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Evaluation of the mechanisms of rare earth elements extraction from citrate solutions in the recycling of NdFeB magnets

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ABSTRACT

Recycling rare earth elements (REEs) from secondary resources has gained significant attention due to their classification as critical metals by the European Union and their essential role in sustainable development. This study investigates the extraction of light and heavy REEs from citrate leachate solutions derived from end-of-life NdFeB magnets and examines the underlying mechanisms. Key parameters influencing REEs extraction efficiency are evaluated, including extractant and diluent types, extractant concentration, organic-to-aqueous phase volume ratio, contact time, and equilibrium pH. Results revealed that D2EHPA was the most efficient extractant, achieving approximately 100 % recovery for heavy REEs and 88 % for light REEs, with negligible iron extraction within 10 min. The extraction mechanism was found to differ significantly between light and heavy REEs. The equilibrium constant for heavy REEs (Dy, Y, and Tb) was approximately 50 times higher than for light REEs (Nd and Pr), indicating stronger interactions with the extractant. This difference is further supported by the smaller ionic radii of heavy REEs compared to light REEs, which result in higher charge density and stronger coordination preferences for heavy REEs. Moreover, it was observed that the extracted forms vary, with LREEs forming LREE $H_{1.6}$ Cit.$R_{1.6}$ $(RH)_2$ complexes and HREEs forming HREE $H_{2.4}$ Cit.$R_{2.4}$ $(RH)_{0.4}$ complexes. These differences contribute to the overall efficiency of the extraction process, with the final oxide product containing approximately 82 % REEs and only 0.1 % iron, demonstrating the high selectivity of the process.

1. Introduction

Rare earth elements (REEs) are essential raw materials due to their unique magnetic, electrical, chemical, and optical properties. They are crucial in producing advanced equipment, energy solutions, and new materials in various industries (Yu et al., 2024). Also, REEs are fundamental in manufacturing batteries, permanent magnets, fluorescent lamps, specialized alloys, and catalysts, and they are a vital component of the green economy and advanced technologies (Shakiba et al., 2023).

Due to their widespread use in advanced industries, the demand for REEs is rapidly increasing (Papagianni et al., 2022). However, production is concentrated in a few countries (with China alone supplying 60 % of the global market), posing significant supply risks (Belfqueh et al., 2024). Extracting REEs from ores involves using strong and hazardous reagents as well as high processing temperatures, resulting in substantial environmental challenges. This process also brings disadvantages, such as the simultaneous extraction of impurities and the presence of radioactive elements, making it difficult to achieve the desired product purity (Reisdörfer et al., 2019; Shakiba et al., 2023). Therefore, recovering and recycling REEs from secondary sources not only reduces environmental impact but also helps maintain market stability (Kołodyńska et al., 2023).

NdFeB magnets comprise approximately 30 % of light REEs (LREEs such as Nd and Pr) and small quantities of heavy rare earth elements (HREEs such as Dy, Tb, Y). These elements, combined with 60–70 % iron, are coated with corrosion protection based on transition metals such as Ni and Co (Kaya, 2024; Nayebossadri et al., 2024). The unique interaction between the unsaturated 3d-4f orbitals in transition metals and REEs results in high crystalline magnetic anisotropy, facilitating the production of high-tech products on a small scale (Kumari et al., 2018). NdFeB magnets are essential components in wind turbine generators, hard disk drives, electric motors, and cell phones (Kumari and Sahu, 2023; Romano et al., 2023). Due to their increasing demand, difficulty in replacing, significant volume, and potential waste stream, the European Rare Earths Competency Network (ERECON) has prioritized recycling NdFeB magnets (Belfqueh et al., 2023). Besides end-of-life NdFeB waste, the inherent brittleness and hardness of permanent magnets lead to considerable raw material waste and defective products during

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Table 1
The summary of some previous research works in the field of REEs extraction.

Leaching reagent	Source of REEs	Type of Extractants	Remarked results	Ref
Acetic acid	NdFeB magnets	TODGA	– High recovery rates for Nd (92 %), Pr (88 %), and Dy (99 %) were achieved using TODGA. – TODGA selectively recovered HREEs over LREEs, unaffected by salting-out agents or other metals. – $NaNO_3$ as a salting-out agent significantly enhanced the distribution co-efficients, extraction yields, and kinetics of REEs during extractions.	(Belfqueh et al., 2024)
Citric acid	NdFeB magnets	D2EHPA	– Electrochemical dissolution of NdFeB magnets in citric acid significantly enhanced the leaching process compared to conventional methods. – Selective extraction with D2EHPA produced mixed REE oxides of 99.9 % purity with iron oxide as a byproduct of 98.6 % purity. – The electrochemical process offered environmental and energy benefits.	(Kumari et al., 2021b)
Hydrochloric acid	Synthetic solution	Cyanex 572 /TBP	– The mixture of TBP and Cyanex 572 exhibited the synergistic effect for extracting HREEs from chloride solutions. – Slope analysis and FT-IR measurements confirmed the complex formation mechanism of extraction Er and Tb using TBP and Cyanex 572. – Cyanex 572 alone effectively extracted HREE, whereas TBP was ineffective.	(Dashti et al., 2021)
Nitric acid /Sulfuric acid	Mine tailings	Cyanex 923 /Hydrochloric acid	– A D2EHPA and Cyanex 923 blend enhanced overall extraction and minimizes iron co-extraction, solving a major REEs extraction challenge. – Cyanex 923 and TODGA were highly efficient in nitric acid, whereas D2EHPA and Cyanex 572 were effective across all acids. – Acidic extractants showed superior selectivity in REE recovery, while selective stripping with nitric acid or diluted hydrochloric acid effectively separated REEs from iron.	(Tunsu et al., 2019)
Citric acid	Synthetic solution	D2EHPA	– Higher D2EHPA concentration boosted Er, La, and Pr extraction from citric acid while increasing citric acid concentration reduced extraction efficiency. – Conditional extraction constants confirmed Er > La ≥ Pr, correlating with experimental results and validating effective extraction for these REEs. – In the organic phase, predominant species included [La(H_2Cit).2A(HA)], [Pr(H_2Cit).2A(HA)], and free cationic Er species Er^{3+}, extracted via D2EHPA.	(Mustafa et al., 2019)
Glycolic acid / Maleic acid /Ascorbic acid	NdFeB magnets	TBP / D2EHPA /Cyanex 272 /Cyanex 923 /TODGA	– Glycolic and maleic acids were superior to ascorbic acid for leaching REEs, achieving nearly complete dissolution. – Increasing acid concentration and temperature and reducing the	(Gergoric et al., 2019)

(*continued on next page*)

Table 1 (*continued*)

Leaching reagent	Source of REEs	Type of Extractants	Remarked results	Ref
			S/L ratio improved leaching efficiency. – TBP, Cyanex 272, and Cyanex 923 performed poorly in glycolic and maleic leachates, whereas TODGA selectively extracted REEs from the maleic leachate and D2EHPA effectively extracted from both leachates. – As nonpolar aliphatic diluents, Pentane and hexane significantly boosted extraction efficiency.	
Citric acid /Acetic acid	NdFeB magnets	D2EHPA	– Citric acid achieved ~100 % leaching efficiency for REEs within 24 h, while acetic acid at the same concentration leached over 95 % of the REEs. – D2EHPA exhibited a stronger affinity for Nd over Fe in both acetic and citric acid leachates, with particularly effective extraction observed in acetic acid.	(Gergoric et al., 2018)
Hydrochloric acid	Synthetic solution	Cyanex 272	– Lactic acid enhanced the extraction of REEs from chloride media with Cyanex272 by acting as a complexing agent, even at low concentrations. – Auxiliary agents like acetic acid, citric acid, and Titriplex III influenced the extraction process. – While acetic acid as an auxiliary agent increased efficiency, citric acid, and Titriplex III decreased it. – Titriplex III improved the	(Kashi et al., 2018)

