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The recycling of secondary resources containing rare earth elements (REEs) is a crucial strategy for meeting the growing demand for these critical materials and reducing reliance on primary mining. In recent years, organic acids (citric, maleic, acetic, malic, and oxalic acid) have been applied as sustainable lixiviants for the leaching of REEs; however, downstream purification of the resulting solutions remains less explored. In this work, solvent extraction was employed to recover and purify REEs from malic acid leachates of NdFeB magnets using different types of extractants: acidic (D2EHPA, Cyanex 272), ion-pair (Aliquat 336), and solvating (TBP). Among the tested extractants, di-(2-ethyl hexyl) phosphoric acid (D2EHPA) showed the highest extraction efficiency, although co-extraction of Fe was also observed. Optimal stripping was achieved using 0.7 mol L^{-1} HCl at 20°C, an aqueous/organic (A/O) ratio of 1, and 10-min contact time, yielding an aqueous solution containing 3.1 g L^{-1} Nd, 1.4 g L^{-1} Pr, and 0.1 g L^{-1} Dy, with a relative purity of 99.3 wt.% for REEs. These findings demonstrate the potential of combining malic acid leaching with D2EHPA-based solvent extraction as a sustainable route for REE recovery. However, challenges remain regarding the efficient stripping of Fe from D2EHPA, which requires further investigation to improve process performance.

INTRODUCTION

Rare earth elements (REEs) are critical components for clean energy technologies such as wind turbines, electric vehicles, and advanced electronics.[1–3] Their global supply is currently dominated by primary mining,[4] leading to environmental concerns and supply risks due to the generation of radioactive by-products[5,6] and market concentration.[7] China has been the world's largest producer of rare earths, accounting for about 60% of global production in 2024.[8,9] To ensure a sustainable supply, recycling of secondary sources (NdFeB magnets, LED lamps, rechargeable batteries, and televisions) has become essential.[10,11] Among these, NdFeB magnets stand out for their high REEs content (up to 30%) and widespread use in renewable energy systems and electronics.[12] The magnets are demagnetized to eliminate magnetic fields and avoid interference during processing.[13] Comminution is then applied to increase the surface area, thereby enhancing the efficiency and effectiveness of subsequent extraction processes, such as leaching.[14] While pyrometallurgy enables direct metal recovery, it often requires high temperatures (500–2000°C)[15] and additional purification steps.[16]

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Therefore, hydrometallurgy has gained attention as a more selective and potentially sustainable alternative.

In hydrometallurgical processes, REEs are commonly leached from solid matrices using strong mineral acids such as sulfuric, nitric, or hydrochloric acid.[17–19] However, the use of these acids raises environmental and operational concerns, including the formation of corrosive residues and complex effluent management.[20] Moreover, separating REEs from co-leached impurities, particularly Fe and Co, remains challenging, often requiring multiple extraction and stripping stages.[21] Developing cleaner, more efficient leaching and separation systems is, therefore, a critical step toward sustainable REE recycling.

Recent studies have investigated organic acids such as acetic,[12,22] citric,[23,24] maleic,[25] and oxalic,[26] as environmentally friendly lixiviants. These acids can be obtained from renewable sources such as plants or microorganisms.[27,28] Organic acid-based leach liquors can be further purified by solvent extraction (SX),[29,30] which remains the most effective technique for large-scale REEs separation due to its high selectivity and operational flexibility.[31,32] Extractants, such as di-(2-ethylhexyl) phosphoric acid (D2EHPA),[33,34] bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272),[35] operate mainly via cation-exchange mechanisms, while tributyl phosphate (TBP)[36,37] acts as a solvating extractant by coordinating neutral REE species. Methyltrioctylammonium chloride (Aliquat 336)[38] extracts REEs through ion-pair formation and has also demonstrated a strong affinity for REEs. Gergoric et al.[25] reported preliminary tests of REEs separation from maleic and glycolic acid leachates using D2EHPA in hexane. At 1.0 mol L^{-1} D2EHPA and pH 1.5, good separation between Nd and Fe was achieved. Rahmati et al.[39] obtained an extraction of nearly 100% for heavy REEs and about 88% for light REEs from a citric acid leach liquor using 50% (v/v) D2EHPA in heptane at pH 3.2. These advances highlight the potential of organic acid systems but also reveal the need to optimize separation efficiency and to understand extractant behavior under milder chemical conditions.

Despite the progress with organic acids, REE separation from malic acid leach liquors has not yet been reported. Malic acid is an environmentally benign lixiviant that has demonstrated high efficiency for NdFeB magnet dissolution,[40] making it an attractive alternative to conventional mineral acids. Compared to other carboxylic acids, malic acid exhibits the same leaching efficiency as acetic acid and avoids the formation of insoluble residues commonly observed with citric acid systems. In our previous study,[12] complete dissolution of NdFeB magnets required 3.0 mol L^{-1} acetic acid concentration at 50°C, solid-to-liquid (S/L) ratio of 1:12 for 2 h, while Reisdörfer et al.[40] reported that unroasted NdFeB powder could be leached with 1.0 mol L^{-1} malic acid, achieving 99% Nd recovery after 360 min at 90°C and a 1:20 S/L ratio. In contrast, leaching with citric acid under similar conditions resulted in a thick sludge due to strong Fe-citrate complexation, hindering solid-liquid separation. These results demonstrate that malic acid enables efficient REE recovery and more environmentally friendly conditions, making it a promising lixiviant for sustainable hydrometallurgical processes. Therefore, the objective of this study was to evaluate the extraction and separation of Nd, Pr, and Dy from a malic acid leach liquor of NdFeB magnets by solvent extraction. The study further aimed to investigate the influence of key operational parameters, such as extractant concentration, A/O, and contact time, as well as the stripping step, for efficient recovery of the metals. By using an organic acid leachate rather than a conventional inorganic medium, this work provides insights into developing more environmentally friendly hydrometallurgical routes for rare-earth recovery and magnet recycling.

