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Hydrometallurgical recycling of waste NdFeB magnets: design of experiment, optimisation of low concentrations of sulphuric acid leaching and process analysis

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ABSTRACT
Efficient recovery of rare earth elements (REEs) from scrap NdFeB magnets is a significant requirement for a circular economy. Therefore, the development of a cost-effective and environmentally friendly leaching process for the dissolution of iron and REEs has received extensive interest. In this study, the dissolution of NdFeB magnet powders in sulphuric acid solution was investigated in detail. Taguchi orthogonal array was employed for the first time to define and optimise the influence of sulphuric acid concentration, solid-to-liquid ratio and stirring speed on the extraction of iron and rare earth elements (REEs). The acid concentration of sulphuric acid was determined as a key factor for iron and REEs dissolution, while solid-to-liquid ratio and stirring speed slightly affected the dissolution of REEs and iron. Maximum iron and REEs extraction were achieved under optimal conditions as the sulphuric acid concentration of 1 M, solid-to-liquid ratio of 1/15 and stirring speed of 350 rev min^{-1}. Consequently, after the validation experiment, it was proved that the design of experiments based on Taguchi orthogonal array is an efficient way for the optimisation of process parameters.

La récupération efficace des éléments de terres rares (ETR) à partir d’aimants rebuts de NdFeB est une exigence importante pour l’économie circulaire. Par conséquent, le développement d’un procédé de lixiviation rentable et écologique pour la dissolution du fer et des ETR a reçu un grand intérêt. Dans cette étude, on a examiné en détail la dissolution des poudres d’aimant de NdFeB dans une solution d’acide sulfurique. On a utilisé un tableau orthogonal de Taguchi la première fois pour définir et optimiser l’influence de la concentration d’acide sulfurique, du rapport solide à liquide et de la vitesse d’agitation sur l’extraction du fer et des éléments de terres rares (ETR). On a déterminé que la concentration en acide de l’acide sulfurique était un facteur clé pour la dissolution du fer et des ETR alors que le rapport solide à liquide et la vitesse d’agitation affectaient légèrement la dissolution des ETR et du fer. L’extraction maximale du fer et des ETR a été obtenue sous les conditions optimales d’une concentration d’acide sulfurique de 1 M, d’un rapport solide à liquide de 1/15 et d’une vitesse d’agitation de 350 tr/min. Par conséquent, après l’expérience de validation, on a prouvé que le plan d’expériences basées sur un tableau orthogonal de Taguchi est une manière efficace d’optimiser les paramètres du procédé.

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KEYWORDS
Leaching; rare earth elements; NdFeB magnets; design of experiment; Taguchi method

1. Introduction

The development of high-added technological devices provides humanity with progress in technological advancement. One of the essential sources of economic development, both on the basis of countries and on a global scale, is a result of new generation technology products such as high efficiency and performance electronic devices, renewable energy systems, magnetic imaging devices etc. Rare earth elements (REEs) are crucial components for the production and development of new generation technological products in consideration of green energy production and low carbon emission. NdFeB permanent magnets, which contain ∼30% rare earth elements, have a wide range of engineering applications with the new generation technology. Rare earth elements, especially Nd, Dy and Pr are the main components of NdFeB permanent magnets which are widely used in green energy technologies and consumer electronics owing to their high magnetic performance. Rare earth elements are considered as critical raw materials due to increased demand and supply risk, as the NdFeB permanent magnet industry grows 20% annually [1]. Rare earth metals have been identified as the metals with the highest supply risk among the 41 elements on the critical metals list in Europe. China supplies 80–95% of the rare earth metal resource needed

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for the production of NdFeB permanent magnets. Considering the increase in the demands of REEs such as Nd and Pr over the past years, the quota applied by China in 2009 indicated the adversities that may be accomplished in the supply chain of permanent NdFeB magnets [1]. The critical importance of permanent magnets and rare earth elements has led to an increase in efforts to ensure the sustainability of the raw material. The recycling of end-of-life NdFeB magnets, or scrapped magnets due to a process failure, is the most effective alternative in recuperating the raw material supply complications. Recycling processes enable the recovery of many metals [2–4] and REEs from secondary raw materials. Various recycling techniques have been applied by researchers for recovering REEs from waste NdFeB magnets including pyrometallurgical, hydrometallurgical and electrometallurgical methods [5–10].