Table 1 (*continued*)

Leaching reagent	Source of REEs	Type of Extractants	Remarked results	Ref
			separation factor and enhanced the REE separation process from other elements.	
Hydrochloric acid	Synthetic solution	D2EHPA /EHEHPA	– A mixture of EHEHPA and D2EHPA enhanced Nd extraction at 0.15 mol/L, and the highest efficiency was achieved at a lower concentration of Nd. – Nd complexation released 1–2 hydrogen ions and bound one D2EHPA dimer, while Y and Dy released 2–3 hydrogen ions and bound two extractant dimers. – Complexation involved extractant dimers, monomers, aggregated REE species, and REE chloride complexes.	(Mohammadi et al., 2015)

manufacturing (industrial scraps) (Yu et al., 2024).

REEs recovery can be accomplished through pyrometallurgical, hydrometallurgical, or combined methods. Pyrometallurgical methods (typically applied to industrial scraps and high-concentration wastes) involve high temperatures and energy consumption, which present significant environmental challenges (Truong et al., 2023). In contrast, hydrometallurgical methods offer a greener alternative with lower energy consumption and the flexibility to tailor processes for NdFeB waste, resulting in high-purity products (Astuti et al., 2023; Rahmati et al., 2024a). Most hydrometallurgical studies have concentrated on direct leaching (Bandara et al., 2016) or roasting followed by leaching (Ho-Sung, 2003) of permanent magnets using inorganic acids such as sulfuric and hydrochloric acids, as well as organic acids like citric, formic, and acetic acids (Belfqueh et al., 2023; Gergoric et al., 2018; Reisdörfer et al., 2019). Recent advancements have highlighted a growing preference for organic acids as leaching agents over mineral acids. Organic acids are favored due to their enhanced controllability, lower hazard levels, and reduced emission of toxic gases (Belfqueh et al., 2023; Stein et al., 2022).

Solvent extraction (SX) is one of the most important and effective techniques for separating REEs (Traore et al., 2023). Many studies have utilized various extractants to separate REEs from different aquas media. Table 1 highlights some previous studies on REE separation using the SX process.

Neutral extractants such as N,N,N′,N′-tetraoctyl diglycolamide (TODGA), Cyanex 923, and tributyl phosphate (TBP) have effectively extracted REEs selectively. These extractants can be employed individually or in combination with others. In some instances, combining neutral and acidic extractants has shown a significant synergistic effect, improving extraction efficiency and selectivity. The nature of the

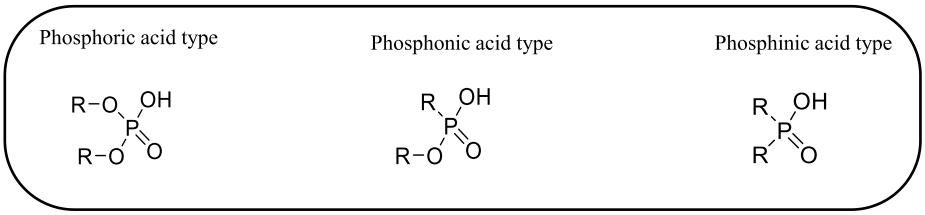


Fig. 1. Three main categories of acidic extractants.

leachate and extraction media also plays a crucial role in determining extraction outcomes. As a result, studies have focused on evaluating the performance of extractants in organic and inorganic leachate media. Leaching metals with organic acids often results in the formation of complexes that improve the extraction process. Furthermore, organic acid leachates do not cause saponification of organophosphorus acidic extractants, thus avoiding complications during the stripping stage (Erust et al., 2021; Zhang et al., 2022).

Organophosphorus acids, such as di (2-ethylhexyl) phosphoric acid (D2EHPA), Cyanex 272, and PC88A, are highly regarded for their extensive use and commercialization in industry. These extractants selectively separate REEs through a cation exchange mechanism (Zhang et al., 2020), enabling them to extract metals from the aqueous phase with greater efficiency than anionic and neutral extractants (Botelho Junior et al., 2023; Merroune et al., 2024). D2EHPA, in particular, has been a key player in REE separation since 1960 (Zhang et al., 2022). Acidic extractants can be categorized based on their chemical structure into three groups (Fig. 1): phosphoric, phosphonic, and phosphinic acids. The unique structural features of each group influence their extraction properties and selectivity. The metal extraction process relies on the formation of coordination bonds between the free electrons of oxygen in these acids and the metal ions or complexes (Merroune et al., 2024; Xie et al., 2014; Yudaev et al., 2021).

Numerous studies have examined how various parameters, including extractant concentration, type of diluent, and pH, affect the extraction efficiency of REEs (Ni'am et al., 2020; Pradhan et al., 2020; Quinn et al., 2015). After the extraction process, the loaded organic phase releases the metal when it comes into contact with a stripping agent, which causes the metal to either dissolve into the aqueous phase or precipitate out. Stripping agents can be strong mineral acids or organic acids. Once the stripping process is complete, the organic phase can be reused in the extraction cycle (Rahmati et al., 2024b).

While prior research has primarily focused on REE extraction from synthetic solutions or mineral acid leachates, this study uniquely examines the selective extraction of REEs from citrate-based leach solutions (an environmentally friendly alternative) derived from recycled NdFeB magnets with D2EHPA. Conducted as part of the INSPIREE project, the first EU industrial plant for REE recovery from spent NdFeB magnets, this work investigates a range of extractants (D2EHPA, Cyanex 272, and Cyanex 572) and diluents (n-heptane, kerosene) to determine optimal conditions for both efficiency and selectivity in REE extraction. Additionally, this study provides a novel analysis of the chemical mechanisms underlying REE-citrate complex extraction with D2EHPA, showing how ionic radius and equilibrium pH conditions influence the separation of LREEs and HREEs. These findings suggest a multistage extraction approach to address challenges in REE separation. Furthermore, this research completes recycling by recovering REEs as REE oxides, supporting sustainable NdFeB magnet recycling.