MATERIALS AND METHODS

Sample Preparation

The feed solution used in the SX experiments was obtained by leaching NdFeB magnets (Brisingi, Denmark) with 2.0 mol L^{-1} malic acid (99%, Sigma-Aldrich, Germany). The leachate was obtained from the malic acid leaching of NdFeB magnets, performed at a solid-to-liquid ratio (S/L) of 1/15, at 75°C, and a leaching time of 2 h under magnetic stirring. The leaching conditions were selected based on preliminary optimization performed by the authors to obtain a representative malic-acid pregnant leach solution for the present solvent-extraction study. The resulting leach liquor is shown in Table I, containing 4.29 g L^{-1} of REEs (29.9 mmol), with a measured pH of 3.1 ± 0.1 and redox potential around 130 mV. All experiments were carried out in triplicate, with the results reported as mean values.

A speciation diagram was constructed using Python programming, since available databases in conventional speciation software do not include reliable parameters for this acid. The equilibrium constants (pKa values and stability constants, log K) were obtained from Martell and Smith's compilation.[41] The model assumes an aqueous system at 25°C (ionic strength = 0). Species distribution was calculated by iteratively solving the charge and mass balance equations over the pH range. The results were validated by comparison with the speciation profiles reported for other carboxylic acids under similar conditions, showing consistent equilibrium trends.

Solvent Extraction

The SX experiments were carried out by pipetting 1 mL organic phase and 1 mL aqueous phase into a 3.5-mL glass vial.[42] The vials were sealed with a

Table I. Elemental composition of the leach liquor from NdFeB magnets with malic acid

Element	Concentration (g L^{-1})	Concentration (mol L^{-1})
Fe	9.62 ± 0.01	0.172 ± 0.017
Nd	3.27 ± 0.14	0.023 ± 0.003
Pr	1.04 ± 0.01	0.007 ± 0.001
Dy	0.04 ± 0.01	3.10^{-4} ± 3.10^{-3}
B	0.15 ± 0.01	0.013 ± 0.006
Co	0.15 ± 0.01	0.003 ± 0.001
Cu	0.02 ± 0.01	0.001 ± 0.001

polyethylene cap and shaken (1500 rpm) using an IKEA VIBRAX VXR Basic at room temperature (20°C ± 1°C) for 10 min. After shaking, the samples were centrifuged at 5000 rpm for 5 min (Ohaus—Frontier™ 5000 Series Multi Pro). After phase separation, the aqueous phases were sampled and diluted in 3% HNO_3 (Sigma-Aldrich) and analyzed by inductively coupled plasma atomic emission s
pectrometry (ICP-OES) at the Industrial Material Recycling group at Chalmers University of Technology (Sweden).

Preliminary solvent extraction tests were first performed using D2EHPA, the most widely reported extractant for REE recovery in the literature,[30,33,43] to evaluate its performance and the potential need for phase modifiers. To this end, TBP was studied as a modifier in combination with D2EHPA.[44] Subsequently, D2EHPA, TBP, Aliquat 336, and Cyanex 272 were tested for the separation of REEs from contaminants (Fe, B, Co, Cu). D2EHPA, TPB, and Cyanex 272 were diluted in Isopar-L, whereas Aliquat 336 was diluted in toluene because of its higher solubility in aromatic diluents.[45] For comparison, all extractants were tested at a concentration of 0.5 mol L^{-1}.

After selecting the extractant, the effects of the organic phase composition (extractant concentration, modifiers), aqueous/organic phase ratio (A/O), and contact time were investigated. Extractant concentration was varied at 0.1, 0.2, 0.3, 0.4, and 0.5 mol L^{-1}.[22] A/O ratios of 1, 1.5, 2, and 2.5 were tested, as well as the contact time of 5 min, 10 min, 15 min, 20 min, 25 min, and 30 min. The initial pH of the aqueous phase was adjusted by adding H_2SO_4 (2.0 mol L^{-1}) and NaOH (5.0 mol L^{-1}). After contact between the organic and aqueous phases, the pH was also measured. The extraction efficiency of the elements was calculated according to Eq. 1, where C_o is the initial concentration in solution, and C is the concentration after extraction.

$$\text{Extraction } (\%) = 100\left(\frac{C_o - C}{C_o}\right) \tag{1}$$

The extraction coefficient (D_i) and the separation factor (SF) were calculated to evaluate the efficiency and selectivity of the SX process. The extraction coefficient for each metal was determined using Eq. 2, where $[M_i]_{org}$ and $[M_i]_{aq}$ are the concentrations of metal in the organic and aqueous phases, respectively, at equilibrium. The separation factor was then calculated to assess the separation of REEs from Fe, based on the Eq. 3, where D_i and D_j are the extraction coefficients of the metals i and j (with Fe as j).

$$D_i = \left(\frac{[M_i]_{org}}{[M_i]_{aq}}\right) \tag{2}$$

$$SF_{ij} = \frac{D_i}{D_j} \tag{3}$$

Stripping Experiments

Sulfuric acid (H_2SO_4)[46] and hydrochloric acid (HCl)[47,48] were evaluated as stripping agents at concentrations of 0.1 mol L^{-1}, 0.3 mol L^{-1}, 0.5 mol L^{-1}, and 0.7 mol L^{-1}. The stripping experiments followed the same procedure as the SX experiments described in section "Solvent Extraction." In this case, the aqueous phase consisted of fresh H_2SO_4 or HCl solution, whereas the organic phase corresponded to the metal-loaded phase.[31] After stripping, the aqueous phases were diluted in 3% HNO_3 (Sigma Aldrich) and quantified by ICP-OES. The stripping efficiency was calculated based on the initial concentration in solution, as shown in Eq. 4, where C_i is the final concentration after stripping.

