



Research article

Optimization of rare earth magnet recovery processes using oxalic acid in precipitation stripping: Insights from experimental investigation and statistical analysis

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ABSTRACT

Recycling the valuable metals found in spent permanent magnets (REPMs) poses a significant global challenge for the future. This study examines the efficiency of back extraction of rare earth elements (REEs) by oxalic acid solution from di-(2-ethylhexyl) phosphoric acid (D2EHPA) in recycling REPMs. To evaluate the efficiency of this process, several experiments were carried out using designed BOX-Behnken methodology to investigate the effects of various operational and chemical parameters, including stripping solution to loaded organic phase volume ratio (in the range of 1.0–2.0), oxalic acid concentration (ranging from 0.25 to 0.75 M), the stirring rate (ranged between 150 and 350 rpm), and stripping time (ranging from 15 to 45 min) on the REEs recovery and the purity of final production. Analysis of variance was applied to rigorously examine the results statistically. The results showed that more than 85 % of light and 80 % of heavy REEs can be recovered under optimal conditions. Moreover, the final product contained 43.5 % REEs and approximately 0.1 % iron. The stripping experiment using phosphoric acid as the reagent demonstrated ~57 % light and ~4 % heavy REEs recovery. Additionally, the recyclability of the organic phase showed its effective reuse for up to four cycles. This study underscores significant progress in the selective recovery of rare earth elements through a relatively straightforward process consuming mild reagents.

1. Introduction

The unique physical, chemical, and structural properties of rare earth elements (REEs) make them indispensable raw materials for advanced technologies and equipment in various industries. These elements are critical in producing permanent magnets, high-tech alloys, rechargeable batteries, catalysts, and optical equipment [1]. The European Commission has classified some REEs as critical elements because of their high economic importance and supply risk (more than 95 % originate from China) [2–5].

Due to the high energy density and low cost of rare earth permanent magnets (REPMs or NdFeB), NdFeB magnets are widely used in electrical and mechanical devices such as hard disk drives, digital versatile discs, wind turbine generators, and hybrid cars [6]. It should be noted that more than 90 % of the total REE demand is for producing NdFeB magnets. The concentration of REEs in these magnets is 30–35 %, significantly higher than their concentration in ore (0.2–1.4 %) [7]. Given the critical supply situation of REEs, the potential of permanent magnets as a secondary source has attracted considerable attention.

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2. Material and methods

2.1. Materials

Table 1 presents the composition of the permanent magnet swarf used in this research. In the extraction experiments, the mixture of D2EHPA (SIGMA-Aldrich, USA) as the extractant and n-Heptane (AppliChem, Germany) as the diluent was used as the organic phase. Citric acid (SIGMA-Aldrich, USA) and oxalic acid (SIGMA-Aldrich, USA) were also employed to prepare the leaching and stripping solutions. All reagents were of analytical grade, and solutions were prepared using distilled water. The chemical and physical properties of the consumed reagents are shown in Table 2. Aqua regia (with a 3:1 ratio of HCl: HNO₃) was used to dissolve the metals of solid samples for measurement.

2.2. Experimental design

To dissolve REEs from REPMs, a solution of citric acid (1.45 M) as the leaching reagent was added to demagnetized (at 350 °C for 2 h) and ground (−212 μm) REPMs sample with a leach solution to solid ratio of 10 L/kg. The leaching time and stirring rate were set at 3 h and 250 rpm, respectively. Romano et al. [37] reported that increasing the citric acid concentration from 0.5 to 1.45 M improved leaching efficiency, but further increases beyond 1.45 M did not result in significant changes. Additionally, metal dissolution by this method reached equilibrium after 120–180 min. The results showed dissolving efficiencies of 77.9 % for Fe, 84.5 % for Dy, 94.3 % for Nd, 93.9 % for Tb, 95.8 % for Y, 82.5 % for B, and 75.7 % for Pr under the conditions of 1.45 M citric acid, a stirring rate of 250 rpm, and a leaching time of 3 h. The PLS and residual material were separated through a vacuum filtration system. Subsequently, distilled water (50 % of the used leach solution volume) was introduced to the filtered residue to enhance metal recovery and neutralize the pH of residual materials. To use homogenized PLS in the solvent extraction experiments, the main and wash solutions of all experiments were mixed.

During the extraction stage, the homogenized PLS was mixed with the organic phase to transfer REEs ions from the aqueous phase to the organic phase. The organic phase comprised D2EHPA as the extractant and n-Heptane as the diluent in equal proportions. The volume ratio of aqueous to organic phase in the solvent extraction experiments was equal to 1. Extraction time and stirring rate were set at 20 min and 250 rpm, respectively, with a settling time of 10 min for phase separation. The loaded organic phase from all experiments was collected and combined to form a homogenized loaded organic phase for subsequent stripping experiments.

Several experiments were designed based on response surface methodology (RSM) and carried out on a laboratory scale to investigate the influence of chemical and operational parameters on the precipitation stripping process efficiency. Notably, to avoid incorporating decimal or negative levels in the experimental conditions, the Box-Behnken (BBD) design was utilized to optimize the stripping stage [38,39]. The achieved results of designed experiments were used to evaluate the effects of operational and chemical parameters, such as S/LO, oxalic acid concentration in the stripping reagent (M), stripping time (minutes), and stirring rate (rpm), as well as their interactions on stripping efficiency. The coded values (xi) of parameters and the non-linear predicted model (Y) of each response were determined using Equations (1) and (2), respectively [40–42].

$$x_i = \frac{(X_i - X_0)}{(\Delta X_i)} \quad (1)$$

$$Y = \beta_0 + \sum_{i=0}^4 \beta_i x_i + \sum_{j=0}^4 \beta_{ii} x_i^2 + \sum_{i=0}^4 \sum_{j=0}^4 \beta_{ij} x_i x_j \quad (2)$$

where, X_i , X_0 , and ΔX_i represent actual, central, and step change values, respectively. Also, β_0 , β_i , β_{ii} , β_{ij} are model constant, linear coefficient, quadratic coefficient, and cross-product coefficient, respectively.

Table 3 shows the range of parameters investigated. It is important to note that the appropriate range of these parameters was determined based on preliminary experiments.

In the precipitation stripping experiments, 25 mL of the loaded organic phase and the required stripping reagent were introduced into an Erlenmeyer flask and mixed using an orbital shaker at room temperature based on stripping time. The achieved mixture from the experiments was then transferred to a Falcon tube and centrifuged for 5 min at 4000 rpm to separate the phases. In the next step, the mixture of liquid and solid phases (the wash water to stripping reagent volume ratio of 50 %) was filtered. Subsequently, the obtained oxalate powder was dried in an oven at 105 °C for 24 h. Also, the dried oxalate powder was subjected to a muffle furnace at 850 °C for 1 h to convert it into oxide form.

The concentrations of main metals (Fe, B, Pr, Nd, Dy, Tb, and Y) in the solutions, such as PLS, raffinate, and obtained from dissolving metals in aqua regia, were measured using ICP-OES (Agilent, model 5100). It should be noted that rare earth elements can be classified as light (such as La, Ce, Pr, Nd, Sm, Eu) and heavy (such as Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Sc, and Y) rare earth elements [43].

Table 1

The metal concentration of permanent magnet swarf measured by ICP-OES (average of 5 repetitions).

Metal	Fe %	B %	Pr %	Dy %	Nd %	Tb	Y %	Rb %
Permanent magnet swarf	63.43	0.87	4.24	2.82	20.29	0.31	0.11	0.00

Table 2
The properties of the used reagents.

Name	Formula	Assay (%)	Molecular Weight (g/mol)	Density (g/cm ³)
Citric acid monohydrate	C ₆ H ₈ O ₇ ·H ₂ O	>99.5	210.14	–
Oxalic acid dihydrate	C ₂ H ₂ O ₄ ·2H ₂ O	>99.5	126.07	–
Bis (2-Ethylhexyl) hydrogen phosphate	C ₁₆ H ₃₅ O ₄ P	95	322.42	–
n-Heptane	C ₇ H ₁₆	>99	100.21	0.684

Table 3
The main parameters and their level at RSM experiments.

Parameter	Symbol	Unit	Low level (–1)	Medium level (0)	High level (+1)
Stripping reagent to the loaded organic phase volume ratio (S/LO)	X ₁	L/L	1.0	1.5	2.0
Oxalic acid concentration (in the stripping reagent)	X ₂	Mol/L	0.25	0.50	0.75
Stripping time	X ₃	min	15	30	45
Stirring rate	X ₄	rpm	150	250	350

To evaluate the efficiency of the precipitation stripping process, the overall metal recoveries of light and heavy REEs (MR_L and MR_H), the total grade of REEs in the oxalate powder, and the selectivity of the stripping stage for both light and heavy REEs via iron (S_L and S_H) were chosen as the responses of RSM experiments. The MR_{L/H} and S_{L/H} responses were calculated using Equation (3) and Equation (4), respectively [44,45].

$$MR_{L/H} = \frac{100 * \sum p_{mi} * W_o}{\sum pf_{mi} * V_{PLS}} \quad (3)$$

$$S_{L/H} = \frac{MR_{L/H}}{MR_{Fe}} = 100 * \frac{f_{Fe} * \sum p_{mi}}{p_{Fe} * \sum pf_{mi}} \quad (4)$$

where *f* and *p* represent the concentration of interested metal (*mi*) in the PLS and the oxalate powder, respectively, and *W_o* and *V_{PLS}* denote the weight of the achieved oxalate powder and the consumed volume of PLS in each experiment, respectively.