2. Materials and methods

2.1. Materials

The end-of-life NdFeB magnet sourced from spent hard disk drives (HDDs) served as the input material for the leaching phase. Citric acid

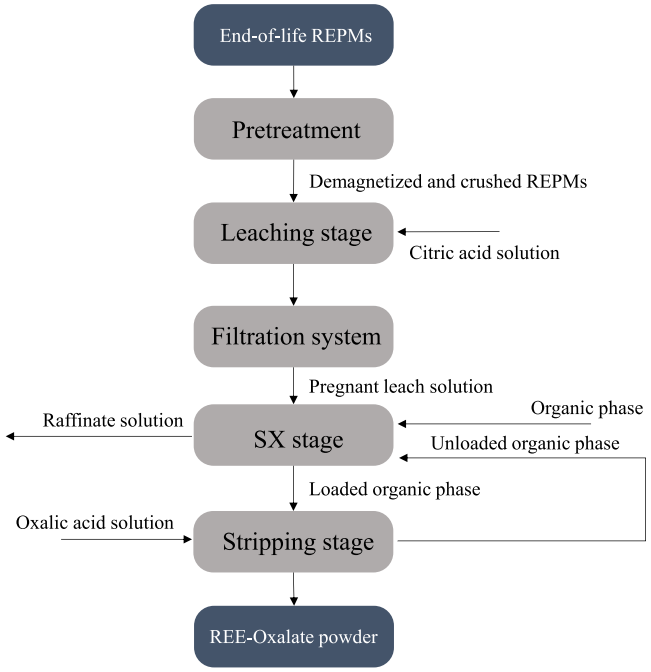


Fig. 2. The flow diagram of the hydrometallurgical approach to recover REEs from end-of-life NdFeB magnets.

(Sigma-Aldrich Co., Austria) was dissolved in distilled water to form the leaching solution.

In the solvent extraction experiments, analytical grade D2EHPA (Thermo Scientific Co.), bis (2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272, Cytec Co.), and a blend of phosphonic and phosphinic acids (Cyanex 572, Cytec Co.) were used as the extractants.

Analytical-grade n-heptane (AppliChem Co., Germany) and kerosene (Carlo Erba Reagents group, Italy) served as diluents to prepare the organic phase. All extractants and diluents were used without additional purification or pre-treatment. A precipitation stripping stage was conducted by adding an oxalic acid solution (SIGMA-Aldrich, USA) to recover REEs from the loaded organic phase.

2.2. Experimental design

Fig. 2 illustrates the stages employed in this study to recover REEs from end-of-life NdFeB magnets. The recovery process consists of three main stages: leaching, extraction and purification, and precipitation stripping.

2.2.1. Leaching stage

According to previous investigation on the leaching of NdFeB magnets with citric acid (Romano et al., 2023; Romano et al., 2024), a 1.45 M citric acid solution was introduced to the demagnetized and crushed NdFeB magnet sample with a solid content of 10 %. The mixture was agitated for 3 h using an orbital rotary shaker at ambient temperature. Following the leaching stage, a vacuum filtrate system was

Table 2
The investigated parameters and their levels at the solvent extraction stage.

Parameter	Type (Unit)	Levels/Type								
Extractant type	Categorical	D2EHPA				Cyanex 272		Cyanex 572		
Diluent type	Categorical	n-Heptane				Kerosene				
Extractant concentration	Numeric (% v/v)	10		25		40		50		
O/A phase ratio	Numeric (v/v)	0.5		1.0		1.5		2.0		
Equilibrium pH	Numeric	0.5	0.9	1.7	2.3	3.0	3.5	4.0	5.0	5.7
Contact time	Numeric (Min)	2	5	7	10	15	20	30	40	50

Table 3
The concentration of elements presented in the NdFeB magnet sample and resulting PLS at the leaching stage.

	Fe	Light REEs		B	Heavy REEs		
		Nd	Pr		Dy	Tb	Y
NdFeB magnet sample	64.4 %	20.3 %	4.3 %	0.9 %	2.8 %	0.3 %	0.1 %
PLS	37.804 g/L	12.342 g/L	2.487 g/L	507.92 mg/L	1.976 g/L	227.54 mg/L	81.88 mg/L

employed to separate PLS from leaching residue. To improve dissolving efficiency and neutralize the pH of the leaching residue, 30 % washing water (distilled water) was used. The combined primary and wash solution were subjected to the solvent extraction stage. Metal concentrations in the resulting PLS were measured using inductively coupled plasma-optical emission spectrometry (ICP-OES, Agilent model:5100).

2.2.2. Solvent extraction stage

At the solvent extraction stage, the obtained PLS was reacted with the organic phase to separate REEs. The aqueous and the organic phases were placed in a glass flask and mixed using an orbital rotary shaker at 250 rpm. Following the mixing step, the mixture of phases was introduced to a separation funnel with a retention time of 20 min to separate the loaded organic phase from the raffinate solution. The metal concentrations in the resulting raffinate solutions were determined using the ICP-OES instrument. In this research, the effects of various chemical and operational parameters on the extraction of REEs from citrate-base PLS, including the composition of the organic phase (types of extractants and diluents, along with extractant concentration), the volume ratio of the organic phase to aqueous phase (O/A phase ratio), contact time, and the pH of the aqueous phase, were investigated. Table 2 shows the investigated parameters and their respective levels in the solvent extraction experiments.

The metal extraction efficiency (E) and distribution coefficient (D) at this stage were calculated using Eqs. 1 and 2, respectively (Tunsu et al., 2019). Additionally, to estimate the extraction efficiency from the distribution coefficient, Eq. 3 can be employed (which is derived from Eqs. 1 and 2) (Gharabaghi et al., 2013).

$$E_i = 100 * \frac{(l_i - r_i)}{l_i} \quad (1)$$

$$D_i = \frac{O_i}{r_i} = \frac{(l_i - r_i)}{r_i} \quad (2)$$

$$E_i = 100 * \frac{D_i}{D_i + 1} \quad (3)$$

where l_i, r_i, and o_i represent the concentration of interesting element (i) in the leach, raffinate, and loaded organic phases, respectively.

2.2.3. Metals recovery stages

To recover the extracted REEs in the precipitation stripping stage, a 0.75 M oxalic acid solution was introduced to the loaded organic phase (O:A of 1:2) (Rahmati et al., 2024b). The phases were thoroughly mixed for 45 min at a stirring rate of 150 rpm to ensure optimal interaction. Subsequently, the mixture of phases was subjected to a separation funnel, allowing for the separation of the unloaded organic phase (retention time of 20 min). The REEs-oxalate powder was then collected using a vacuum filtration system and subsequently dried in an oven at 90 °C for 24 h.

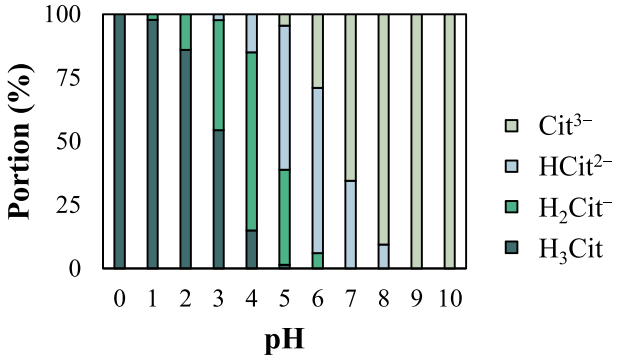


Fig. 3. The portion of citrate species via solution pH.