$$\text{Stripping } (\%) = 100\left(\frac{C_o - C_i}{C_o}\right) \tag{4}$$

The relative purity (RP) of REEs was calculated as the ratio between the amount of that element and the total amount of metals analyzed in solution, expressed in either moles or weight, according to Eqs. 5 and 6, where m_i is the number of moles of the element, and n_i is its mass.

$$RP(\%) = 100\left(\frac{n_i}{\Sigma_j n_i}\right) \quad (5)$$

$$RP^*(\%) = 100\left(\frac{m_i}{\Sigma_j m_i}\right) \quad (6)$$

RESULTS AND DISCUSSION

The leaching of REEs with malic acid occurs through the gradual deprotonation of the acid, releasing H^+ into the solution and enabling metal complexation, as shown in Eqs. 7–9.[23,49] At the experimental pH of 3.1, all three protonation states of malic acid (H_2Mal, $HMal^-$, and Mal^{2-}) can coexist (see supplementary Fig. S1), which influences the complexation equilibria with M^{3+} ions. Nd was chosen as a representative element to discuss the speciation behavior of REEs. Based on the speciation diagram proposed by Sukhno et al.,[50] at pH 3.1, the predominant complexes expected in solution are Nd^{3+}, $NdHMal^+$ Eq. 7, NdH_2Mal^{2+} Eq. 8, and $Nd(HMal)_2^-$. However, malic acid lacks selectivity, leading to the co-leaching of impurities, such as Fe, Co, Cu, and B. Therefore, SX was applied as a subsequent step to achieve REE separation.

$$M^{3+}_{(aq)} + C_4H_6O_{5(aq)} \rightleftharpoons MH_2C_4H_4O^{2+}_{5(aq)} + H^+_{(aq)} \quad (7)$$

$$M^{3+}_{(aq)} + C_4H_6O_{5(aq)} \rightleftharpoons MHC_4H_4O^{+}_{5(aq)} + 2H^+_{(aq)} \quad (8)$$

$$M^{3+}_{(aq)} + C_4H_6O_{5(aq)} \rightleftharpoons MC_4H_4O_{5(s)} + 3H^+_{(aq)} \quad (9)$$

To evaluate the behavior of organic acids in the aqueous phase, 0.5 mol L^{-1} D2EHPA in Isopar-L was selected for preliminary tests at 20°C ± 1°C, an A/O ratio of 1, and a contact time of 10 min.[33] However, a third phase was observed, preventing the separation and quantification of metals. This behavior can be associated with the formation of a microemulsion.[51] Polar complexes formed between REEs and D2EHPA tend to aggregate into nanoscale clusters (reverse micelles) in an attempt to minimize contact with Isopar-L, a highly nonpolar diluent.[44,52] The limited solubility of these polar complexes in the aliphatic medium creates a strong thermodynamic driving force for aggregation. Once these aggregates reach a critical size due to the high metal loading, the organic phase loses thermodynamic stability and splits into two distinct organic layers, leading to third-phase formation.[53] Rodríguez et al.[44] reported the same phenomenon during the extraction of REEs with D2EHPA, in which third-phase formation occurs at pH values > 2. This is consistent with the present study, cconducted at pH 3.1 ± 0.1, where third-phase formation was also observed.

To suppress this phenomenon, TBP was investigated as a phase modifier. TBP primarily acts as a cosolvent and anti-aggregation agent, with a role that extends beyond merely increasing the solubility of polar species.[54] It interferes directly with the nucleation and growth mechanism of reverse micelles. Being more polar than the Isopar-L diluent, TBP specifically interacts with the polar cores of the REE–D2EHPA complexes and with co-extracted water molecules.[55] This interaction stabilizes the forming aggregates, preventing them from reaching the critical size necessary for third-phase separation. In addition, the butyl chains of TBP embed into the "shell" of the aggregates, introducing steric hindrance that inhibits the coalescence of smaller aggregates into larger, insoluble structures. Efficient metal extraction was only achieved at TBP concentrations > 3% v/v, since at 1% v/v the amount of TBP was insufficient to provide adequate interfacial stabilization and solvation of the complexes. At 3% v/v, the TBP concentration was sufficient to saturate the aggregate interfaces, stabilizing the system and allowing a stable biphasic extraction.

At 3% v/v, 100% of Nd, Pr, and Dy was extracted, with co-extraction of 60% Fe and 66% Cu. Increasing the TBP concentration to 5% v/v kept the REE extraction constant, while Fe extraction increased by approximately 5%. Since 3% and 5% v/v TBP showed similar efficiencies, 3% v/v was selected for subsequent SX experiments.

Effect of Extractant

Preliminary experiments showed that SX could effectively recover REEs but also indicated the need for process optimization due to Fe co-extraction. Therefore, different extractants were evaluated, including acidic (D2EHPA, Cyanex 272), ion-pair (Aliquat 336), and solvating (TBP).[56] Table II presents the extraction efficiencies and SF results of REEs and Fe using different extractants (0.5 mol L^{-1}) at 20°C, with an A/O ratio of 1 and a contact time of 10 min. The uncertainty of the equilibrium pH measurements was estimated at ± 0.1.