Hydrometallurgical techniques, which include leaching, precipitation and solvent extraction for the recovery of REEs from secondary raw materials have been widely preferred. Hydrometallurgical methods are used for high purity grade recovery of REEs from lower grade raw materials. The separation of REEs *via* using the hydrometallurgical method can be achieved with higher selectivity than *via* using other methods. Furthermore, compared to the pyrometallurgical techniques, the scale-up hydrometallurgical equipment performs at a low cost [11]. Nevertheless, many additional steps are needed to obtain the high purity product *via* using hydrometallurgical routes. Furthermore, in the industrial scale applications for recovery of REEs, both the amount and prices of the chemicals used are high in some cases [9,12–14].

Various studies have been carried out on the recovery of REEs from secondary raw materials *via* using hydrometallurgical methods [7,8]. Bandara et al. [15] studied the HCl leaching process for motors containing RE magnets, steel and copper. After the demagnetisation and shredding of the scrap NdFeB magnet, the powders were leached in HCl, H_2SO_4, acetic acid, oxalic acid, formic acid and lactic acid for 24 h at room temperature. It is proved that 4M HCl has higher efficiency for the dissolution of NdFeB magnets. Eventually, the oxalate precipitation route was proposed by the addition of oxalic acid. In this step, 99% yield of $(RE)_2\ (C_2O_4)_3$ was achieved and the total REE recovery rate was calculated as 82% through different reduction potentials of steel, copper and RE magnets [15]. Lyman and Palmer [16] studied the recycling of scrap NdFeB magnets by sulphuric acid (H_2SO_4), and precipitation of rare earth salts with (NaOH) and ammonium hydroxide (NH_4OH). The weight ratio of acid-to-scrap was held at 2:1 or higher to dissolve the magnet powders and to keep on a low pH for avoiding Fe (II) oxidation to Fe (III). Afterwards, REEs were precipitated as sodium sulphate double salt ($Nd_2(SO_4)_3{\cdot}Na_2SO_4{\cdot}6H_2O$) and ammonium sulphate double salt ($Nd_2(NH_4)_2(SO_4)_4{\cdot}8H_2O$) by NaOH and NH_4OH, respectively. The recovery of Nd, about 95%, was achieved between the pH values of 1.5 and 2, using NaOH. However, a remarkable amount of Fe was precipitated above the pH value of 5. Furthermore, in the case of NH_4OH, the recovery of Nd was about 70% owing to the solubility of its salt in the solution. Tian et al. [17] proposed a method for the recovery of REEs from NdFeB by avoiding iron precipitation. During the HCl leaching, chelating agents such as tartaric acid and hexamethylenetetramine (HMTA) were employed to prevent iron precipitation. Subsequently, the precipitation of rare earth elements was investigated by oxalic acid [17]. Venkatesan et al. focused on the conversion of Fe (II) to Fe (III) by the electro-oxidative process. First, NdFeB magnets were dissolved by HCl; then, the conversion of Fe (II) to Fe (III) which is significant for selectively REEs precipitation, was performed by the electrochemical method. Finally, oxalic acid was employed to form rare-earth oxalates. After the precipitation with oxalic acid, approximately a 99% of purity rare earth oxide was produced [18]. Likewise, Önal et al. [19], investigated the complete leaching process by H_2SO_4, to recover valuable metals (Ni, Co and Cu) and REEs. MnO_2 was preferred to oxidise Fe (II) to Fe (III) at an ambient temperature. Iron was precipitated by adjusting the pH using $Ca(OH)_2$ or MnO. After that, REEs and Co were selectively precipitated as oxalate and sulphide forms, respectively. Lin et al. reported that waste NdFeB magnets were leached with HCl, H_2SO_4 and HNO_3, and subsequently, hematite precipitation was performed in a hydrothermal reactor. While iron in the nitric acid solution was selectively precipitated in the reactor, hematite formation was not observed in sulphuric acid and hydrochloric acid solution [20].