3. Results and discussion

To apply a homogenous loaded organic phase as a feed in precipitation stripping experiments, the required amount of REPMs swarf was leached using citric acid, and the resulting PLSs and wash solutions were combined. The average portion of leaching residue in these experiments was 21.4 % (g/g). Also, the average dissolving efficiency for Fe, B, light REEs, and heavy REEs in this step were 81.6 %, 85.6 %, 90.9 %, and 88.6 %, respectively. Thus, it can be concluded that citric acid can efficiently dissolve metals presented in spent REPMs.

In the next stage, REEs were separated from PLS using D2EHPA. All experiments' resulting loaded organic phase was mixed to use a similarly loaded organic phase in stripping experiments. Metal concentrations in the raffinate solution and the loaded organic phase are detailed in Table 4. Notably, the extraction efficiency of this stage for light REEs, heavy REEs, Fe, and B were 91.4 %, 99.7 %, 26.6 %, and 2.7 %, respectively. The results indicate a selective extraction of rare earth elements by D2EHPA. Furthermore, nearly all the boron and a significant portion of the iron remained in the aqueous phase.

The efficiency of the precipitation stripping process, such as selectivity, metal recovery, and purification of REE-Oxalate powder, was investigated through laboratory-scale experiments designed by BBD. Experiment conditions and outcomes are presented in Table 5. Stripping experiments of D2EHPA by oxalic acid yielded four distinct phases: unloaded organic phase, middle solid phase, stripping solution, and oxalate precipitate (Fig. 1). A centrifuge facilitated the separation of these phases, given the prolonged separation time observed in the separatory funnel.

The analysis of the middle solid phase showed concentrations of rare earth elements and iron similar to those found in the REE-oxalate product. However, the formation of this phase could be attributed to differences in anodic composition. The precipitation occurring in two distinct phases may be due to variations in density between the stripping solution and the two mentioned solid components.

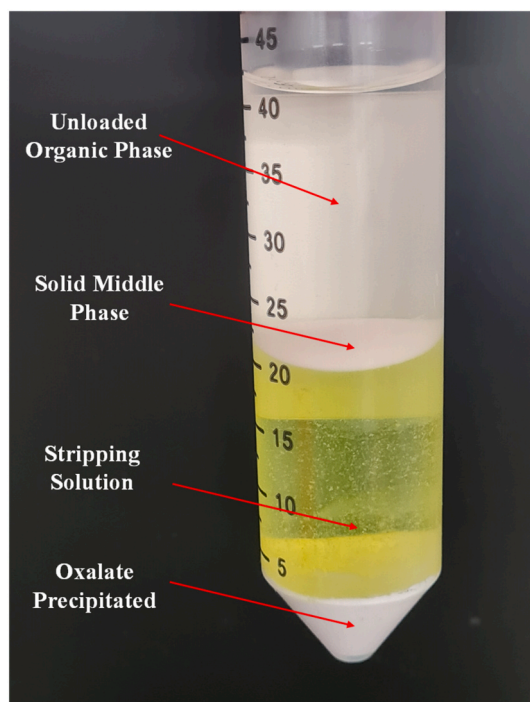
Table 4
The metal concentration in the leaching and solvent extraction branches.

Branch	Fe (mg/L)	B (mg/L)	Pr (mg/L)	Dy (mg/L)	Nd (mg/L)	Tb (mg/L)	Y (mg/L)
The mixture of PLS	36,414	515	2773	1632	14,282	189	62
Raffinate solution	26,729	501	321	4	1144	1	0
Loaded organic phase	9685	14	2452	1628	13,138	188	62

Table 5

Designed Conditions of the stripping experiments and their results (X_1 = Stripping reagent to the loaded organic phase volume ratio (1.0, 1.5, and 2.0), X_2 = oxalic acid concentration in stripping reagent (0.25, 0.5, and 0.75 M), X_3 = stripping time (15,30, and 45 Mins), X_4 = stirring rate (150, 250, and 350 rpm)).

No	X_1	X_2	X_3	X_4	S_H	S_L	MR_H (%)	MR_L (%)	Total REEs grade (%)
1	-1	-1	0	0	85	141	43.8	72.7	34.1
2	1	-1	0	0	310	394	66.7	84.8	36.9
3	-1	1	0	0	320	305	86.4	82.2	41.5
4	1	1	0	0	602	556	88.0	81.2	43.9
5	0	0	-1	-1	337	561	28.6	47.4	29.1
6	0	0	1	-1	423	519	63.6	78.2	42.6
7	0	0	-1	1	519	601	70.5	81.6	40.4
8	0	0	1	1	364	381	73.9	77.1	36.7
9	-1	0	0	-1	377	566	48.1	72.2	39.1
10	1	0	0	-1	384	517	60.8	81.8	40.1
11	-1	0	0	1	213	219	72.9	74.9	35.9
12	1	0	0	1	592	585	83.9	83.1	39.9
13	0	-1	-1	0	194	252	68.5	89.0	39.8
14	0	1	-1	0	472	461	74.7	72.9	41.3
15	0	-1	1	0	184	261	44.8	63.7	35.5
16	0	1	1	0	582	550	64.7	61.2	41.3
17	-1	0	-1	0	213	200	79.3	74.5	40.0
18	1	0	-1	0	473	695	43.5	63.9	38.6
19	-1	0	1	0	291	269	62.9	58.0	37.4
20	1	0	1	0	457	478	80.0	83.7	40.2
21	0	-1	0	-1	175	389	36.0	79.8	36.0
22	0	1	0	-1	612	733	63.3	75.8	41.1
23	0	-1	0	1	482	444	98.4	90.6	36.8
24	0	1	0	1	154	215	49.5	69.1	35.4
25	0	0	0	0	418	448	80.8	86.5	41.4
26	0	0	0	0	410	385	88.7	83.5	40.1
27	0	0	0	0	388	384	82.3	81.4	40.1



B. S. S.

Fig. 1. The phases produced at the stripping stage of loaded D2EHPA by oxalic acid.

3.1. Model analysis

Analysis of variance (ANOVA) was applied to the results to evaluate the main and interaction effects of parameters on the responses of the precipitation stripping process by oxalic acid (Table 6). All responses were modeled without any transformation and found to be significant, with a confidence level exceeding 99 %. The models' R-squared values (i.e., the coefficient of multiple determination) of models were 0.82, 0.80, 0.45, 0.56, and 0.51 for S_L , S_H , MR_L , MR_H , and the total REEs grade in oxalate powder, respectively. Also, adjusted R-squared and predicted R-squared coefficients were close for S_L , S_H , and MR_L models. Additionally, the adequate precisions were greater than four for all models, indicating a satisfactory fit of the derived models to the responses [46–48]. Also, the results indicate the significance of the interaction effects of the parameters, which shows the necessity of considering their simultaneous effects. The resulting quadratic models are expressed by Equations (5)–(9) (based on the coded values).

$$S_H = +371.53 + 109.94*X_1 + 109.36*X_2 + 1.41*X_4 + 92.96*X_1*X_4 - 191.13*X_2*X_4 \quad (5)$$

$$S_L = +385.22 + 127.13*X_1 + 78.26*X_2 - 69.91*X_4 + 104.09*X_1*X_4 - 143.14*X_2*X_4 + 92.15*X_4^2 \quad (6)$$

$$MR_H (\%) = +66.84 + 5.69*X_2 + 12.40*X_4 - 19.08*X_2*X_4 \quad (7)$$

$$MR_L (\%) = +79.97 + 3.64*X_1 - 0.62*X_3 + 3.43*X_4 + 9.07*X_1*X_3 - 8.79*X_3*X_4 - 9.04*X_3^2 \quad (8)$$

$$\text{Total REEs grade (\%)} = +38.71 + 2.13*X_2 + 0.38*X_3 - 0.24*X_4 - 4.32*X_3*X_4 \quad (9)$$

where X_1 to X_4 are the investigated parameters described in Table 3.

The selectivity of heavy and light REEs recovery via iron recovery was examined using ANOVA analysis, as presented in Table 6. Oxalic acid concentration, the S/LO ratio, and the interaction of stirring rate with oxalic acid concentration and the S/LO ratio were found to be significant for both responses (with a confidence level exceeding 98 %). Additionally, the effect of stirring rate on the selectivity of light REEs recovery was deemed significant. As can be seen in Table 5, the selectivity of heavy REEs recovery ranged from 86 to 618, while the selectivity of light REEs recovery varied between 171 and 887. It should be noted that the minimum selectivity was observed at the low levels of chemical parameters (oxalic acid concentration of 0.25 M and S/LO ratio of 1.0) and the medium levels of

Table 6

The ANOVA table for S_H , S_L , MR_H , MR_L , and total REEs grade. X_1 = stripping reagent to the loaded organic phase volume ratio, X_2 = oxalic acid concentration in stripping reagent, X_3 = stripping time, X_4 = stirring rate.