Among the extractants studied, D2EHPA showed higher selectivity and efficiency for the REEs than the others, as evidenced by the higher separation factors (REE/Fe) obtained under the same experimental conditions (Table II). Although Cyanex 272, like D2EHPA, is an acidic extractant, it exhibited lower extraction performance. Using D2EHPA, nearly 100% of the REEs was extracted, whereas with Cyanex 272, only 62% Dy, 35% Pr, and 24% of Fe and Nd were recovered. The SF confirms this difference quantitatively: 97.1, 72.9, and 31.2 for Nd, Pr, and Dy with D2EHPA compared to 0.9, 2.4, and 5.2 with Cyanex 272, respectively. The higher efficiency of D2EHPA can be attributed to both the extraction mechanism and molecular structure. The

Table II. Effect of different extractants in the purification step of REEs (20°C, A/O: 1, 10 min) (analytical uncertainty and D: see supplementary Table S1)

			Extraction (%)				SF		
Extractant	**Diluent**	**pH**	**Nd**	**Pr**	**Dy**	**Fe**	**Nd/Fe**	**Pr/Fe**	**Dy/Fe**
D2EHPA	Isopar-L	2.5	100	100	100	50.6	97.1	72.9	31.2
Cyanex 272	Isopar-L	2.9	22.8	34.8	61.8	23.9	0.9	2.4	5.2
Aliquat 336	Isopar-L	2.8	0.0	7.4	13.3	33.8	0.0	0.2	0.3
TBP	Toluene	2.9	0.0	2.8	0.1	1.3	0.0	2.2	0.0

extraction with acidic extractants occurs through a proton-exchange mechanism,[57] in which M^{3+} ions replace H^+ from the extractant, releasing protons into the aqueous phase Eq. 10.[33] The larger pH drop observed with D2EHPA (2.5) compared to Cyanex 272 (final pH 2.9) indicates a greater extent of metal exchange (2.9).

$$M^{3+}_{(aq)} + m(HA)_{2(org)} \rightleftharpoons MR_3(HR)_{2m-3(org)} + 3H^+ \quad (10)$$

This behavior can also be attributed to the molecular structure of the extractants. The presence of oxygen atoms and the linearity of the alkyl chain enhance extraction efficiency by increasing the electron density and favoring the cation exchange between M^{3+} and H^+ ions. D2EHPA contains more oxygen atoms, which facilitate electron donation and metal complexation.[58] In contrast, the more branched alkyl chain of Cyanex 272 decreases the electron density around the donor atom and introduces steric hindrance, thereby reducing its extraction efficiency.[59] The molecular structures of D2EHPA and Cyanex 272 are shown in Fig. S2 (see supplementary data file).

Aliquat 336 and TBP showed negligible interaction with the REEs in solution. As the predominant species in the liquor are cationic, as suggested in Eqs. 8 and 9, extraction with a basic extractant (Aliquat 336) is disfavored, which explains its low efficiency.[60] For TBP, a solvating extractant, metal transfer typically proceeds via complexes formed with counter-ions.[56] Therefore, the TBP is hindered by the absence of simple cation-anion pairs available to form neutral complexes, as malate ligands already stabilize REEs in the aqueous phase.[25,61] Considering the performance of the four extractants in REEs extraction, D2EHPA was selected for further evaluation of the process parameters because of its superior efficiency and selectivity toward REEs.

Although the focus of this study was on REE extraction, Fe was also coextracted at significant levels (51%). Given the strong affinity of D2EHPA for Fe(III),[62] such coextraction was expected, since Fe is present as Fe^{3+} in malate complexes after leaching with malic acid.[49] The extraction of Fe^{3+} by D2EHPA follows the same cation-exchange mechanism described for REE^{3+} Eq. 10, as both species exhibit the same trivalent charge. Consequently, Fe^{3+} competes with REEs for the available extractant, reducing the overall selectivity of the system. Similar behavior was reported by Rahmati et al.,[23] who observed Fe co-extraction from a citric acid medium and noted that increasing D2EHPA concentration diminished the selectivity between REEs and Fe due to the higher availability of extraction sites. Therefore, based on the results (Table II), the effect of D2EHPA concentration on Fe co-extraction is investigated in the following section to understand its role in the performance of the SX system.

Effect of the Extractant Concentration

Once the extractant was defined, the effect of extractant concentration was evaluated. Considering that the aqueous phase contained 0.21 mol L^{-1} of total metals (0.03 mol L^{-1} REEs), the D2EHPA concentration ranged from 0.05 mol L^{-1} to 0.5 mol L^{-1} in Isopar-L (3% v/v TBP). The other variables were kept constant: 20°C, A/O ratio of 1-, and 10-min contact time. The extraction behavior of REEs and Fe is shown in Fig. 1, and Table III presents the D and SF for each metal.

Although D2EHPA shows higher affinity for REEs than Fe (extraction coefficient, Table III), it was not fully selective, since Fe extraction was also observed. At concentrations < 0.2 mol L^{-1}, no extractions > 60% were observed. The extraction efficiency is directly related to the availability of D2EHPA molecules in the organic phase. Considering that 3 mols of D2EHPA are required to extract 1 mol of M^{3+} Eq. 10,[43,56] the concentration of 0.05 mol L^{-1} is insufficient for the complete complexation of the REEs present in solution (0.03 mol L^{-1}). Although 0.1 mol L^{-1} is already higher than the minimum required, competition with Fe is observed, reducing selectivity. A significant improvement in extraction was observed when the concentration was increased up to 0.3 mol L^{-1}, reaching 100% for Dy and 95% for Nd and Pr, with 47% Fe co-extracted. At 0.5 mol L^{-1}, all REEs were completely extracted but accompanied by higher Fe co-extraction, resulting in lower selectivity.

