallium it was 180 minutes. Using this leaching agent none of the factors investigated, in the assessed rage, affected the response variable for cerium and yttrium with statistical significance within a 95% confidence interval. For gallium it was reported that the acid concentration and the quadratic factor of the temperature affected the response.

The literature shows that for recovering cerium from more complex crystal structures severe conditions must be used, or pretreatments need to be applied to transform the structure of cerium into oxides. However, the present research shows that almost 80% of cerium could be extracted by adding hydrogen peroxide and maintaining temperature and concentration in milder conditions.

Using nitric acid, the most favorable leaching conditions for cerium (25.47%) and gallium (51.77 mg kg^{-1}) was 40°C, 1 mol.L$^{- 1}$ and 25 g.L^{-1}, and, for yttrium (11.02%) it was 40°C, 4 mol.L^{-1}, and 100 g.L^{-1}. The factors that effected with statistical significance the response for cerium was the interaction factor between acid concentration and solid-liquid ratio, for yttrium were the acid concentration and the quadratic factor of the temperature. For gallium the acid concentration and the interaction factor between acid concentration and solid-liquid ratio influenced the extraction with statistically significance.

Using sulfuric acid, the condition that most extracted these three elements was 55°C, 2.5 mol.L$^{- 1}$ and 25 g.L^{-1}. For cerium none of the factors affected the response variable with statistical significance. For yttrium and gallium, the temperature had statistically significant influence. Additionally, the solid-liquid ratio also influenced the extraction of gallium.

Beyond the higher extraction, using the association of sulfuric acid and hydrogen peroxide extracted REE more selectively. The extraction of base metals had a different order of leaching agents, HNO_3 > H_2SO_4+H_2O_2 > H_2SO_4. Despite sulfuric acid having a lower extraction of base metals, it also had the lowest extraction of REE, thus, not being the ideal option. Precious metals were poorly extracted in leaching agents and conditions tested, not reaching higher than 10% of extraction.

As the range evaluated for each variable was determined based on other WEEE, the results of this research can be used to improve the values assessed, dislocating the range based on the experiment with higher extractions. It is suggested higher temperatures, similar acid concentration and higher solid-liquid ratios.

Also, as future research, it can be suggested the comprehension of the dissolution behavior of the yellow phosphorus in its pure form, following with the application of the optimal conditions for the residues. It can be beneficial for understanding the influence of the composition of the residue in the extraction.

Additionally, a combination of two leaching steps is suggested. First step to remove base metals and concentrate the REE in the solid matrix and a second step using an oxidative leaching to extract the critical elements. Alternatively, adding a mechanical separation process to remove the conducting fraction is also a possibility.

It is worth noting that, as stated in Chapter 2, the hydrometallurgical processes have environmental drawbacks concerning liquid waste and acid management. Thus, besides not being the focus of the chapter, it is crucial to perform environmental assessments and also analyze the waste treatment processes.

CAPÍTULO 4

CONCLUSIONS AND RECOMMENDATIONS

This research aimed to assess three leaching agents to extract REE from end-of-life LED lamps, evaluating the optimal conditions and the influence of temperature, acid concentration and solid-liquid ratio.

In Chapter 2 a review of the recovery of REE and critical elements from different WEEE showed that these elements are considered critical due to a high demand and supply risk. Among the REE, yttrium, cerium and neodymium are the most recovered in the literature. Still, among the WEEE, NiMH batteries and NdBFe magnets are the most investigated residues.

As gaps in the research field, it was possible to highlight the necessity to develop economical assessments on the REE recovery. Also, the need of integration of the REE recovery process with the recovery of base and precious metals.

In the LED lamp residues, it was clear the lack of investigation of REE recoveries, being that mostly gallium and indium were evaluated.

Thus, Chapter 3 fills part of the gap in the LED residue studies, assessing different conditions of temperature, acid concentration and solid-liquid ratio for three leaching agents for the extraction of cerium and yttrium.

The higher leaching results were achieved using 2.5 mol.L^{-1} of sulfuric acid with the addition of 10% of hydrogen peroxide, a solid-liquid ratio of 100 g.L^{-1} at a 55°C temperature. For this leaching agent, in the range adopted, temperature, acid concentration and solid-liquid ratio did not have statistically significant effect in the extraction results of cerium and yttrium.

It is noticeable that different residues return different extraction results. As only few of the studies using LED lamps extracted cerium and yttrium, it was not possible to compare these results directly with the same residue. Still, the determination of the methodology was based on other residues, thus not surprising that different behavior occurred.

As limitations of this research, it is highlighted the lack of pH assessment during the whole extraction process, of constant temperature measurements and the control of the emitted gasses. Additionally, it is possible to point out that an analysis of the solid remaining after leaching could have been beneficial. In the early stages of the research a deeper understanding of the powder composition with complementing methods of characterization such as XRD analysis could be beneficial in the understanding of the results and the selection of processes to be tested.

As future researches we highlight the need of expand the experimental plan beginning from the higher extraction condition. For the temperature it is suggested the evaluation of higher ranges, reaching 100°C. The solid-liquid ratio should also be increased as it would be economically beneficial, for example assessing from 100 to 300 $g.L^{-1}$. Regarding the acid concentration, as the central point was part of the higher extraction a milder increase in the range is suggested, using 2.5 $mol.L^{-1}$ as the lower level in the experimental plan.

Another possibility suggested is to evaluate the effect of the residue composition in the extraction, by analyzing the behavior of pure yellow phosphorus under the leaching conditions and then the extraction in more complex matrixes.

Moreover, understanding the composition of the residue regarding silicon and other polymers is necessary to determine with more certainty whether silica formation could have impacted in the extraction.

Additionally, a combination of processes could be assessed, first concentrating the REE in the solid by performing mechanical separation or a first leaching step (using nitric acid, for example), secondly leaching REE by an oxidizing leaching process.

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