Response	Parameters					Fitted model			
	Variable	Sum of Squares	df	F Value	p-Value	R ²	Adj R ²	Pred R ²	Adeq Precision
S_H	Model	479800	5	19.30	<0.0001	0.8213	0.7787	0.6326	18.282
	X_1	148300	1	29.83	<0.0001				
	X_2	146700	1	29.51	<0.0001				
	X_4	24	1	0.0048	0.9450				
	X_1X_4	35339	1	7.11	0.0145				
	X_2X_4	149400	1	30.05	<0.0001				
	Residue	104400	21						
S_L	Model	745100	6	12.98	<0.0001	0.7957	0.7344	0.5835	14.407
	X_1	284500	1	29.74	<0.0001				
	X_2	107800	1	11.27	0.0031				
	X_4	86028	1	8.99	0.0071				
	X_1X_4	63563	1	6.64	0.0180				
	X_2X_4	120200	1	12.57	0.0020				
	X_4^2	83037	1	8.68	0.0080				
Residue	191300	20							
MR_H (%)	Model	2577.08	3	6.21	0.0030	0.4476	0.3756	0.1848	11.627
	X_2	271.36	1	1.96	0.1746				
	X_4	1288.48	1	9.32	0.0056				
	X_2X_4	1017.24	1	7.36	0.0124				
	Residue	3179.86	23						
MR_L (%)	Model	1490.53	6	4.25	0.0064	0.5603	0.4284	0.0745	7.569
	X_1	159.69	1	2.73	0.1141				
	X_3	4.65	1	0.080	0.7808				
	X_4	141.15	1	2.41	0.1360				
	X_1X_3	329.58	1	5.64	0.0277				
	X_3X_4	309.83	1	5.30	0.0322				
	X_3^2	545.63	1	9.33	0.0063				
	Residue	1169.65	20						
Total REEs grade (%)	Model	131.43	5	5.78	0.0025	0.5125	0.4239	0.0383	9.165
	X_2	54.45	1	9.58	0.0053				
	X_3	1.76	1	0.31	0.5832				
	X_4	0.67	1	0.12	0.7355				
	X_3X_4	74.55	1	13.12	0.0015				
	Residue	125.00	22						

operational parameters (stripping time of 30 min and stirring rate of 250 rpm). Conversely, the maximum selectivity was achieved at an oxalic acid concentration of 0.75 M, S/LO ratio of 1.5, stripping time of 30 min, and stirring rate of 150 rpm.

The stirring rate and its interaction with oxalic acid concentration were the main significant parameters influencing the overall metal recovery of heavy REEs, with a confidence level of more than 98 %. Moreover, the ANOVA results indicated that stripping time, as well as its interaction with the S/LO ratio (X_1X_3) and stirring rate (X_3X_4), were identified as the main parameters affecting the overall metal recovery of light REEs, with a confidence level of higher than 98 %. Within the examined conditions (as shown in Table 5), the overall recovery of light REEs ranged from 47.4 % to 90.6 %, while for heavy REEs it changed from 28.6 % to 98.4 %. The maximum overall metal recovery for both light and heavy REEs was achieved at a S/LO volume ratio of 1.5, oxalic acid concentration of 0.25 M, stripping time of 30 min, and stirring rate of 350 rpm.

Another critical response of the precipitation stripping process was the total REEs grade (the sum of all studied REEs) in the oxalate powder. This response ranged from 29.4 % (the S/LO volume ratio, oxalic acid concentration, stripping time, and stirring rate of 1.5, 0.5 M, 15 min, and 150 rpm, respectively) to 44.0 % (the S/LO volume ratio, oxalic acid concentration, stripping time, and stirring rate of 2.0, 0.75 M, 30 min, and 250 rpm, respectively). The main parameters influencing it were identified as the oxalic acid concentration and the interaction of stripping time with stirring rate (operational parameters).

The following sub-sections present the findings of the stripping stage and elucidate the effect of chemical and operational parameters on this process. It needs to be pointed out that the influence of these parameters on the responses was evaluated at the medium level of the other parameters.

3.2. Effect of chemical and operational parameters on the precipitation stripping stage efficiency

3.2.1. Effect of stripping reagent to loaded D2EHPA volume ratio

The effect of the S/LO volume ratio in the range of one to two on the selectivity, metal recovery, and the overall grade of REEs in the achieved REE-oxalate powder during the stripping process was investigated using the results of RSM experiments. Results showed that this parameter significantly influenced the selectivity of heavy and light REEs recovery via iron at this stage (Fig. 2a and b, respectively). By increasing the S/LO volume ratio from one to two, the selectivity for heavy REEs (S_H) and light REEs (S_L) rose from 262 to 481 and 258 to 512, respectively. The heightened selectivity shows that the high concentration of oxalate ions ($C_2O_4^{2-}$) led to a more efficient separation and precipitation of REEs (light and heavy) via iron ions, i.e., facilitating the extraction of all REEs from D2EHPA. While the S/LO ratio significantly affected the selectivity of REEs recovery, its influence on the overall REEs recoveries and the total REEs grade in the oxalate powder was found to be insignificant. Therefore, it can be concluded that this parameter might have a considerable effect on the iron concentration in the resulting oxalate powder during these experiments.

3.2.2. Effect of oxalic acid concentration in the stripping reagent

The effect of oxalic acid concentration in the stripping reagent on the precipitation stripping process of loaded D2EHPA was investigated in the range of 0.25–0.75 M using BBD-designed experiments. It should be noted that the oxalic acid solution is saturated at ~ 0.9 M at 25 °C. Table 6 illustrates that oxalic acid concentration significantly affected S_H , S_L , and the total REEs grade in the oxalate precipitated responses (Fig. 3a, b, and 3c, respectively). Dissolving oxalic acid follows the following two-step dissociation equilibrium (Equations (10) and (11)) [32].



The equilibrium constants of Equations (10) and (11) are 5.9×10^{-2} and 6.40×10^{-5} , respectively. The forms of oxalate species depend on the pH of the solution. It has been reported that at a pH of less than one, the main species of dissolving oxalic acid is $H_2C_2O_4$ [49,50]. Thus, the reaction of oxalic acid with REEs is in Equation (12) [51].

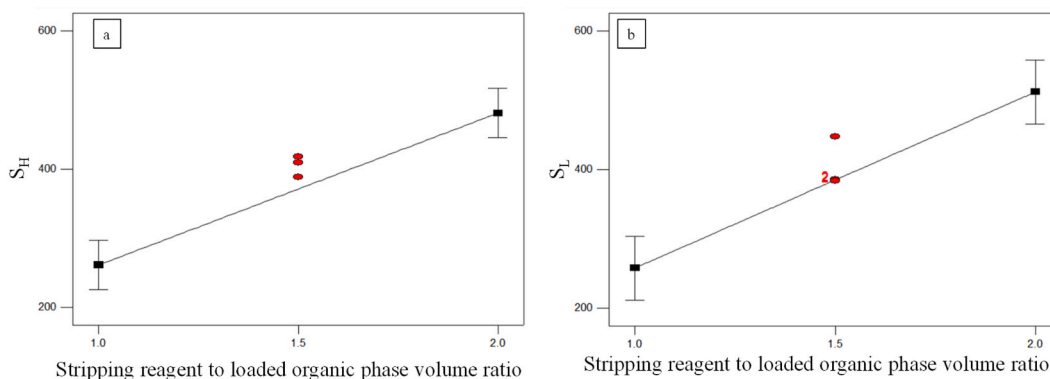


Fig. 2. The effect of stripping reagent to loaded D2EHPA volume ratio on the a) S_H and b) S_L .

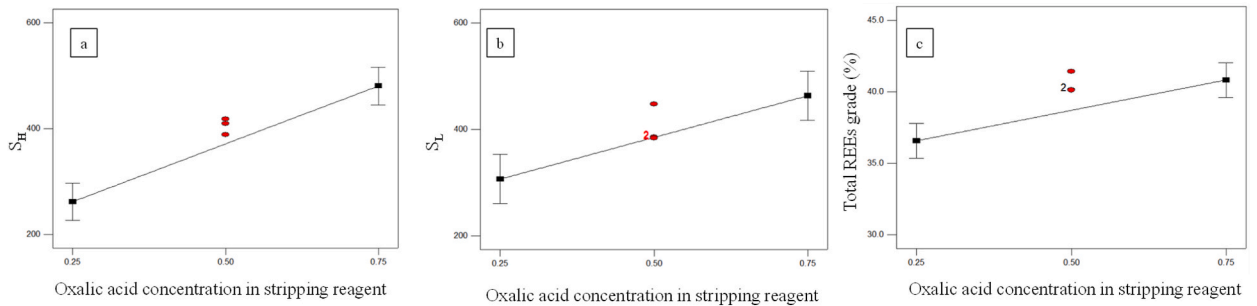


Fig. 3. The effect of oxalic acid concentration of stripping reagent on the a) S_H , b) S_L , and c) the total REEs grade of oxalate powder.



Results showed that enhancing the oxalic acid concentration from 0.25 to 0.75 M led to the growth of the S_H value from 262 to 481 and the S_L value from 307 to 463. Increasing both the S/LO (X_1) and the concentration of oxalic acid in the stripping solution (X_2) improved the selectivity of the precipitation stripping process for rare earth elements, augmenting the amount of $\text{C}_2\text{O}_4^{2-}$ for a consistent volume of the loaded organic phase, leading to a greater formation of REE-oxalate compared to iron-oxalate. Reacting oxalic acid with iron (Equation (13)) produces the complex $\text{Fe}(\text{C}_2\text{O}_4)_3^{3-}$, which is soluble in an oxalic acid solution [52].



Fig. 3c indicates that raising the oxalic acid concentration from 0.25 to 0.75 M elevated the total REEs grade in the oxalate powder from 36.6 to 40.8 %. It means that the stripping process product at a higher concentration of oxalic acid improves the quality of REE-oxalate for subsequent processes. Moreover, the rise in the overall REEs grade resulting from an increase in oxalic acid concentration underscores the effect of higher $\text{C}_2\text{O}_4^{2-}$ levels in the stripping reagent, leading to the precipitation of a greater quantity of REEs than iron, as previously mentioned. Jorjani and Shahbazi [35] also reported that the REEs grade in the final product is strongly dependent on the oxalic acid concentration, with REEs oxide increasing from 61.2 % to 89.1 % as the oxalic acid concentration rises from 5 % to 15 %.

3.2.3. Effect of stripping time

To investigate the effect of stripping time on the efficiency of the precipitation stripping process, several experiments were carried out by varying this parameter in the range of 15–45 min. While the main effect of stripping time was only significant on the overall metal recovery of light REEs (MR_L), its interaction with the S/LO ratio and stirring rate proved noteworthy. As shown in Fig. 4, increasing the stripping time from 15 to approximately 30 min increased the metal recovery of light REEs from 71.6 to 80.0 %. However, extending the stripping time beyond 30 decreased this response to 70.3 %. Zhang et al. [53] and Harvianto et al. [54] indicated that increasing the stripping time can enhance stripping efficiency to a maximum value. The reduction in overall metal recovery with stripping times ranging from 30 to 45 min can be attributed to a reverse reaction, leading to the dissolution of precipitated light REE-oxalate. To put it another way, the extended experiment duration within this range may contribute to the dissolution of precipitated light REEs, transferring them back into the stripping solution.