3. Results and discussion

The demagnetized and crushed NdFeB magnets were subjected to a leaching process with a citric acid solution. Table 3 presents the concentrations of metals in the NdFeB magnet sample and in the resulting PLS (which consists of a mixture of main and wash solutions). The results indicate that the dissolution efficiencies for Fe, B, light REEs, and heavy REEs were 76.3 %, 73.4 %, 78.4 %, and 92.8 %, respectively. The following equations show the three stages of citric acid (H_3Cit) dissociation in both acidic and neutral solutions (Burdzy et al., 2022; Younesian-Farid and Sadeghnejad, 2020):

$$H_3Cit \leftrightarrow H_2Cit^- + H^+, \quad K_{a1} = 7.4 \times 10^{-4} \quad (4)$$

$$H_2Cit^- \leftrightarrow HCit^{2-} + H^+, \quad K_{a2} = 1.7 \times 10^{-5} \quad (5)$$

$$HCit^{2-} \leftrightarrow Cit^{3-} + H^+, \quad K_{a3} = 4.0 \times 10^{-7} \quad (6)$$

Fig. 3 shows the distribution of citrate species at various pH levels (Ji et al., 2022; Olvera-Venegas et al., 2017). Since the pH of the resulting PLS was 3.2, the probabilities of the citrate species present are as follows: H_3Cit (citric acid) at 44 %, H_2Cit^- (monoprotonated citrate) at 52 %, and $HCit^{2-}$ (deprotonated citrate) at 4 %. Consequently, chelating and dissolution of REEs by citric acid can occur according to the following equations (Gergoric et al., 2018; Ke et al., 2020; Kumari et al., 2021a; Reisdörfer et al., 2019; Wan et al., 2024):

$$REE^{3+} + H_3Cit \leftrightarrow REEH_2Cit^{2+} + H^+ \quad (7)$$

Table 4
Extraction efficiency of the solvent extraction stage using various extractants and diluents (50 % extractant concentration and equal aqueous to organic volume ratio).

Run	Extractant type	Diluent type	Extraction efficiency (%)						
			Nd	Pr	Dy	Tb	Y	Fe	B
1	D2EHPA	n-Heptane	88.7	87.7	99.8	99.6	99.7	27.8	2.0
2	Cyanex 272	n-Heptane	0.0	7.1	48.1	35.8	66.4	7.6	5.3
3	Cyanex 572	n-Heptane	13.9	13.2	98.2	97.0	97.8	7.4	1.9
4	D2EHPA	Kerosene	91.7	93.1	99.7	99.3	100.0	36.1	6.3
5	Cyanex 572 and D2EHPA (1:1)	n-Heptane	89.0	90.6	98.0	92.0	94.7	59.9	0.0
6*	D2EHPA	n-Heptane	84.9	86.0	1.3	1.4	2.1	81.1	7.4

* Two-stage extraction: the raffinate of run #3 was used as the feed of the second stage

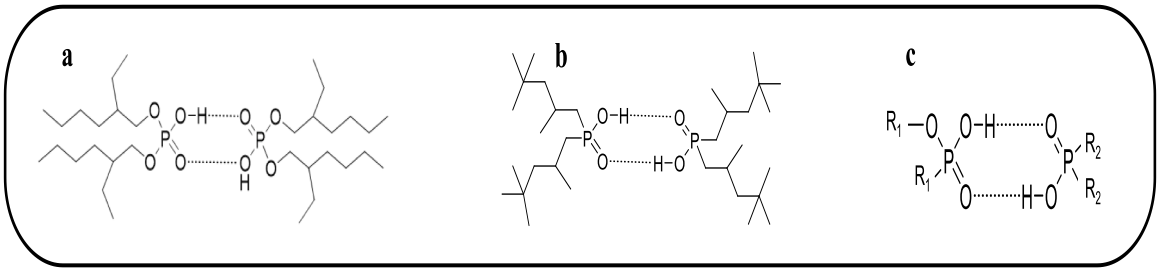


Fig. 4. The chemical structure of D2EHPA (a), Cyanex 272 (b), and Cyanex 572 (c).

$$REE^{3+} + H_3Cit \leftrightarrow REEHCit^{+} + 2H^{+} \quad (8)$$

$$REE^{3+} + H_3Cit \leftrightarrow REECit + 3H^{+} \quad (9)$$

$$REE^{3+} + H_3Cit \leftrightarrow REEH_3Cit^{3+} \quad (10)$$

Furthermore, the resulting solution was significantly enriched in iron (37.8 g/L), while the total concentrations of light and heavy REEs were 14.829 g/L and 3.022 g/L, respectively. This underscores the need for a selective extraction process to effectively separate REEs and facilitate the production of purified products. Consequently, a solvent extraction stage was implemented to concentrate and purify the obtained solution. In the following sub-sections, the effects of various chemical and operational parameters on REEs extraction, as well as the mechanism involved in the extraction of these metals using D2EHPA, were evaluated.

3.1. Organic phase composition

A series of solvent extraction experiments were carried out to assess the influence of organic phase composition on the separation efficiency of REEs, Fe, and B from the citrate leach solution. To evaluate this effect, various cationic extractants (D2EHPA, Cyanex 272, and Cyanex 572) and diluents (n-Heptane and kerosene) were used to prepare the organic phase. Cationic extractants, such as organophosphorus acids, glycol amide acids, and carboxylic acids, are known to outperform anionic and solvating extractants in REE separation, especially at pH levels below 6 (He et al., 2021). All experiments (presented in Table 4) were conducted in parallel to evaluate the influence of varying extractants and diluents on the REE extraction. The experimental conditions were kept constant, featuring an organic-to-aqueous phase ratio of 1:1, an extractant concentration of 50 %, and an extraction time of 20 min.

Table 4 illustrates the effect of the investigated extractants and diluents on the extraction efficiency of Fe, light REEs (Nd and Pr), heavy REEs (Dy, Y, and Tb), and B. Among the extractants, Cyanex 572 and D2EHPA (runs #1 and #3) achieved high extraction efficiencies for heavy REEs, approximately 98 % and 100 %, respectively. In contrast, the extraction efficiencies for light REEs differed significantly: D2EHPA obtained ~ 89 %, while Cyanex 572 achieved only ~ 14 %.

Cyanex 272 exhibited poor extraction capability compared to the other extractants for both heavy and light REEs (run #2). The varying extraction efficiencies can be attributed to the chemical properties of these components. Fig. 4 shows the chemical structure of investigated extractants (Belova et al., 2021; Fan et al., 2021; He et al., 2021). Cyanex 572, a commercial extractant from CYTEC Industries Inc., is a proprietary blend of phosphinic and phosphonic acids with an undisclosed alkyl group composition (Agarwal et al., 2018; Nazari et al., 2018; Tunsu et al., 2016). The primary distinction among these extractants lies in their structure's number of oxygen atoms.

The high electronegativity of oxygen enhances cation exchange and strengthens coordination with metal cations, thereby improving extraction efficiency. As oxygen atoms increase, cation exchange becomes more efficient, leading to better extraction performance (Anisyabana et al., 2021; Pusparini et al., 2021). Additionally, the structure and properties of the substituted alkyl group in the extractant significantly impact its efficiency. Longer alkyl chains enhance extraction by increasing solubility in the organic phase, improving electron-donating capabilities, and reducing dimerization of the extractant molecules (Batchu et al., 2021; Kolařík and Pankova, 1966).

Branched chains, on the other hand, can introduce steric hindrance, reducing their capacity and overall extraction efficiency (Batchu et al., 2021). Furthermore, research shows that alkyl substitutions at the α and β carbon positions affect extraction efficiency, with ethyl groups at these positions having a stronger effect than methyl groups (Du et al., 2016). Consequently, D2EHPA exhibits higher extraction efficiency than both Cyanex 572 and Cyanex 272, attributable to its greater number of oxygen atoms and a more linear structure and ethyl substituent in the β position. Similarly, Cyanex 572 outperforms Cyanex 272 for the same reasons.