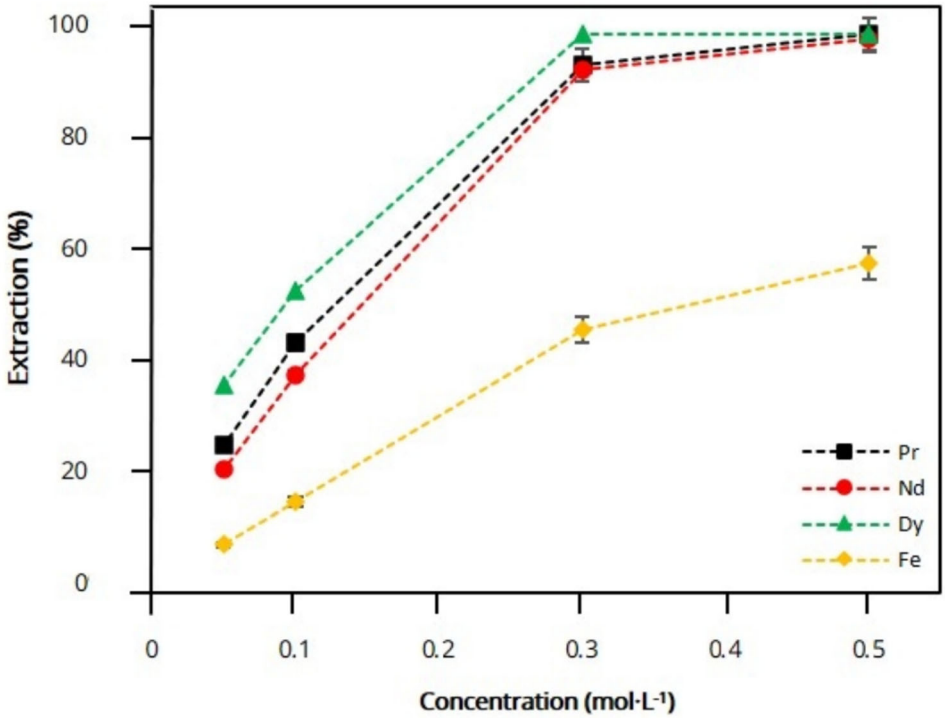

Fig. 1. Effect of extractant concentration in the SX of REEs and Fe (D2EHPA 3%v/v TBP, 20°C, A/O: 1, 10 min).

Table III. Coefficient extraction and separation factors for REEs, Fe, and Cu varying D2EHPA concentration

		D					SF			
C (mol•L^{-1})	pH	Nd	Pr	Dy	Fe	Cu	Nd/Fe	Pr/Fe	Dy/Fe	Cu/Fe
0.05	3.0	0.3	0.4	0.6	0.1	5.0	3.0	3.8	6.2	52.2
0.1	3.0	0.6	0.8	1.2	0.2	4.0	3.3	4.2	6.0	20.3
0.3	2.9	14.7	17.5	44.9	0.9	1.5	16.5	19.7	50.4	1.6
0.5	2.8	139.8	104.9	44.9	1.4	1.9	97.1	72.9	31.2	1.3

Effect of the A/O Ratio

To better understand the influence of the phase volume ratio on extraction efficiency, the effect of the A/O ratio on REE separation was investigated at the selected extractant concentration. The conditions were fixed at 20°C, 0.3 mol L^{-1} D2EHPA in Isopar-L (3%v/v TBP), with 10 min contact time, while the A/O ratio was varied from 1 to 2.5. The extraction percentages of the elements are shown in Fig. 2, and the D and SF are shown in Table IV.

Evaluating the influence of the A/O ratio on REE extraction, it was observed that increasing the proportion of the aqueous phase resulted in reduced REE extraction. This trend can be related to the molar concentration of metals in solution (Table V). At an A/O ratio of 1.5, the concentration of metals (0.31 mol L^{-1}) is higher than the available concentration of extractant (0.3 mol L^{-1}). This behavior reaffirms the low selectivity of D2EHPA for REEs compared to Fe.[33,63]

Although Dy has a smaller ionic radius and higher charge density than Pr and Nd,[30] which favor its complexation with D2EHPA, the distribution ratio of Dy also decreased with increasing A/O ratio, from 44.9 at A/O = 1 to 16.2 at A/O = 2.5. Nevertheless, Dy remained significantly more extracted than Nd and Pr under all conditions. Moreover, the separation factor Dy/Fe increased markedly (from 50.4 to 130.4), indicating that, despite the reduction in the absolute extraction of Dy, higher A/O ratios enhanced its selectivity over Fe. However, an A/O ratio of 1 was selected to ensure nearly complete extraction of all REEs, even though Dy is one of the elements of interest.

Effect of the Contact Time

The effect of contact time between the phases was also evaluated, ranging from 5 min to 30 min. The extraction of REEs and Fe as a function of contact time is shown in Fig. 3, and the D and SF are presented in Table VI. The experiments were

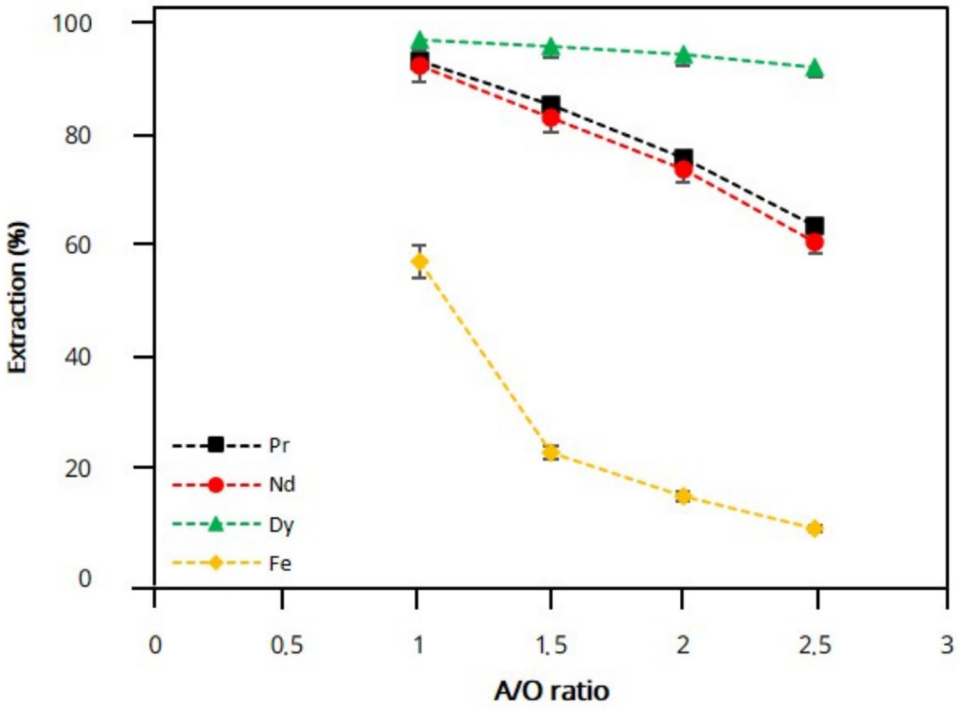

Fig. 2. Effect of A/O ratio in the purification step of REEs (0.3 mol L^{-1} D2EHPA 3%v/v TBP, 20°C, 10 min) (pH: Table V).