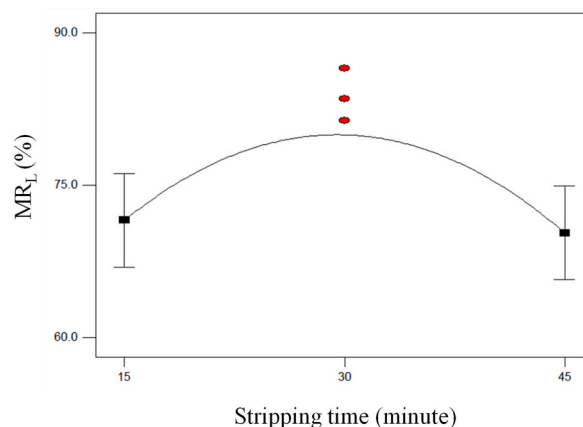


Fig. 4. The effect of stripping time on the MR_L .

3.2.4. Effect of stirring rate

The influence of stirring rate in the range of 150–350 rpm on the stripping process efficiency was examined using ANOVA analysis (Table 6). The results showed a significant effect of stirring rate on S_L and REEs grade in the REE-oxalate product (with a confidence level of more than 99 %). Fig. 5a and b illustrate the effect of the stirring rate on S_H and S_L , respectively.

Although increasing the stirring rate from 150 to ~290 rpm led to a decrease in S_L from 547 to 370, further increasing the stirring rate to 350 rpm slightly improved this response to 407. This behavior can be attributed to the kinetics of transferring ions from the loaded D2EHPA to the stripping solution. High stirring rates facilitate the transfer of all ions in the loaded organic phase to the stripping solution or precipitated powder, reducing the selectivity in the precipitation stripping process.

Moreover, raising the stirring rate from 150 to 350 rpm enhanced the overall metal recovery of heavy REEs from 54.4 to 79.2 %. According to previous achievements, this might show the significant role of stirring rate in the kinetics of Dy, Y, and Tb stripping. Also, the lesser abundance of heavy REEs compared to light REEs in the permanent magnet swarf may have caused the effect of the stirring rate to be insignificant on the selectivity of heavy REEs extraction. It is noteworthy that increasing the stirring rate promotes the dispersion of the stripping reagent, thereby enhancing the contact area between the two phases and improving the stripping efficiency [55].

3.2.5. Interaction effect of volume ratio of S/Lo and stirring rate

The results of ANOVA analysis showed a significant effect of interaction between the volume ratio of S/LO and stirring rate (X_1X_4) on the stripping selectivity of recovering heavy and light REEs (Fig. 6a and b, respectively). Increasing the volume ratio of S/LO from 1.0 to 2.0 at all stirring rate levels resulted in higher values of both S_H and S_L responses. For instance, raising the S/LO from 1 to 2 increased S_H from 355 to 387 and S_L from 524 to 570 at the low level of stirring rate (150 rpm), while S_H was enhanced from 170 to 576 and S_L from 176 to 639 at high level of stirring rate (350 rpm). Therefore, a high S/LO volume ratio is recommended to maximize the selectivity of recovering REEs in the precipitation stripping.

On the other hand, two distinct trends for S_H and S_L were observed concerning the stirring rate. At the low level of S/LO volume ratio (1.0), increasing the stirring rate from 150 to 350 rpm led to a decrease in S_H from 353 to 170 and S_L from 524 to 176. Conversely, at the high level of S/LO volume ratio (2.0), increasing the stirring rate from 150 to 350 rpm enhanced S_H from 387 to 576 and S_L from 570 to 639. This suggests that at lower S/LO ratios, the stripping process tends to form iron-oxalate more than REE-oxalate. Consequently, increasing the stirring rate results in the precipitation of iron oxalate relative to REEs. Notably, the higher amount of $C_2O_4^{2-}$ in the system with an increased S/LO volume ratio favored the formation of REE-oxalate, leading to the improvement of S_H and S_L with higher stirring rates.

3.2.6. Interaction effect of oxalic acid concentration and stirring rate

The interaction effects of oxalic acid concentration and stirring rate (X_2X_4) on S_H , S_L , and MR_H in the final product are shown in Fig. 7a, b, and 7c, respectively. These diagrams exhibit a consistent trend across the parameters. At the low levels of both X_2 and X_4 , an increase in one parameter results in an increase in the mentioned responses. Conversely, at the high levels of each parameter, increasing another parameter leads to a decrease in the responses. For instance, the highest values of S_H (671) and S_L (769) were achieved at a stirring rate of 150 rpm and an oxalic acid concentration of 0.75 M, while the highest value of MR_H (92.6 %) was attained at a stirring rate of 350 rpm and an oxalic acid concentration of 0.25 M.

Increasing the oxalic acid concentration from 0.25 to 0.75 M at a stirring rate of 150 rpm resulted in increases in S_H , S_L , and MR_H from 70 to 671, from 326 to 769, and from 29.7 to 79.2 %, respectively. This augmentation can be attributed to the forming of more REEs-oxalate in the presence of higher values of $C_2O_4^{2-}$. Conversely, augmenting the oxalic acid concentration from 0.25 to 0.75 M at a high stirring rate (350 rpm) led to reductions in S_H , S_L , and MR_H from 455 to 291, from 472 to 342, and from 92.6 to 65.8 %, respectively. Although higher values of oxalic acid concentration led to an increase in the amount of oxalate precipitated, the highest value of stirring rate might cause the dissolution of REE-oxalate and the transfer of these metals to the stripping solution, thereby reducing the selectivity of REEs via iron recovery. Some other researchers have also reported the positive effect of increasing the

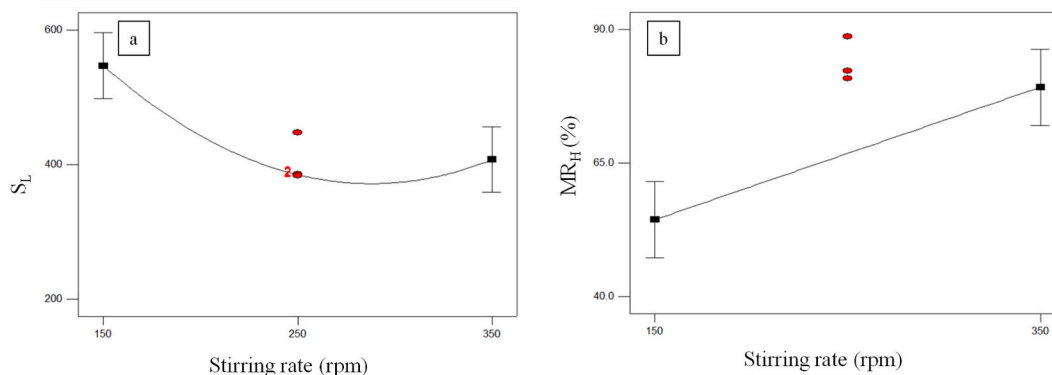


Fig. 5. The effect of stirring rate on the a) S_L and b) MR_H .

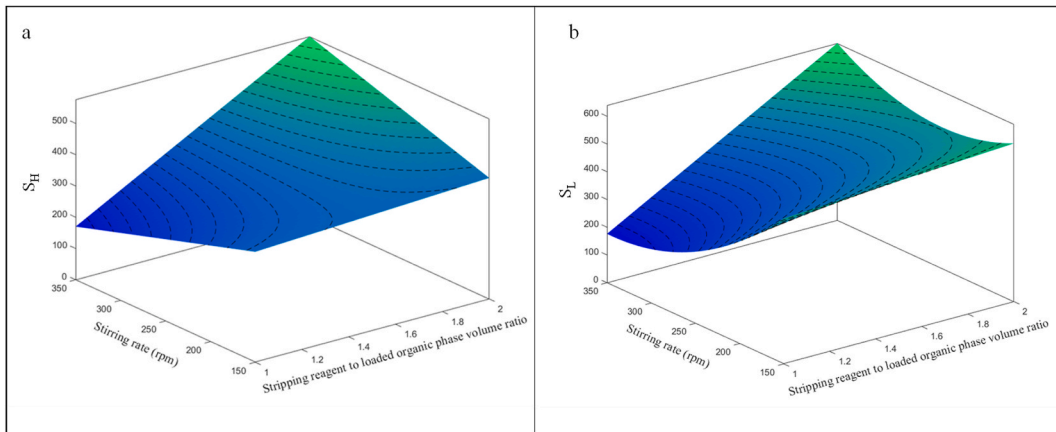


Fig. 6. The interaction effect of stripping reagent to loaded organic phase volume ratio and stirring rate on a) S_H and b) S_L responses.