Given the promising results obtained with D2EHPA and Cyanex 572, the synergistic effect of these extractants was also evaluated (run #5). It was observed that while a slight improvement in the extraction of Nd and Pr occurred, a significant increase in the iron extraction was noted under these conditions. This enhancement in iron extraction resulted in a decrease in the selectivity of the overall extraction process.

The low extraction efficiency of Cyanex 272 and Cyanex 572 in recovering light REEs (Nd and Pr) and the superior results achieved with D2EHPA for extracting REEs have been reported by other researchers (Dashti et al., 2021; Larochelle et al., 2022; Pavon et al., 2018; Seyyed Alizadeh Ganji et al., 2016). Additionally, boron could not be

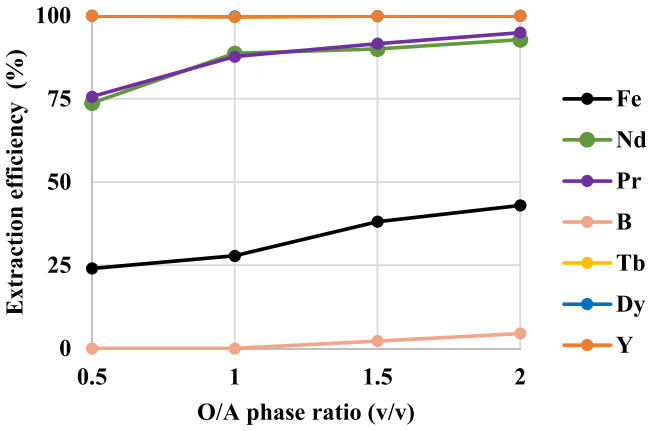


Fig. 5. Effect of A/O phase ratio on metal extraction efficiency.

meaningfully extracted from the PLS using these extractants. As a result, almost all of the boron, along with most of the iron ions, were transferred to the raffinate solution during the solvent extraction stage, necessitating further separation processes.

The results from runs #1 and #4 highlight the effect of using n-heptane (C_7H_{16}) and kerosene (C_nH_{2n+2}, where $9 < n < 17$) as diluents at this stage. The extraction efficiency for heavy REEs with both diluents was nearly identical, reaching approximately 100 %. However, when kerosene was used instead of n-heptane, the extraction efficiency for Pr and Nd improved from 87.7 % to 93.1 % and from 88.7 % to 91.7 %, respectively.

Kerosene also resulted in a higher extraction of Fe and B from the PLS, which reduced the selectivity for REEs extraction due to interference from these barrier ions. The improved extraction efficiency observed with kerosene, in conjunction with n-heptane, can be attributed to enhanced intermolecular interactions between D2EHPA and kerosene. As the hydrocarbon chain length of the solvent increases, the contact area between the hydrocarbon chains of D2EHPA and the solvent becomes more extensive. This leads to more effective interactions, enhancing D2EHPA's miscibility and dispersion in the solvent, and ultimately resulting in improved extraction efficiency (Srirachat et al., 2017).

Although separating light and heavy REEs was not the primary aim of this research, a two-stage extraction experiment was conducted. In the first stage, Cyanex 572 was used to extract heavy REEs, followed by D2EHPA in the second stage to recover light REEs (runs #3 and #6). The results demonstrated that this two-stage solvent extraction effectively separated these two categories of REEs. However, it also led to significant iron extraction during the second stage (along with the light REEs), necessitating a complex process to remove iron from the final products of Nd and Pr.

3.2. *Effect of O/A ratio*

To evaluate the effect of the organic to aqueous (O/A) phase ratio on the extraction efficiency of REEs, boron, and iron from citrate-based PLS derived from spent NdFeB magnets, experiments were performed using O/A ratios of 0.5, 1.0, 1.5, and 2.0 (Fig. 5). Throughout these experiments, the D2EHPA-to-n-heptane ratio was held constant at 1:1, with a mixing rate of 250 rpm, and contact time of 20 min to ensure consistent conditions across trials.

Increasing this O/A phase ratio from 0.5 to 1.0 improved Nd and Pr extraction efficiency from 73.8 % to 88.8 % and 75.6–87.7 %, respectively. However, further enhancing the ratio beyond 1.0 (up to 2.0) did not significantly change the extraction efficiency for Nd (~90.5 %) and Pr (~91.5 %). Furthermore, raising the O/A phase ratio from 0.5 to 2.0 enhanced the iron extraction from 24.1 % to 43.2 %. On the other hand, varying the O/A phase ratio in the range of 0.5–1.5 had a minimal

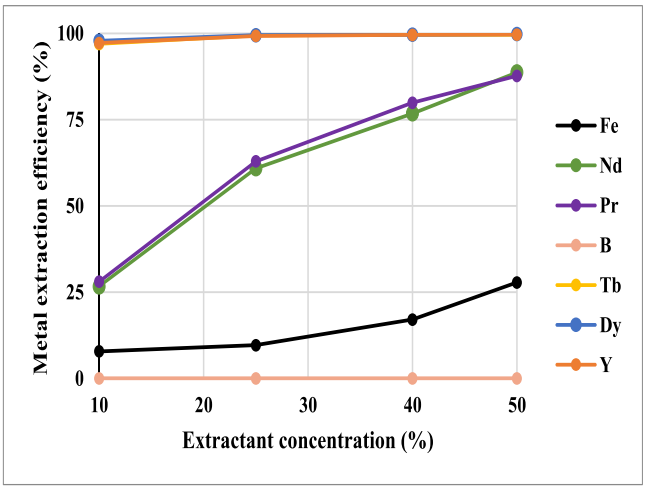


Fig. 6. The effect of extractant concentration on metal extraction efficiency.

impact on the extraction rates of Y, Dy, Tb, and B, with heavy REEs maintaining nearly 100 % extraction and B remaining negligible. The improvement in light REE extraction at a higher O/A phase ratio is likely due to increased extractant loading capacity and more effective phase mixing.

3.3. *Effect of extractant concentration*

Four experiments were conducted to examine the influence of the extractant concentration ranging from 10 % to 50 % on the extraction efficiency of REEs, iron, and boron from the PLS of NdFeB magnets during the solvent extraction stage. An organic phase with more than 50 % D2EHPA exhibits elevated viscosity, which adversely impacts the extraction process in two key ways: (1) it reduces mass transfer efficiency by hindering the mixing of the organic and aqueous phases during extraction, and (2) it prolongs phase separation in the settler step, thereby diminishing overall process efficiency. On the other hand, initial experiments showed that using an organic phase with less than 10 % D2EHPA resulted in extraction efficiencies for Nd and Pr below 25 %, making the process economically unviable due to insufficient recovery of these critical elements. Fig. 6 illustrates the effect of this parameter on the extraction efficiency of these elements, conducted under conditions where the O/A ratio and D2EHPA/n-heptane ratio were set to 1, with a contact time of 20 min.