Table IV. Coefficient extraction and separation factor for REEs, Fe, and Cu varying the A/O ratio

	D					SF			
A/O	Nd	Pr	Dy	Fe	Cu	Nd/Fe	Pr/Fe	Dy/Fe	Cu/Fe
1.0	14.7	17.5	44.9	0.9	1.5	16.5	19.7	50.4	1.6
1.5	5.7	6.9	44.9	0.3	0.7	17.4	21.2	137.8	2.2
2.0	3.1	3.5	27.2	0.2	0.4	15.6	17.4	135.9	2.2
2.5	1.7	1.9	16.2	0.1	0.3	13.4	15.4	130.4	2.8

Table V. Metal concentration and pH in different A/O ratios in the loaded organic phase

A/O ratio	1.0	1.5	2.0	2.5
REE (mol L^{-1})	0.09 ± 0.01	0.14 ± 0.02	0.18 ± 0.01	0.23 ± 0.01
Total metal (mol L^{-1})	0.21 ± 0.10	0.31 ± 0.20	0.41 ± 0.20	0.51 ± 0.20
pH*	2.8	2.9	2.9	3.0

*pH uncertainties: ± 0.1.

carried out at 20°C, using 0.3 mol L^{-1} D2EHPA in Isopar-L (3% v/v TBP) with an A/O ratio of 1.

The extraction of REEs remained nearly constant across all tested contact times (~100%), while Fe extraction fluctuated between 40% and 50%, which may be attributed to analytical uncertainty. These trends are summarized in Table VI, where no significant variations in distribution ratios or separation factors are observed, except for an anomalous value at 30 min, likely due to experimental error. Therefore, a contact time of 10 min was selected. At 20°C, under the optimized conditions, an A/O ratio of 1, and 0.3 mol L^{-1} D2EHPA in Isopar-L (3% v/v TBP) for 10 min, the loaded organic phase contained 4.5 g L^{-1} Fe, 3.1 g L^{-1} Nd, 1.5 g L^{-1} Pr, 0.2 g L^{-1} Dy, 0.01 g L^{-1} B, 0.006 g L^{-1} Co, and 0.01 g L^{-1} Cu.

The low extraction of Cu, Co, and B is due to the selectivity order of the D2EHPA extractant, which prioritizes the extraction of trivalent ions (such as

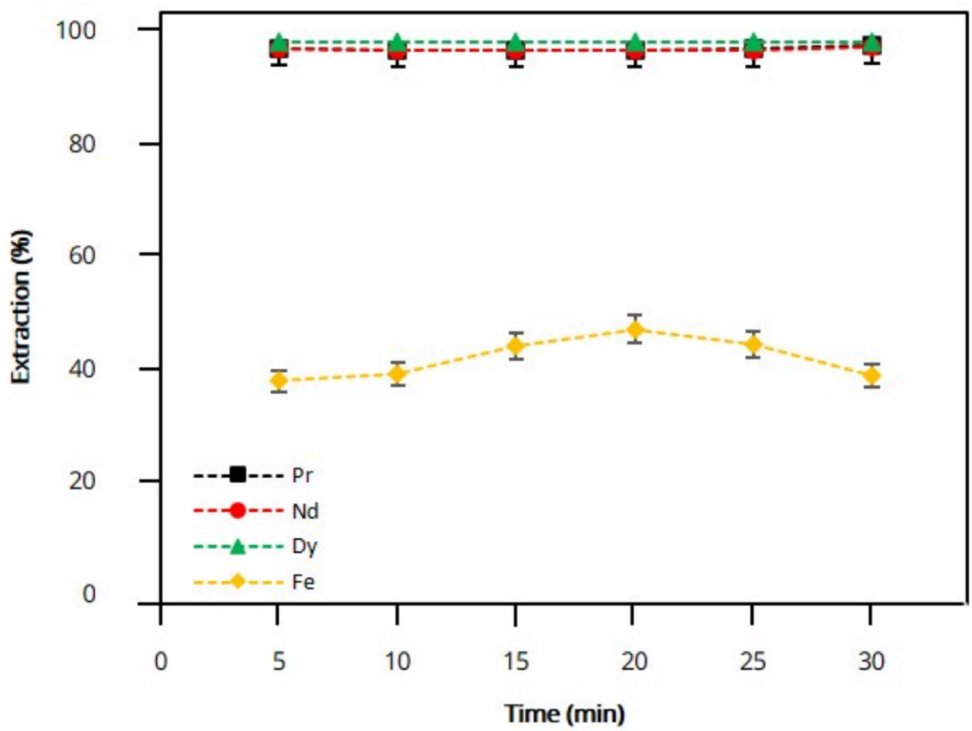

Fig. 3. Effect of time in the purification step of REEs 0.3 mol L^{-1} D2EHPA 3%v/v TBP, 20°C, A/O: 1.