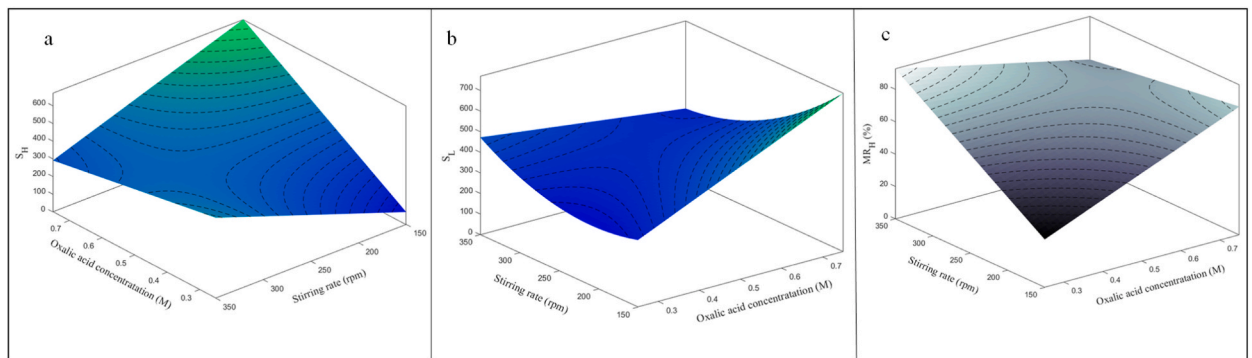


Fig. 7. The interaction effect of Oxalic acid concentration in stripping reagent and stirring rate on a) S_H and b) S_L c) MR_H responses.

concentration of stripping reagents on metal recovery [56–58].

Furthermore, enhancing the stirring rate from 150 to 350 rpm at the low level of X_2 (0.25 M) resulted in an increase in S_H , S_L , and MR_H from 70 to 455, from 326 to 472, and from 29.7 to 92.6 %, respectively. Conversely, at the high level of X_2 (0.75 M), increasing the stirring rate led to decreases in S_H , S_L , and MR_H from 671 to 291, from 769 to 343, and from 79.2 to 65.8 %, respectively. As mentioned earlier, this behavior can be attributed to the reversible chemical reaction of REE-oxalate precipitation and the tendency to dissolve REE-oxalate more than Fe-oxalate.

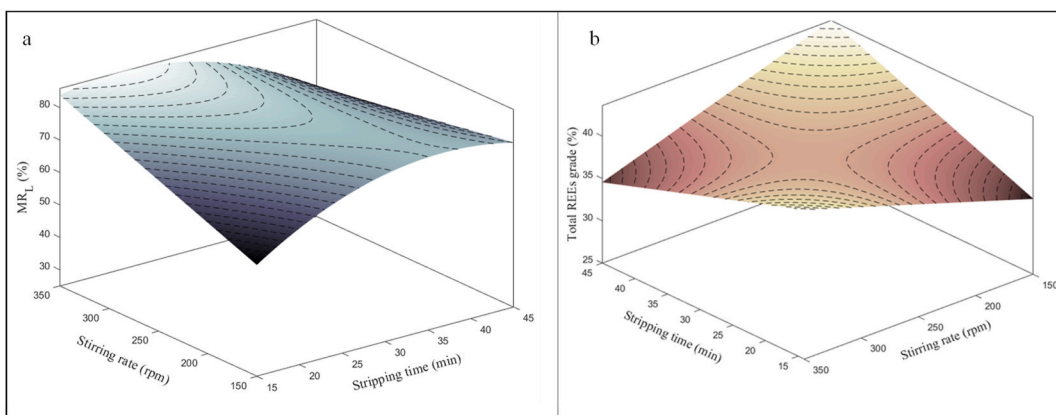


Fig. 8. The interaction effect of stripping time and stirring rate on a) MR_H and b) total REEs grade of oxalate powder responses.

3.2.7. Interaction effect of stripping time and stirring rate

The interaction effect of stirring rate and stripping time (the operational parameters, X_3X_4) on the overall metal recovery of light REEs (Fig. 8a) and the total grade of REEs of the precipitated oxalate product (Fig. 8b) was significant.

The results showed that increasing the stripping time from 15 to 45 min led to an increase in the total REEs grade from 34.2 % to 43.6 % at the stirring rate of 150 rpm, while decreasing this response from 42.4 % to 34.5 % at the stirring rate of 350 rpm. Additionally, a similar trend was observed for the effect of stirring rate. These trends illustrate the opposite performance of these operational parameters. It could be concluded that the REE-oxalate was precipitated in the first step, and a portion of it was dissolved and transferred to the stripping solution in the second step. Thus, although increasing the operational parameters caused an increase in the portion of precipitated REEs (to a maximum value), increasing the agitation of the precipitated material causes the dissolution of the REEs precipitated material.

Furthermore, it was found that increasing the stripping time for all levels of stirring rate led to an increase in the MR_L to a maximum value (beyond a specific stripping time, a slight reduction occurred). Also, increasing the stirring rate between 15 and 35 min of stripping time led to an improvement in the MR_L response, while it decreased in the 35–45 min range. This behavior shows the interaction effect of these parameters on the response of the total grade of REEs.

3.2.8. Interaction effect of volume ratio of S/LO and stripping time

The interaction effect between the S/LO ratio and stripping time was found to be significant in the metal recovery of light REEs, with a confidence level of more than 97 % (Fig. 9). Notably, increasing the S/LO ratio showed an enhancement in MR_L for all stripping time levels. This improvement can be attributed to the presence of more oxalate ions in the system, facilitating the formation of REE-oxalate compounds. Additionally, MR_L was increased with longer stripping times, reaching a maximum threshold dependent on the S/LO ratio. This rise in light REEs recovery is correlated with the time required to achieve maximum precipitation. Conversely, the subsequent reduction in this response with extended stripping times suggests the dissolution of some of the produced REE-oxalate compounds.

The interaction between stripping time, stirring rate, and the S/LO ratio on stripping efficiency highlights the significance of media turbulence in stripping kinetics. Konishi et al. [34] reported that the kinetics of precipitation stripping of Nd with oxalic acid are controlled by the mass transfer in the organic phase, and the amount of oxalic acid in the strip solution does not influence the process rate.

3.2.9. Iron co-precipitation

Although the main goal of this process was to recover REEs by adding oxalic acid, the results showed that a portion of the extracted iron also precipitated. Based on the suggestion that adding deionized hot water (70 °C) can remove iron from loaded D2EHPA [35], an experiment was carried out by adding water as a scrubber for the loaded organic phase. However, the results showed that this method was unsuccessful in removing iron.

In earlier sections, the effect of iron on the selectivity of the process was evaluated. Additionally, the influences of investigated parameters of iron recovery and iron grade in the REE-oxalate product were assessed using ANOVA analysis. The main effects of S/LO, oxalic acid concentration, and stirring rate were meaningful on iron recovery and grade, with a confidence level above 95 %. Fig. 10a and b shows the variation of iron grade and recovery with these parameters, respectively.

As shown, increasing the amount of oxalate ion by raising the S/LO or oxalic acid concentration led to a decrease in both iron grade and recovery. It has been noted that higher amounts of oxalate ions result in better REE recovery than iron. Conversely, increasing the stirring rate increased the iron grade and recovery. This can be attributed to the increase in the turbulence of the stripping medium, consequently increasing the contact surface of phases, as well as the kinetics of the reaction between iron and $C_2O_4^{2-}$. As iron oxalate

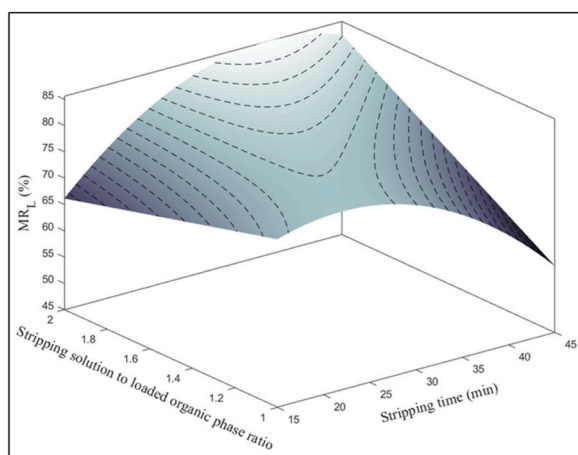


Fig. 9. The interaction effect of stripping time and stripping reagent to loaded organic phase volume ratio on MR_L response.

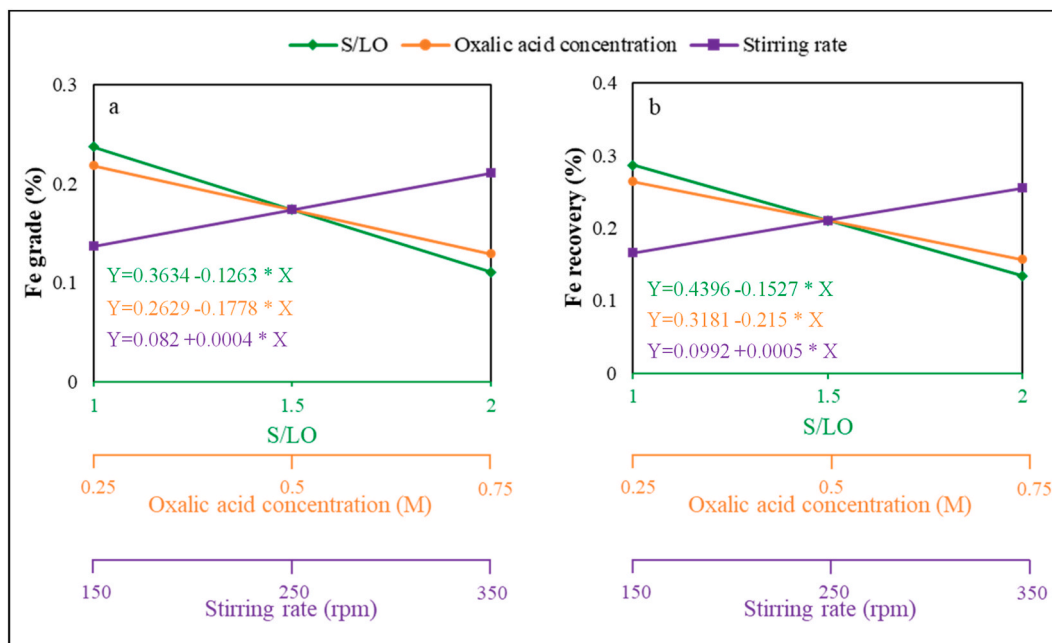


Fig. 10. The effect of S/LO, oxalic acid concentration, and stirring rate on the a: iron grade in REE-oxalate product and b: iron recovery.

remains in the stripping solution during the precipitation of REEs using oxalic acid [59], the resulting REE-oxalate powder typically shows low iron impurities, as observed in this research.