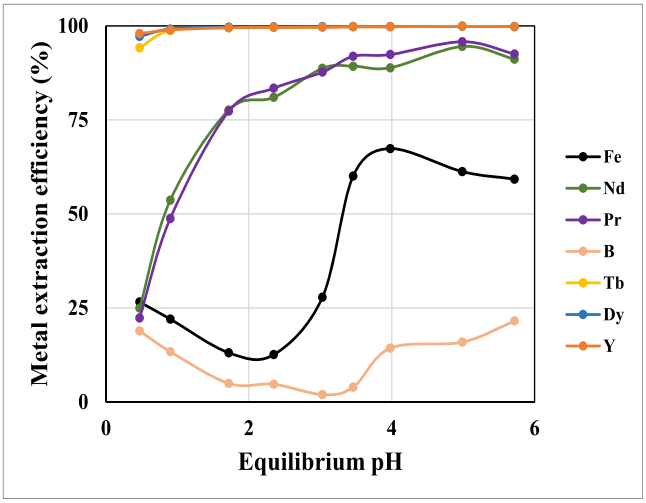


Fig. 7. The effect of the equilibrium pH on the metal extraction.

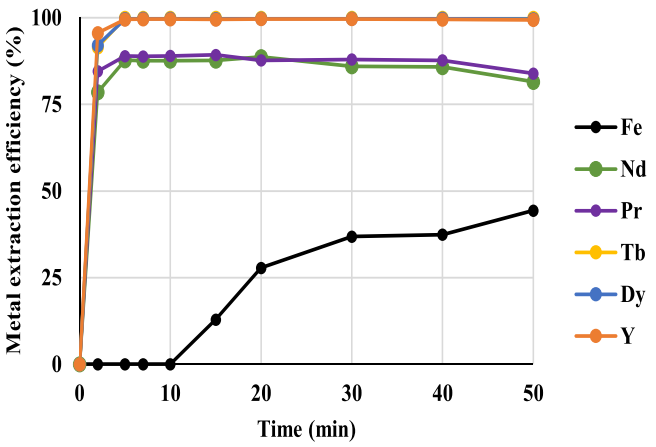


Fig. 8. The extraction efficiency of metals by D2EHPA (A/O:1 and 50 % concentration).

The results indicated that within the investigated range of extractant concentration, nearly all Y, Dy, and Tb were consistently from the PLS, underscoring D2EHPA's high extraction capability for these metals. Conversely, increasing the extractant concentration from 10 % to 50 % notably enhanced the extraction efficiency of Nd, Pr, and Fe, which rose from 26.7 % to 88.7 %, 20.0–87.7 %, and 7.8–27.8 %, respectively. This increase in the extraction efficiency of Nd, Pr, and Fe with higher extractant concentration is likely due to the enhanced loading capacity of the organic phase. In addition, minimal boron extraction suggests that D2EHPA selectively separates REEs from boron ions.

3.4. pH equilibrium

Experiments conducted across a range of pH levels in the aqueous phase elucidated the influence of the pH (i.e., protons concentration) in the PLS on metal extraction efficiency and selectivity during the solvent extraction stage (Fig. 7). The results show that an equilibrium pH above 0.9 enables nearly complete extraction (approximately 100 %) of Dy, Y, and Tb, underscoring the high extractive capacity of D2EHPA for these metals, even at low pH values. Moreover, enhancing the equilibrium pH from 0.5 to 5.0 markedly increased the extraction efficiencies for Nd from 24.9 % to 94.5 % and Pr from 22.3 % to 95.8 %. This correlation aligns with the mechanism of D2EHPA, which releases H^+ ions upon metal extraction, thus lowering solution pH and potentially decreasing extraction efficiency in more acidic environments (Laguel and Samar, 2024; Li et al., 2023).

Iron separation efficiency also exhibited notable pH sensitivity, fluctuating between 12 % and 25 % at an equilibrium pH below 3, but rising sharply as pH increased. In contrast, boron extraction remained relatively low (under 20 %) across the entire pH range, reflecting D2EHPA's selectivity for REEs over boron.

While this study does not directly address the separation of heavy and light REEs, the findings suggest that sequential solvent extraction using varied PLS pH conditions could serve as a viable strategy for differentiating these REE groups.

3.5. The effect of contact time

A series of experiments were conducted at extraction times of 2, 5, 7, 10, 15, 20, 30, 40, and 50 min to evaluate the effect of contact time on the extraction efficiency of D2EHPA for REEs and Fe (Fig. 8). In these experiments, the O/A ratio was maintained at 1, the extractant concentration was at 50 % (using n-heptane as a diluent), and the stirring rate was at 250 rpm.

The results showed that the extraction of REEs peaked within the first 5 min, reaching a maximum that remained stable through 50 min of contact time. During this period, extraction efficiencies for heavy REEs (Tb, Dy, and Y) approached 100 %, while light REEs (Nd and Pr) reached approximately 88 %.

In contrast, Fe extraction was minimal within the initial 10 min but increased significantly, reaching 44.4 % after 50 min. This limited early extraction is likely due to the slow kinetics associated with D2EHPA's iron extraction process. While D2EHPA is effective for iron extraction, studies indicate that it requires extended time to reach equilibrium (Ciceri et al., 2014; Grigorieva et al., 2023; Yang et al., 2014). Furthermore, the presence of hydrated iron-citrate complexes, such as $[Fe2(Cit)_2(H_2O)_2]^{2-}$ and $[Fe_9O(Cit)_8(H_2O)_3]^{7-}$, at acidic pH slows down extraction. These complexes are stabilized by hydration, reducing their availability for coordination with D2EHPA (Silva et al., 2009), limiting the ion-exchange process and lowering the extraction rate (Sato et al., 1985). These findings indicate that for selective separation of REEs from PLS in the presence of Fe, the extraction time should ideally be kept

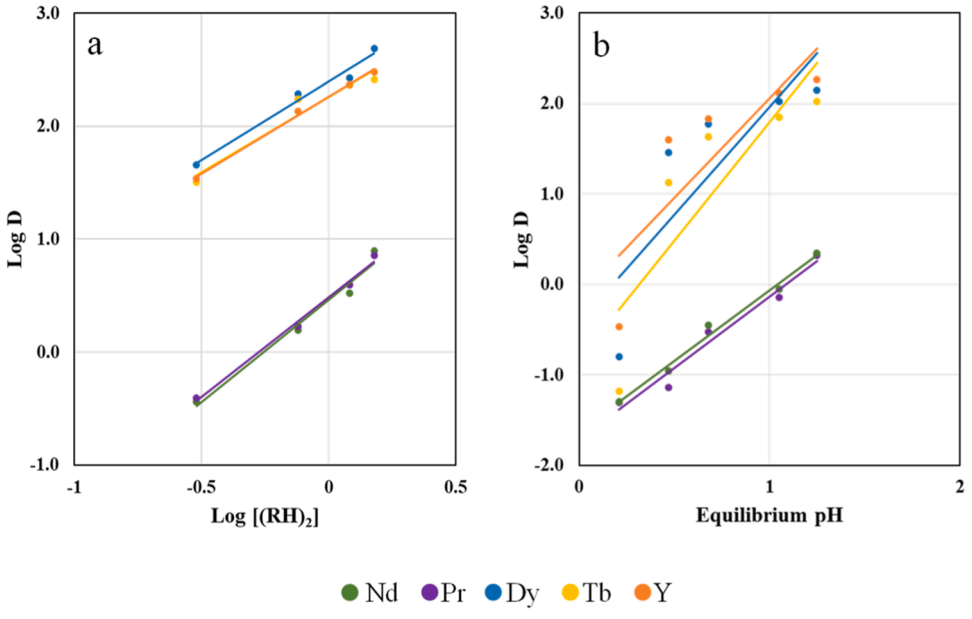


Fig. 9. The plot of the logarithm of distribution vs a: logarithm extractant concentration and b: equilibrium pH.