Table VI. Coefficient extraction and separation factors for REEs, Fe, and Cu, varying the contact time

	D					SF			
Time (min)	**Nd**	**Pr**	**Dy**	**Fe**	**Cu**	**Nd/Fe**	**Pr/Fe**	**Dy/Fe**	**Cu/Fe**
5	70.8	70.7	45.6	0.7	0.7	107.8	107.6	69.4	1.1
10	66.2	67.5	45.6	0.7	0.8	95.6	97.4	65.8	1.2
15	64.0	65.3	45.6	0.8	0.8	75.4	76.9	53.7	0.9
20	63.8	65.5	45.6	1.0	0.7	66.8	68.5	47.7	0.8
25	67.3	68.4	45.6	0.9	0.8	78.2	79.5	53.0	0.9
30	98.5	115.2	45.6	0.7	4.5	144.6	169.2	66.9	6.6

Fe^{3+} and REE^{3+}) in more acidic pH ranges.[64] At pH 3.1, the conditions predominantly favor the extraction of trivalent metals, whereas divalent metals, such as Cu2+ and Co2+ , require a higher pH (generally above 4) to achieve maximum extraction.[65] This occurs because the extraction of divalent ions requires the release of two protons per complexed metal ion, as illustrated by the reaction shown in Eq. 11, necessitating a lower concentration of free H^+ ions in the solution (i.e., a higher pH).[66] The behavior of B is distinct; it does not form extractable cationic species via D2EHPA under these acidic conditions, remaining predominantly in the aqueous phase, resulting in negligible extraction.[67]

$$M^{2+}_{(aq)} + 2(HA)_{2(org)} \rightleftharpoons M(HA_2)_{2(org)} + 2H^+ \qquad (11)$$

REEs Stripping

Stripping experiments were carried out to selectively recover them from the loaded organic phase after extraction with 0.3 mol L^{-1} D2EHPA in Isopar-L (3% v/v TBP). H_2SO_4 and HCl were tested as stripping agents to transfer the REEs back into a fresh aqueous phase, with concentrations ranging from 0.1 mol L^{-1} to 0.7 mol L^{-1}. The experiments were carried out at 20°C ± 1°C, with an A/O ratio of 1 for 10 min. The stripping results are presented in Table VII.

The concentration of the stripping agent was a key factor for the back-extraction of REEs. For HCl, increasing the concentration from 0.1 mol L^{-1} to 0.7 mol L^{-1} enhanced Nd stripping from 24.4% to 100%. This behavior is consistent with Eq. 10, where the increase in $[H^+]$ shifts the equilibrium to

Table VII. Stripping performance of REEs from the loaded organic phase using (a) H_2SO_4 and (b) HCl media (analytical uncertainties, see supplementary Table S2)

		Stripping (%)						
Conc (mol L^{-1})		B	Co	Cu	Dy	Fe	Nd	Pr
HCl	0.1	39.5	–	93.8	6.2	–	24.4	32.3
	0.3	55.6	–	92.3	40.0	–	54.31	59.9
	0.5	55.4	–	97.7	76.4	–	73.6	79.2
	0.7	64.7	3.7	100	72.2	0.2	100	96.5
H_2SO_4	0.1	–	–	94.5	24.7	–	66.7	74.5
	0.3	–	–	96.8	79.3	0.1	77.6	83.2
	0.5	–	–	94.2	88.7	0.1	75.8	90.74
	0.7	–	–	100	90.2	0.2	74.2	76.2

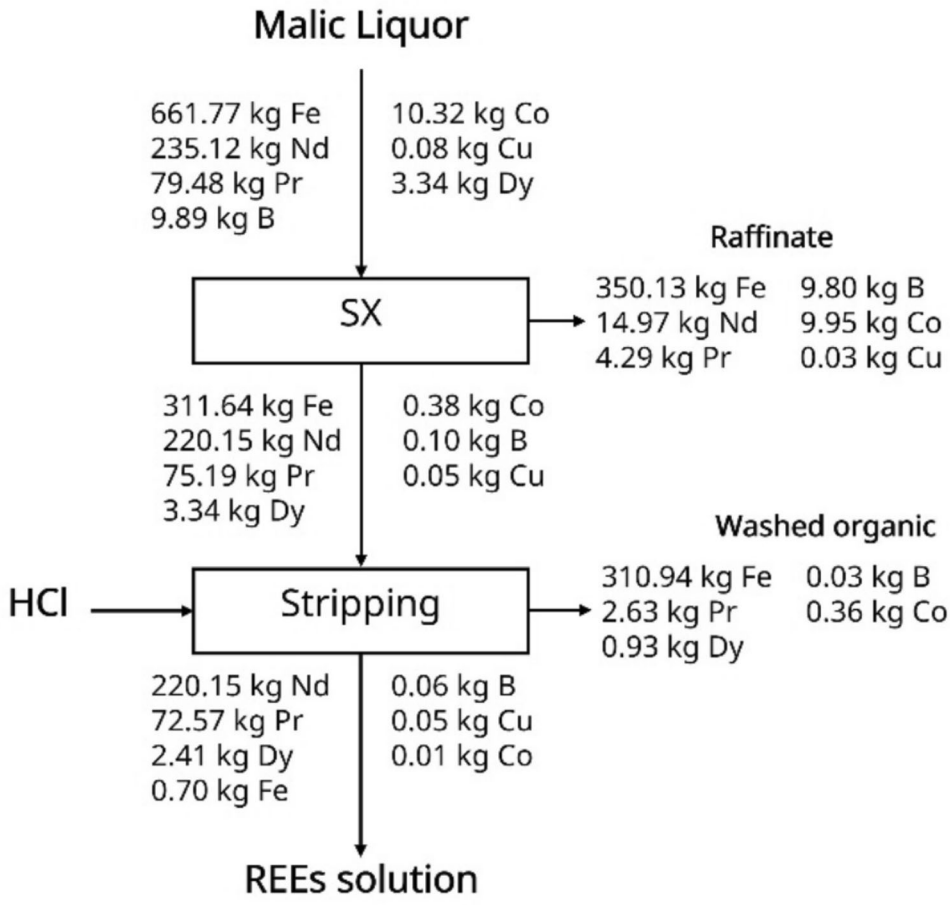

Fig. 4. Flowchart of the REE recovery process from magnets, including SX and stripping steps, with the corresponding mass balances.

the left, favoring the release of REEs into the aqueous phase.[31]

Co-stripping of Cu was also observed, with a stripping efficiency > 92% for all concentrations tested with both acids. The re-extraction of Cu from the organic phase has been reported in the literature using sulfuric acid solutions (0.1–0.5 mol L^{-1}), achieving up to 99% Cu recovery,[68] consistent with the results obtained in this study (Table VII). However, although 100% of the Cu present in the organic phase was stripped, given its initial concentration in the leachate and the extraction efficiency of 59%, the final concentration after stripping was < 0.01 g L^{-1} Cu.