The design of experiments (DOE) is used in various fields due to the fact that it reduces testing costs and creates optimal conditions. One of the most utilised methods to optimise the process parameters is the Taguchi method. This method is considered economical compared to the other methods in terms of the number of experiments. Moreover, it allows to optimise the process with the best performance. Subsequently, the statistical and mathematical methods provide a broad range of information with a lower number of experiments [21–25].

In the present study, we aim to define the optimal process parameters of the NdFeB magnet powders leaching experiment to achieve a higher leaching efficiency with low concentrations of sulphuric acid. To evaluate the effects of the influencing variable on the leaching efficiency, an experimental design technique based on the Taguchi orthogonal array was employed. Afterwards, the statistical method supplied the information regarding the most significant process parameters. Moreover, to prove the reparability and consistency of the results of the leaching experiments, the validation experiment was carried out.

Table 1. Experimental designs with a 3-factor, 3-level L_9 orthogonal layout.

Number of experiments	Acid concentration (M)	Solid-to-liquid ratio ($g\ l^{-1}$)	Stirring speed ($rev\ min^{-1}$)
1	0.25	1/20	200
2	0.25	1/15	350
3	0.25	1/10	500
4	0.50	1/20	350
5	0.50	1/15	500
6	0.50	1/10	200
7	1.00	1/20	500
8	1.00	1/15	200
9	1.00	1/10	350

2. Materials and methods

2.1. Materials

Waste NdFeB permanent magnets were obtained from Arçelik A.Ş. (Turkey) and used as a raw material for magnet powder. H_2SO_4 (95–98% purity, Merck quality, Germany) was used for leaching. De-ionised water (produced from Milli-q, ITU, Turkey) was used.

2.1. Sample pretreatment

Sample preparation prior to the leaching experiments affects the leaching efficiency [1]. Initially, magnetism removal of the waste NdFeB magnets was required, since the demagnetisation of waste NdFeB magnets is an important step before grinding. The demagnetisation process was conducted at 350°C for 30 min in a muffle furnace (Nabertherm). After the demagnetisation process, waste NdFeB magnet samples were subjected to the grinding process. Vibration milling was used to obtain the powder form of NdFeB magnets and to demagnetise them. The grinding process was applied for 3 min for 50 g bulk magnets.

2.2. Leaching experiments

Sulphuric acid was used to complete the leaching of waste demagnetised NdFeB magnet powders. The Taguchi experimental design method was applied to obtain an optimum leaching parameter between specific limiting conditions. Our Taguchi experimental design, which is of $L_9(3^3)$ layout, has 3 factors and each factor has 3 levels. Acid concentration, stirring rate and S/L ratio were investigated by changing three variables. Table 1 represents the details of the experimental design. About 200 mL of sulphuric acid was consumed for each leaching experiment. In each experimental set, the time was kept constant for 30 min and the temperature was set as room temperature (~ 25°C). The leaching processes were carried out in a heat-controlled heating mantle (Weightlab, WF-BDK500), overhead mixer (IKA Yellow Line) and using a 3-necked quartz reactor, after the leaching leach residue and pregnant leach liquor were separated using a vacuum filtration system. Final filtration was practiced through 0.45 µm and 0.22 µm filters using a syringe. After leaching and filtration, the pregnant leach liquor solutions were stocked to 1L with distilled water. The leaching efficiency was calculated with the insoluble powder weight *via* using Equation (1). Figure 1 shows the experimental set-up for leaching. Figure 2 presents the experimental processes.

$$\%\text{The leaching efficiency} = \frac{\begin{array}{c}\text{total amount of powder fed into the leaching process(g)}-\\ \text{insoluble particle weight (g)}\end{array}}{\text{total amount of powder fed into the leaching process(g)}} \times 100 \qquad (1)$$