Table 5
The slopes of log D vs equilibrium pH and [(RH)2] for studied metals.

Element	Log D vs. $[(RH)_2]$		Log D vs. equilibrium pH	
	Slope (m)	R^2	Slope (S)	R^2
Nd	1.8	0.98	1.6	0.99
Pr	1.8	0.99	1.6	0.97
Dy	1.4	0.98	2.4	0.69
Y	1.3	0.94	2.2	0.70
Tb	1.4	0.99	2.6	0.71

below 10 min to achieve efficient REE recovery while minimizing Fe co-extraction.

3.6. Mechanisms of extraction of REEs from citrate leachate solution

The extraction mechanisms of light and heavy REEs from citrate solutions were found to be complex and depend on various factors, including the chemical properties of the REEs, the structure of the citrate complexes, and the nature of the extractant used. In the case of NdFeB magnet recycling, citrate acts as a chelating agent that forms stable complexes with REEs during the leaching process. Once formed, these complexes can be extracted by D2EHPA, but extraction efficiency depends significantly on the specific REE, the concentration of citrate, and the pH of the solution. It should be noted that the presence of various interfering ions in the citrate PLS derived from spent NdFeB magnets makes the REEs extraction mechanisms by D2EHPA (RH) more complex than in synthesized solutions. Building on Eqs. 7 to 10, the general extraction equation for REEs is expressed in Eq. 11, allowing the equilibrium constant (K) to be calculated using Eq. 12 (Mohammadzadeh et al., 2022). It should be noted that RH forms as a dimer in non-polar solvents, such as n-heptane and kerosene. Due to the absence of hydrogen donor or acceptor groups in these solvents, there is minimal interaction between the extractant and the solvent molecules, prompting D2EHPA to stabilize through self-association and form dimers (Kolarik, 2010).

$$(REEH_s\mathrm{Cit})^{s+} + m\ (RH)_2 \rightleftarrows [(REEH_s\mathrm{Cit}.R_s(RH)_{2m-s}] + s\ H^+ \quad (11)$$

$$K = \frac{[(REEH_s\mathrm{Cit}.R_s(RH)_{2m-s}] \times [H^+]^s}{[(REEH_s\mathrm{Cit})^{s+}] \times [(RH)_2]^m} \quad (12)$$

where s represents the number of protons released from the ionization of citric acid during the leaching stage (ranging from 0 to 3).

The following equations can be achieved by linearization of Eq. 12:

$$\mathrm{Log}K = \log \frac{[(REEH_s\mathrm{Cit}.R_s(RH)_{2m-s}]}{[(REEH_s\mathrm{Cit})^{s+}]} + s\log[H^+] - m\log[(RH)_2] \quad (13)$$

$$\mathrm{Log\ D} = \mathrm{Log}K + spH + m\log[(RH)_2] \quad (14)$$

The values of s and m for each REEs element can be determined by plotting the results of Log D against equilibrium pH and Log $[(RH)_2]$, respectively (Fig. 9) (Song et al., 2020; Zhu et al., 2021). The values of m and s are crucial for assessing the extraction mechanisms of REEs using D2EHPA. The slopes and corresponding R^2 values for the fitted lines of each element are shown in Table 5.

Based on these results and Eq. 11, the average extraction process for all studied elements with D2EHPA can be represented by the following equations:

$$(NdH_{1.6}\mathrm{Cit})^{1.6+} + 1.8\ (RH)_2 \rightleftarrows [(NdH_{1.6}\mathrm{Cit}.R_{1.6}(RH)_2] + 1.6\ H^+ \quad (15)$$

$$(\mathrm{Pr}H_{1.6}\mathrm{Cit})^{1.6+} + 1.8\ (RH)_2 \rightleftarrows [(\mathrm{Pr}H_{1.6}\mathrm{Cit}.R_{1.6}(RH)_2] + 1.6\ H^+ \quad (16)$$

Table 6
The equilibrium constant of extracting REEs from citrate PLS by D2EHPA at a pH of 3.2.

	Nd	Pr	Dy	Y	Tb
K	5.28×10^{-5}	4.80×10^{-5}	3.29×10^{-3}	1.73×10^{-3}	2.04×10^{-3}

$$(DyH_{2.4}\mathrm{Cit})^{2.4+} + 1.4\ (RH)_2 \rightleftarrows [(DyH_{2.4}\mathrm{Cit}.R_{2.4}(RH)_{0.4}] + 2.4\ H^+ \quad (17)$$

$$(YH_{2.2}\mathrm{Cit})^{2.2+} + 1.3\ (RH)_2 \rightleftarrows [(YH_{2.2}\mathrm{Cit}.R_{2.2}(RH)_{0.4}] + 2.2\ H^+ \quad (18)$$

$$(TbH_{2.6}\mathrm{Cit})^{2.6+} + 1.4\ (RH)_2 \rightleftarrows [(TbH_{2.6}\mathrm{Cit}.R_{2.6}(RH)_{0.2}] + 2.6\ H^+ \quad (19)$$

As the leaching stage of NdFeB magnets with citric acid produces a mixture of REEs-citrate complexes, the resulting extraction equations reflect an averaged behavior of these species. Extraction mechanisms differ between light REEs (Nd and Pr) and heavy REEs (Dy, Tb, Y). For instance, Eq. 17 suggests that the primary complex for Dy is $(DyH_3\mathrm{Cit})^{3+}$, with lower amounts of $(DyH_2\mathrm{Cit})^{2+}$ and $(DyHCit)^{+}$ also formed during the dissolving stage. According to Fig. 3, the citrate species distribution at pH 3.2 consists of $(H_3\mathrm{Cit})$, $(H_2\mathrm{Cit})^{-}$, and $(HCit)^{2-}$, contributing 44 %, 52 %, and 4 % to the total composition, respectively. The weighted average net charge of the system is −0.6, supporting these findings.

The linear fit of log D versus equilibrium pH for heavy REEs such as Dy, Y, and Tb yielded an R^2 value of approximately 0.7. This deviation from ideal linearity likely stems from the low concentrations of these elements in solution, coupled with their near-complete extraction at low pH, which amplifies minor variations in pH. Additionally, the similar ionic radii of these heavy REEs may contribute to inter-element interactions, further influencing the correlation.

For light rare earth elements such as Nd^{3+} and Pr^{3+}, the predominant citrate complex in solution was typically mono- or di-citrate species (e.g., $NdH_{1.6}\mathrm{Cit}^{1.6+}$). The larger ionic radii of LREEs (Nd^{3+}: 0.995 Å, Pr^{3+}: 1.01 Å) resulted in less stable complexes with citrate, making these elements less compatible with the organic phase. Therefore, higher concentrations of D2EHPA were required for effective extraction. In contrast, heavy rare earth elements such as Dy^{3+}, Tb^{3+}, and Y^{3+} formed more stable citrate complexes (e.g., $DyH_{2.4}\mathrm{Cit}^{2.4+}$) due to their smaller ionic radii (Dy^{3+}: 0.908 Å, Tb^{3+}: 0.923 Å, Y^{3+}: 0.900 Å) (Kinraide and Yermiyahu, 2007)). This size disparity makes LREEs more incompatible and concentrated in the continental crust than HREEs (Battsengel et al., 2018; Gergoric et al., 2017).