On the other hand, Fe remained strongly bound in the organic phase, showing no significant

variation with either the type or concentration of the stripping acid, allowing effective REE separation. This behavior reflects the strong affinity of D2EHPA for Fe^{3+}, forming highly stable complexes in the organic phase.[62] Similar difficulties in stripping Fe(III) from D2EHPA-loaded phases have been widely reported,[69] since high concentrations of stripping agents are often required, which may also promote D2EHPA degradation.[70] The persistence of Fe in the organic phase presents a significant challenge for industrial implementation, primarily impacting the long-term process viability and the regeneration efficiency of the D2EHPA extractant, potentially leading to operational costs and a decrease in extraction capacity over multiple cycles to overcome this limitation. Alternative strategies have been investigated, including the use of complexing organic acids such as oxalic acid,[71] modification of the organic phase (e.g., addition of proton-donor additives or saponification of D2EHPA),[72] and reductive stripping by introducing reducing agents during the aqueous contact.[73]

Comparing the two stripping agents, HCl showed higher REE recovery, achieving 100% Nd, 96.5% Pr, and 72.2% Dy. The lower Dy recovery can be attributed to its smaller ionic radius and higher charge density, which lead to stronger complexation with the extractant, thereby hindering its stripping efficiency.[30,74] It may also be related to the mild stripping conditions applied, since literature reports indicate that higher H^+ concentrations favor the displacement of REEs from D2EHPA to the aqueous phase.[31,75] Therefore, the use of 0.7 mol L^{-1} HCl may limit Dy recovery under the present conditions. Although HCl was selected for the subsequent purification steps because of its higher efficiency, it is worth noting that using H_2SO_4 could represent a more cost-effective and operationally safer alternative (lower corrosivity and lower volatility), which might achieve comparable recoveries under optimized conditions.[27] The final aqueous solution consisted mainly of Nd, Pr, and Dy, representing 99.6 wt% ± 0.1 by mass and 97.6% ± 0.3 by mole of the dissolved metals (see supplementary Table S3). The recovered REE solution reached a purity of 99.3 wt.%, indicating its potential for use as a precursor for rare-earth oxide synthesis or other downstream recovery processes. Further investigations on the conversion of this solution into magnet-grade materials and evaluation of their magnetic performance are recommended for future studies.

Mass Balance and Scalability

Based on the optimal SX and stripping conditions, a mass balance of the process was calculated. The calculation considered a pregnant leach solution containing 1000 kg of dissolved metals (317.94 kg of REEs). This value refers to the mass after the leaching step, already including all leaching losses, meaning that the initial mass of NdFeB magnets would be higher. Under these conditions, the system enables the separation of REEs from Fe, yielding a solution with 99.3 wt.% ± 0.1 REE purity with only a single extraction and stripping stage. After the complete SX-stripping process, 257.48 kg of REEs was recovered, as shown in the process flowchart and mass balance (Fig. 4). After stripping, Fe remains loaded in the organic phase. This represents a well-known challenge, as the currently available methods for Fe removal are not yet efficient enough for industrial application and require further optimization (washed organic). The mass balance analysis of the process indicates a loss of 7.2% of REEs (22.8 kg), mainly due to incomplete extraction (94% Nd and 95% Pr) and low Dy stripping efficiency (72.2%). Additional contacts are suggested to mitigate these losses.

From a scalability standpoint, the proposed process relies on conventional solvent extraction equipment (e.g., mixer-settlers or pulsed columns), which facilitates its transition to larger scales. However, economic feasibility will depend on minimizing REE losses and developing a cost-effective strategy for Fe removal and organic phase regeneration. Despite these challenges, the use of an environmentally benign lixiviant (malic acid) and the potential for selective, high-purity recovery make this route a promising alternative to conventional mineral acid-based systems, especially with further process optimization. Future work will focus on investigating re-extraction strategies and alternative stripping conditions, aiming to further enhance the environmental performance and overall sustainability of the process.

CONCLUSION

In this study, the separation of REEs from a malic acid leachate containing Fe, Co, Cu, and B was investigated using D2EHPA as the extractant and HCl as the striping agent. The extraction with 0.3 mol L^{-1} D2EHPA in Isopar-L (3% v/v TBP), followed by a stripping step with 0.7 mol L^{-1} HCl, enabled the efficient recovery of REEs. Under the optimized conditions (20°C, A/O ratio of 1-, and 10-min contact time), Nd and Pr were completely stripped, while Dy recovery reached 72%, limited mainly by its smaller ionic radius. These results highlight the potential of combining D2EHPA and HCl as an efficient approach for REE recovery and purification from malic acid leachates. Furthermore, the use of organic acids as leaching agents underscores the potential to develop a more sustainable, environmentally friendly hydrometallurgical route for REE recycling. However, challenges remain in this approach, particularly regarding the co-extraction of Fe, the careful control of D2EHPA concentration, and the optimization of stripping conditions to maximize REE recovery while minimizing impurities. Among thestrategies reported in the literature, reductive stripping stands out as

particularly promising for the malic acid-D2EHPA system, as reducing Fe^{3+} to Fe^{2+} weakens its interaction with D2EHPA and may enable more efficient regeneration of the organic phase. Future studies should therefore focus on evaluating this approach to improve long-term process viability. Addressing these issues is crucial to developing an efficient and scalable process.

SUPPLEMENTARY INFORMATION

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