3.3. Optimization

In this section, the precipitation stripping process was optimized by applying ANOVA analysis to the results. To achieve this goal, various responses, including the selectivity of REEs via iron recovery (S_L and S_H), overall REEs recovery (MR_L and MR_H), and the total REEs concentration in the precipitated powder, were chosen to reach maximum levels. The optimization suggested that the highest efficiency could be achieved with a S/LO ratio of 2, oxalic acid concentration in the stripping reagent of 0.75 M, stripping time of 44 min, and stirring rate of 150 rpm. Since the predicted optimal conditions differed from those designed in the RSM experiments, an additional experiment was carried out at the predicted conditions to validate the desirable responses. The pH of the oxalic acid solution before reacting with the loaded organic phase (0.75 M) was 0.79, and after the reaction was 0.70. As shown in Equation (12), recovering REEs by oxalic acid causes a decrease in the pH of the solution.

The metal concentration of oxalate and oxide powders achieved at the optimum conditions and the optimal responses are shown in Tables 7 and 8, respectively. The test results obtained under optimal conditions showed a strong correlation with the predicted responses, confirming the reliability of the optimization process. The high values of the responses show the high efficiency of the precipitation stripping stage using oxalic acid. Fig. 11a shows the scanning electron microscopy (SEM) image of the REEs-oxalate powder obtained under the optimum levels of parameters. As can be seen, the REEs-oxalate precipitated in a tetragonal shape with dimensions of approximately 2 μm by 6 μm . Smith [33] reported that REE oxalate produced using oxalic acid as the precipitation stripping reagent forms tetragonal structures.

To convert REEs-oxalate to REEs-oxide, the materials were subjected to a furnace at 850 $^{\circ}\text{C}$ for 1 h. It was observed that approximately 81.8 % of the REEs-oxide powder consists of REEs, indicating the high purity of the product. Additionally, Fig. 11b shows the X-ray diffraction (XRD) pattern of the REEs-oxide powder. As can be seen, the oxide forms of Nd, Pr, and Tb are the main components of this product.

Additionally, an experiment was carried out using phosphoric acid to evaluate the effect of this stripping reagent. The values of S_H , S_L , MR_H , MR_L , and the total REEs grade in the oxalic product using the phosphoric acid experiment were 38, 574, 3.8 %, 56.9 %, and 46.8 %, respectively. Comparatively, the metal recovery and selectivity of rare earth elements (S_L and S_H) with oxalic acid were found to be higher than with phosphoric acid. In addition, it was observed that almost all heavy rare earth elements were not recovered and

Table 7

The metal concentration of oxalate and oxide powders at the optimum condition.

Metal	Fe %	B %	Pr %	Dy %	Nd %	Tb	Y %
Oxalate powder	0.12	0.01	4.80	3.64	34.56	0.33	0.05
Oxide powder	0.15	0.01	11.96	6.86	61.91	0.92	0.13

Table 8

The values of parameters and related responses in the optimum conditions: S/LO volume ratio of 2.0, the oxalic acid concentration in the stripping reagent of 0.75 M, stripping time of 44 min s, and the stirring rate of 150 rpm.

	S_H	S_L	MR_H (%)	MR_L (%)	The total REEs grade (%)
Calculated	688	792	79.2	88.4	45.5
Experimented	647	701	80.3	86.8	43.4
Error	-6.2 %	-13 %	+1.5 %	-1.8 %	-4.4 %

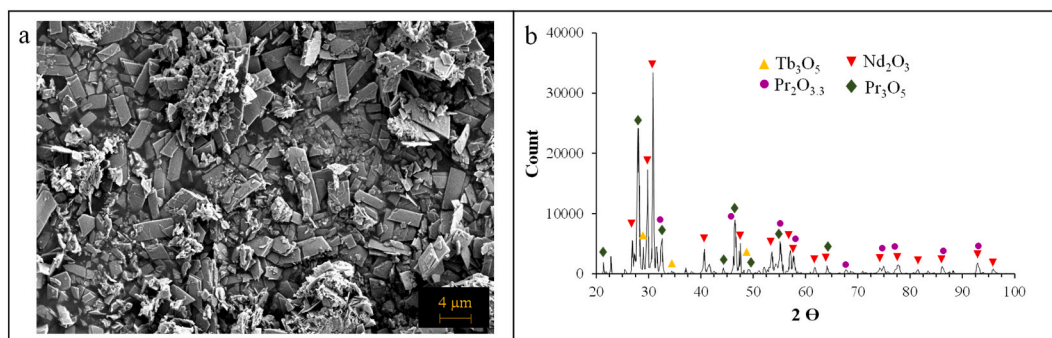


Fig. 11. a: The SEM image of REE-oxalate and b: the XRD pattern of REE-oxide products of using oxalic acid as the stripping reagent of loaded D2EHPA.

remained in the organic phase using phosphoric acid as the stripping reagent. Conversely, the oxalate powder obtained from the phosphoric acid reaction was slightly purer than the powder produced by adding oxalic acid.

Although approximately 25 % of the iron was extracted by D2EHPA during the solvent extraction, a small fraction was stripped by oxalic acid and precipitated as oxalate. This issue contributed to achieving high selectivity in this process, marking it as one of the main advantages of this method.

3.4. Recyclability of the organic phase

To evaluate the recyclability of the unloaded organic phase obtained from the precipitation stripping stage and its reuse in the solvent extraction stage, several experiments were conducted under two conditions: a) with 20 % makeup and b) without any makeup. It should be noted that the chemical and operational parameters were set at optimum levels (section 3-3). During the recycling investigation, it was observed that an intermediate precipitated phase was formed during the extraction experiments. Analysis via ICP-OES (Table 9) indicated that most of this powder consisted of iron (with a neodymium concentration of less than 0.5 %). Indeed, the presence of iron in this powder and its yellow color indicates that a fraction of the iron in the PLS may be precipitated as Fe-oxalate ($C_6Fe_2O_{12}$) during the extraction stage. It is important to highlight that the ferric oxalate complex ion exhibits high stability in aqueous phases, whereas ferrous oxalate is significantly insoluble in oxalic acid solutions [52]. Notably, the loss of these elements in this part was negligible due to the low concentration of REEs in this intermediate phase.

The results obtained from the extraction and stripping stages over four recycling steps of the organic phase (with and without makeup) for S_H , S_L , MR_H , MR_L , and total REEs grade in the precipitated particles are presented in Fig. 12a, 12b, 12c, 12d, and 12e, respectively. While there wasn't a significant alteration in the extraction and precipitation stripping efficiency for both series of recycling organic phase experiments in cycles 2 and 3, the results were dropped in the 4th recycle. Harvianto et al. [54] also found that solvent extraction efficiency decreased notably when the organic phase was recycled more than three times. The changes in organic phase viscosity during recycling experiments (pre- and post-addition of solvent to makeup) are presented in Fig. 13.

It was impossible to continue the experiment beyond the fourth cycle due to the high viscosity of the recycled organic phase, reaching 70 kg/m.s. The increased viscosity of the recycled organic phase could be the primary reason for the reduced stripping efficiency in the 4th recycle experiment. Additionally, the accumulation of iron ions in each cycle might contribute to a decrease in the loading capacity of the organic phase. The high viscosity of the organic phase reduces the turbulence of phases and thus diminution the efficiency of the process in the extraction and separation stages. Furthermore, heightened viscosity prolongs the phase separation duration in the settler stage. The rise in the viscosity of the organic phase can be ascribed to the evaporation of n-Heptane (which has a low boiling point) in the recycling experiments, resulting in an elevated concentration of D2EHPA. Therefore, adding only diluent to the organic phase or using higher makeup ratios can potentially solve the problem of high viscosity in the recycled organic phase.

Fig. 14 proposes an efficient flowsheet for recovering valuable metals from permanent magnet swarf based on the results of this research.

This research demonstrated that using oxalic acid for precipitation stripping loaded D2EHPA from the recycling process of end-of-life permanent magnets can efficiently recover REEs with high purity and minimal impurities. The stripping efficiency of light and

Table 9
The metal concentration of yellow powder achieved in the extraction stage of the recycled organic phase.