The extraction process was highly dependent on the pH of the solution. During the leaching stage, citric acid released protons, leading to protonated REE-citrate complexes that were more soluble and thus easier to extract. Experimental results showed that increasing the pH improved the extraction efficiency, likely due to reduced proton competition and enhanced interaction between the REE-citrate complexes and D2EHPA. As a cationic extractant, D2EHPA exchanges hydrogen ions in the organic phase with the REE ions in the aqueous phase, facilitating the transfer of REEs into the organic phase. This finding highlighted the importance of pH control as a critical parameter in maximizing the recovery efficiency of both LREEs and HREEs.

Based on the equations achieved, the interaction between the REE-citrate complexes and D2EHPA in the organic phase was governed by the ion exchange mechanism. D2EHPA acted as an extractant, forming complexes with the REEs, but this interaction varied among the REEs studied. The equilibrium constant for REE extraction (Eqs. 15–19) at pH 3.2 and 50 % D2EHPA concentration are presented in Table 6, with HREEs exhibiting significantly higher equilibrium constant values than LREEs. This difference can be attributed to (1) stronger complex

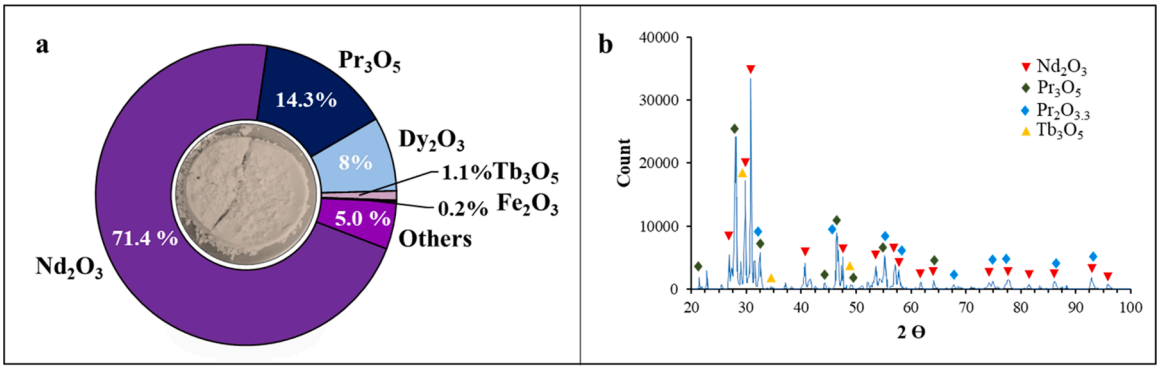


Fig. 10. (a) Composition and (b) XRD pattern of the obtained REE-oxide.

formation of HREEs due to smaller ionic radii, higher electronegativity, and lower polarizability (Alizadeh et al., 2021; José and Ladeira, 2021) and (2) greater thermodynamic favorability of HREE extraction, as indicated by a more negative Gibbs free energy compared to LREEs (Arellano Ruiz et al., 2020; Pereira et al., 2019; Udawattha, 2020).

In summary, the extraction mechanisms for light and heavy REEs differed significantly due to their distinct ionic properties, complexation tendencies, and thermodynamic behavior. The differences in ionic radii, complex stability, and extraction efficiency underscored the importance of tailoring extraction conditions, such as pH and extractant concentration, to achieve selective and efficient recovery of REEs from citrate solutions in recycling NdFeB magnets. This understanding of the distinct extraction behaviors of LREEs and HREEs contributed to the optimization of the recycling process for more selective REE recovery.

Furthermore, the varying extraction behaviors of HREEs and LREEs indicate that employing a multi-step extraction process with optimized conditions could increase selectivity. As illustrated in Fig. 9, lowering the D2EHPA concentration in the organic phase slightly increases the separation between the distribution ratios of HREEs and LREEs, while raising the pH greatly expands this gap. These observations suggest optimization opportunities for achieving more selective REE recovery.

3.7. Recovering REEs

To recover REEs in the precipitation stripping stage, an oxalic acid solution was added to the loaded D2EHPA obtained from the extraction stage (Rahmati et al., 2024b). The resulting REE-oxalate precipitate was then calcinated at 850°C for 1 h, producing REE-oxide as the final product. This process yielded a product with high REE purity, as shown in Fig. 10a, with REEs-oxide and iron-oxide concentrations of approximately 95 % and 0.2 %, respectively, underscoring the high selectivity of the extraction and stripping process. The XRD pattern of the final product (Fig. 10b) confirms that REEs are the predominant constituents.

In this study, oxalic acid was chosen for the stripping step due to its notable advantages in REE processing. As a strong organic acid and effective chelating agent, it exhibits high affinity and exceptional selectivity for REEs (Khawassek et al., 2015), outperforming alternatives like carbonates, which are only effective at high pH and require additional neutralization steps. Oxalic acid's ability to function efficiently at low pH simplifies the process and enhances overall efficiency (Wang et al., 2022). Kenneth N. Han (Han, 2020) highlighted its superior precipitation capabilities compared to other agents, such as phosphates, fluorides, sulfates, and carbonates. Additionally, oxalic acid promotes the conversion of metal oxalates to metal oxides through calcination, speeding up recovery and improving process efficiency. By integrating separation and recovery in a single step, oxalic acid enables selective metal precipitation. Its recyclability further reduces reagent costs and waste, supporting more sustainable processing practices (Rahmati et al., 2024b).

While around 95 % of the product is composed of REEs, the remaining unidentified portion may include residual oxalic acid from the stripping stage and trace elements such as Zr, Nb, Rb, and Ni, which were present in minor amounts in the original magnet material (Romano et al., 2025). Furthermore, the use of organic acids as reagents in both the leaching and stripping stages underscores the environmentally friendly nature of the process, promoting its potential as a green technology.

4. Conclusion

This study extensively explored the extraction of REEs from citrate leach solutions derived from the leaching of spent NdFeB magnets, with a particular focus on the extraction mechanisms and the efficacy of D2EHPA as an extractant. Our findings indicate that D2EHPA not only effectively extracts both heavy and light REEs but does so with significantly higher efficiency compared to Cyanex 572 and Cyanex 272, achieving near-complete extraction for heavy REEs and approximately 88 % for light REEs, all while minimizing iron co-extraction.

Chemical and operational parameters, including organic phase composition, organic-to-aqueous phase ratio, extractant concentration, and pH, were varied, resulting in high selectivity and extraction efficiency. The mechanisms of REE extraction with D2EHPA were thoroughly assessed, revealing variations in the extraction process for light and heavy REEs based on the formation of different complexes and the molarity of the extractant used. The significantly higher equilibrium constant for heavy REEs was noted, underscoring their preferential extraction compared to lighter counterparts.

Overall, this study advances the understanding of REE extraction mechanisms and highlights the potential for sustainable recovery of critical metals. Future research directions should be aimed at exploring the optimization of multistage extraction processes to further enhance operational efficiency and minimize environmental impacts.

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CRediT authorship contribution statement

Francesco Vegliò: Writing – review & editing, Writing – original draft, Validation, Supervision, Funding acquisition, Conceptualization. **Pietro Romano:** Writing – original draft, Software, Methodology, Formal analysis. **Roshanak Adavodi:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Soroush Rahmati:** Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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