Fe %	B %	Pr %	Dy %	Nd %	Tb	Y %
8.76	0.02	0.07	0.00	0.50	0.00	0.00

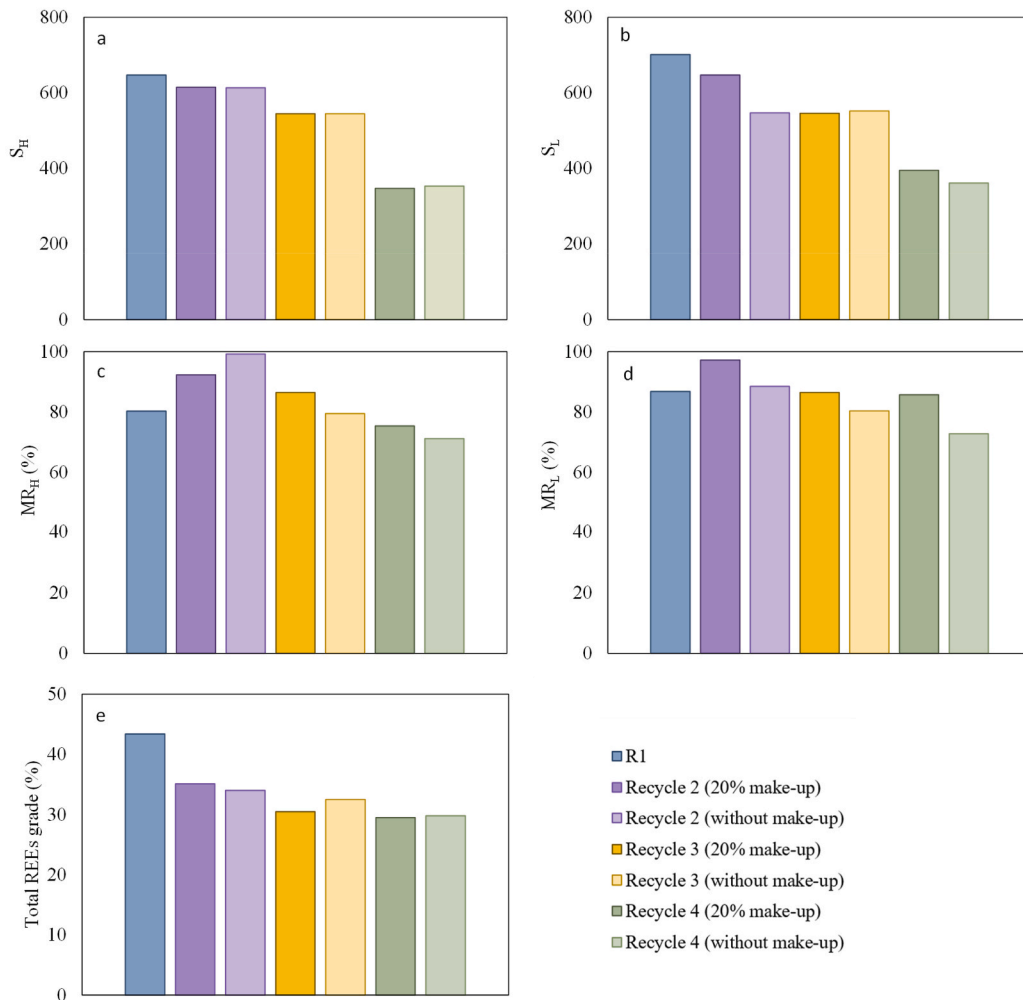


Fig. 12. The efficiency of extraction and stripping processes using recycled organic phase. a) Selectivity of heavy REEs via Iron recoveries, b) Selectivity of light REEs via Iron recoveries, c) overall heavy REEs recovery, d) overall light REEs recovery, e) the total REEs grade in the REE-oxalate powder.

heavy REEs in this method were 87 % and 80 %, respectively. Additionally, the stripping selectivity of REE over iron was greater than 600, resulting in an iron concentration of approximately 0.1 % in the final product. This method eliminates the required stage to convert other REE components into oxalate. Furthermore, the organic phase obtained through this method can be recycled multiple times to extract REEs from REE-citrate solutions. This approach provides the necessary raw materials for the various industries, promoting a circular economy and sustainable development of REPMS.

4. Conclusion

To pursue the recovery of REEs from permanent magnet swarf, the effects of the main parameters of the precipitation stripping process with a method using oxalic acid, including the volume ratio of stripping reagent to loaded organic phase (S/LO ratio), oxalic acid concentration in the stripping reagent, stripping time, and stirring rate, were investigated and optimized. Through rigorous experimentation and using analysis of variance (ANOVA), the following were found as concluding remarks.

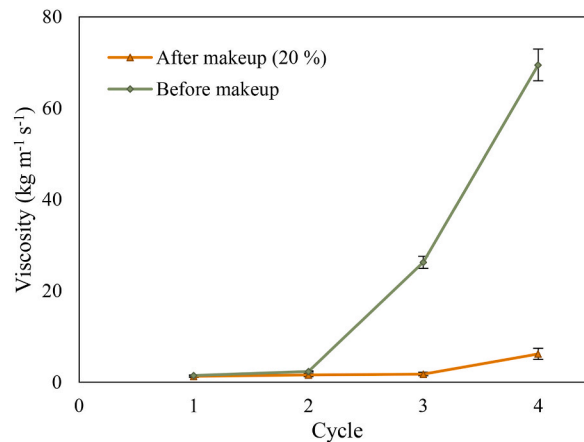


Fig. 13. The viscosity changes of the organic phase during the recycling evaluation.

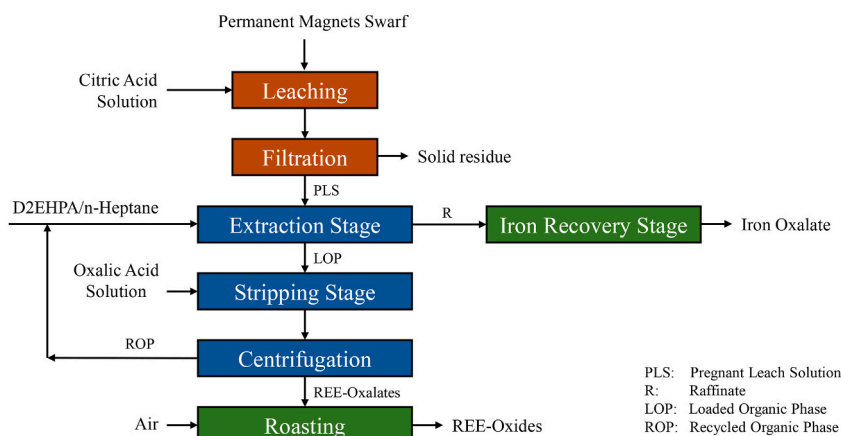


Fig. 14. The block diagram of REEs recycling from permanent magnet swarf.

- Applying oxalic acid as the stripping reagent streamlined the production of REE-oxalate powder from the loaded organic phase and was more efficient than alternative reagents like phosphoric acid. In addition, REEs can be converted to the oxide by being placed in a furnace at 850 °C for 1 h.
- The ANOVA model specified that optimal conditions to maximize the extraction and stripping efficiency could be achieved at a S/LO volume ratio of 2.0, oxalic acid concentration of 0.75 M, stripping time of 44 min, and stirring rate of 150 rpm. Under these conditions, high overall metal recovery of light (88 %) and heavy REEs (80 %), with selectivity favoring REEs recovery via iron (S_L of 792 and S_H of 688), and a final product with high REEs purity (45.5 %) were predicted. Subsequent experimental validation confirmed these findings and highlighted the efficiency of the optimal approach. Remarkably, the resulting REE-oxalate powder contained approximately 43.5 % REEs with minimal Fe (0.12 %), and the REEs oxide form showed a remarkable purity of about 82 % REE.
- Examining the results of the recycled organic phase showed that this method can extract and recover rare earth elements from PLS obtained in continuous mode up to 4 recycles.

In conclusion, this study demonstrates a straightforward and efficient method for recovering REEs from swarf REPMs. The high quality of both REE-oxalate and REE-oxide products, along with the efficient precipitation stripping using oxalic acid solution, demonstrates the method's potential for REE recovery from permanent magnets.

CRediT authorship contribution statement

Soroush Rahmati: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Ionela Birloaga:** Writing – review & editing, Validation, Methodology, Conceptualization. **Pietro Romano:** Writing – original draft, Methodology, Investigation, Formal analysis. **Francesco Veglio:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Funding acquisition, 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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References

- [1] S. Belfqueh, et al., Selective recovery of rare earth elements from acetic leachate of NdFeB magnet by solvent extraction, *Separ. Purif. Technol.* (2024) 126701.
- [2] B. Daigle, S. DeCarlo, Rare earths and the US Electronics sector: supply chain developments and trends, Office of Industries, US International Trade Commission, 2021.
- [3] S. Papagianni, et al., Preprocessing and leaching methods for extraction of REE from permanent magnets: a scoping review, *AppliedChem* 2 (4) (2022) 14.
- [4] G. Reisdörfer, D. Bertuol, E.H. Tanabe, Recovery of neodymium from the magnets of hard disk drives using organic acids, *Miner. Eng.* 143 (2019) 105938.
- [5] E. Commission, Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions Youth Opportunities Initiative, European Commission Brussels, Belgium, 2011.
- [6] A. Kumari, S.K. Sahu, A comprehensive review on recycling of critical raw materials from spent neodymium iron boron (NdFeB) magnet, *Separ. Purif. Technol.* (2023) 123527.
- [7] S. Belfqueh, et al., Evaluating organic acids as alternative leaching reagents for rare earth elements recovery from NdFeB magnets, *J. Rare Earths* 41 (4) (2023) 621–631.
- [8] D. Kołodzyńska, et al., Green extractants in assisting recovery of REEs: a case study, *Molecules* 28 (3) (2023) 965.
- [9] H.S. Kim, et al., Adsorptive recovery of rare earth elements from aqueous solution by citric acid crosslinked carboxymethylated cellulose nanofibril aerogel, *J. Clean. Prod.* 418 (2023) 138189.
- [10] Y. Zhang, et al., Hydrometallurgical recovery of rare earth elements from NdFeB permanent magnet scrap: a review, *Metals* 10 (6) (2020) 841.
- [11] C. Tunsu, 8 - hydrometallurgy in the recycling of spent NdFeB permanent magnets, in: F. Vegliò, I. Birloaga (Eds.), *Waste Electrical and Electronic Equipment Recycling*, Woodhead Publishing, 2018, pp. 175–211.
- [12] O. Diehl, et al., Towards an alloy recycling of Nd–Fe–B permanent magnets in a circular economy, *Journal of Sustainable Metallurgy* 4 (2) (2018) 163–175.
- [13] M. Firdaus, et al., Review of high-temperature recovery of rare earth (Nd/Dy) from magnet waste, *Journal of Sustainable Metallurgy* 2 (4) (2016) 276–295.
- [14] Q. Truong, et al., Leaching of neodymium from recycled NdFeB magnet powders using citric acid, in: *TMS Annual Meeting & Exhibition*, Springer, 2023.
- [15] E. Emil-Kaya, et al., Recycling of NdFeB magnets employing oxidation, selective leaching, and iron precipitation in an autoclave, *RSC Adv.* 13 (2) (2023) 1320–1332.
- [16] S. Rahmati, et al., Efficient metal extraction from dilute solutions: a review of novel selective separation methods and their applications, *Metals* 14 (6) (2024) 605.
- [17] A. Klemettinen, et al., Recovery of rare earth elements from the leaching solutions of spent NdFeB permanent magnets by selective precipitation of rare earth oxalates, *Minerals* 13 (7) (2023) 846.
- [18] C. Erust, et al., A multi-stage process for recovery of neodymium (Nd) and dysprosium (Dy) from spent hard disc drives (HDDs), *Miner. Process. Extr. Metall. Rev.* 42 (2) (2021) 90–101.
- [19] R.T. Stein, A.C. Kasper, H.M. Veit, Recovery of rare earth elements present in mobile phone magnets with the use of organic acids, *Minerals* 12 (6) (2022) 668.
- [20] I. Birloaga, F. Vegliò, Hydrometallurgical process for the treatment of permanent magnets, *IT102018* (2018) 5178.
- [21] M. Gergoric, et al., Leaching and recovery of rare-earth elements from neodymium magnet waste using organic acids, *Metals* 8 (9) (2018) 721.
- [22] Y. Yang, et al., REE recovery from end-of-life NdFeB permanent magnet scrap: a critical review, *Journal of Sustainable Metallurgy* 3 (2017) 122–149.
- [23] S. Dashti, et al., Separation and solvent extraction of rare earth elements (Pr, Nd, Sm, Eu, Tb, and Er) using TBP and Cyanex 572 from a chloride medium, *Miner. Eng.* 161 (2021) 106694.
- [24] A.C. Ni'am, et al., Simultaneous recovery of rare earth elements from waste permanent magnets (WPMs) leach liquor by solvent extraction and hollow fiber supported liquid membrane, *Chemical Engineering and Processing-Process Intensification* 148 (2020) 107831.
- [25] M. Mohammadi, et al., Separation of Nd (III), Dy (III) and Y (III) by solvent extraction using D2EHPA and EHEHPA, *Hydrometallurgy* 156 (2015) 215–224.
- [26] A.C. Ni'am, et al., Simultaneous recovery of rare earth elements from waste permanent magnets (WPMs) leach liquor by solvent extraction and hollow fiber supported liquid membrane, *Chemical Engineering and Processing - Process Intensification* 148 (2020) 107831.
- [27] H.-S. Yoon, et al., Solvent extraction, separation and recovery of dysprosium (Dy) and neodymium (Nd) from aqueous solutions: waste recycling strategies for permanent magnet processing, *Hydrometallurgy* 165 (2016) 27–43.
- [28] B.-J. Rho, P.-P. Sun, S.-Y. Cho, Recovery of neodymium and praseodymium from nitrate-based leachate of permanent magnet by solvent extraction with trioctylphosphine oxide, *Separ. Purif. Technol.* 238 (2020) 116429.
- [29] K. Shah, K. Gupta, B. Sengupta, Selective separation of copper and zinc from spent chloride brass pickle liquors using solvent extraction and metal recovery by precipitation-stripping, *J. Environ. Chem. Eng.* 5 (5) (2017) 5260–5269.
- [30] K.N. Han, Characteristics of precipitation of rare earth elements with various precipitants, *Minerals* 10 (2) (2020) 178.
- [31] Z. Cicek, A.A. Mira, Q. Huang, Process development for the extraction of rare earth elements from an acid mine drainage treatment sludge, *Resour. Conserv. Recycl.* 198 (2023) 107147.
- [32] R.K. Nekouei, et al., Chemical isolation of rare earth elements (as pure rare earth oxides) from Nd-Fe-B magnets and Ni-MH batteries, *J. Environ. Chem. Eng.* 12 (3) (2024) 112596.
- [33] P.M. Smith, High-purity rare earth oxides produced via precipitation stripping, *Metall. Mater. Trans. B* 38 (2007) 763–768.
- [34] Y. Konishi, S. Asai, T. Murai, Precipitation stripping of neodymium from carboxylate extractant with aqueous oxalic acid solutions, *Ind. Eng. Chem. Res.* 32 (5) (1993) 937–942.
- [35] E. Jorjani, M. Shahbazi, The production of rare earth elements group via tributyl phosphate extraction and precipitation stripping using oxalic acid, *Arab. J. Chem.* 9 (2016) S1532–S1539.
- [36] S. Riaño, K. Binnemans, Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets, *Green Chem.* 17 (5) (2015) 2931–2942.
- [37] P. Romano, et al., Leaching of rare earth elements from permanent magnet swarf in citric acid: effects of acid concentration on extraction kinetics, *Metals* 13 (11) (2023) 1801.
- [38] R.L. Mason, R.F. Gunst, J.L. Hess, *Statistical Design and Analysis of Experiments: with Applications to Engineering and Science*, John Wiley & Sons, 2003.
- [39] R. Advodi, G. Dini, Benzotriazolium bis (2-ethylhexyl) phosphate ionic liquid as a catalyst and multifunctional lubricant additive: synthesis, optimization, characterization, and tribological evaluation, *Arabian J. Sci. Eng.* (2024) 1–16.
- [40] S. Rahmati, et al., Optimization of continuous air-assisted solvent extraction for treating dilute Cu leach solutions using response surface methodology, *Miner. Eng.* 131 (2019) 154–163.

- [41] G.C. Chintokoma, Y. Chebude, S.K. Kassahun, Cd²⁺ removal efficiency of activated carbon from *Prosopis juliflora*: optimization of preparation parameters by the Box-Behnken Design of Response Surface Methodology, *Heliyon* 10 (10) (2024) e31357. ISSN 2405-8440.
- [42] L. Yan, et al., Optimization of mix proportions for hybrid fiber engineered cementitious composites based on Box-Behnken design response surface model, *Construct. Build. Mater.* 421 (2024) 135697.
- [43] Y. Nakamura, et al., Differences in behavior among the chlorides of seven rare earth elements administered intravenously to rats, *Toxicol. Sci.* 37 (2) (1997) 106–116.
- [44] C. Hu, et al., Recovery of iron resources from wet-process phosphoric acid and the preparation of high purity ferrous oxalate: solvent extraction and photochemical reaction, *ACS Sustain. Chem. Eng.* 12 (13) (2024) 5061–5074.
- [45] Y. Zhang, et al., A novel technology for producing high-purity V₂O₅ from hazardous vanadium-containing solutions using precipitation and solvent extraction, *Process Saf. Environ. Protect.* 173 (2023) 567–578.
- [46] Y. Yang, et al., Insights to perfluorooctanoic acid adsorption micro-mechanism over Fe-based metal organic frameworks: combining computational calculation with response surface methodology, *J. Hazard Mater.* 395 (2020) 122686.
- [47] M. Adamu, et al., Mechanical performance and optimization of high-volume fly ash concrete containing plastic wastes and graphene nanoplatelets using response surface methodology, *Construct. Build. Mater.* 308 (2021) 125085.
- [48] S. Rahmati, et al., Effect of liquid and air flowrates on the efficiency of a two-stage air-assisted solvent extraction system in pilot scale, *Miner. Eng.* 153 (2020) 106376.
- [49] A. Verma, et al., Metal recovery using oxalate chemistry: a technical review, *Ind. Eng. Chem. Res.* 58 (34) (2019) 15381–15393.
- [50] D. Panias, et al., Mechanisms of dissolution of iron oxides in aqueous oxalic acid solutions, *Hydrometallurgy* 42 (2) (1996) 257–265.
- [51] R.-a. Chi, Z.-g. Xu, A solution chemistry approach to the study of rare earth element precipitation by oxalic acid, *Metall. Mater. Trans. B* 30 (1999) 189–195.
- [52] Q. Liu, et al., High-efficiency simultaneous extraction of rare earth elements and iron from NdFeB waste by oxalic acid leaching, *J. Rare Earths* 39 (3) (2021) 323–330.
- [53] X. Zhang, et al., Stripping of Fe(III) from Aliquat 336 by NaH₂PO₄: implication for rare-earth elements recovery from red mud, *Separ. Sci. Technol.* 56 (2) (2021) 301–309.
- [54] G.R. Harvianto, S.-H. Kim, C.-S. Ju, Solvent extraction and stripping of lithium ion from aqueous solution and its application to seawater, *Rare Met.* 35 (2016) 948–953.
- [55] A. Merroune, et al., Competitive extraction and stripping behaviors of rare earth elements from industrial wet-process phosphoric acid using di-(2-ethyl-hexyl) phosphoric acid solvent: optimization and thermodynamic studies, *J. Mol. Liq.* 367 (2022) 120585.
- [56] M. Ghadiri, S.N. Ashrafizadeh, M. Taghizadeh, Study of molybdenum extraction by trioctylamine and tributylphosphate and stripping by ammonium solutions, *Hydrometallurgy* 144–145 (2014) 151–155.
- [57] P. Halli, et al., Recovery of Pb and Zn from a citrate leach liquor of a roasted EAF dust using precipitation and solvent extraction, *Separ. Purif. Technol.* 236 (2020) 116264.
- [58] Z. Liu, et al., Separation and recovery of vanadium and aluminum from oxalic acid leachate of shale by solvent extraction with Aliquat 336, *Separ. Purif. Technol.* 249 (2020) 116867.
- [59] G. Yu, et al., Recovery of rare earth metal oxides from NdFeB magnet leachate by hydrophobic deep eutectic solvent extraction, oxalate stripping and calcination, *Hydrometallurgy* 223 (2024) 106209.