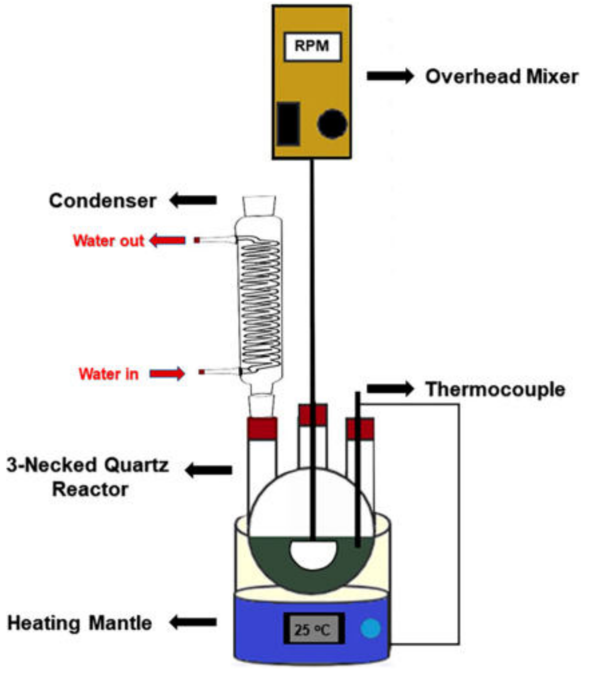

Figure 1. Leaching experiments' set-up.

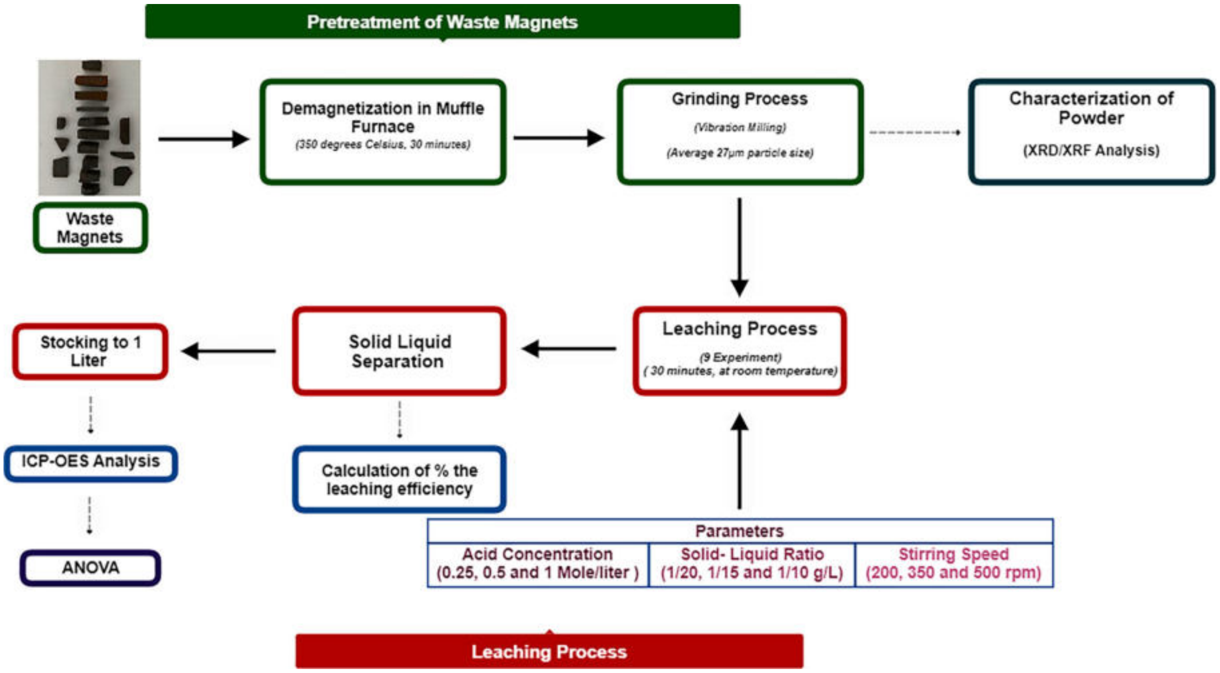

Figure 2. The main schematic of experimental design.

2.3. Characterisation

The waste magnets were Ni-coated and the coating thickness was determined using the SEM (JEOL-JSM 700F) analysis after the demagnetisation process. The particle size distribution of NdFeB magnet powders was determined *via* the DLS analysis (Mastersizer 2000).The XRF (Rigaku ZSX Primus II) analysis was performed to obtain the chemical composition of the magnet powder. The X-ray diffraction analysis (XRD) (Rigaku Miniflex, Cu Kα, $10° \leq 2\Theta \leq 90°$) was performed to reveal the main phases in the powders. The metal ion concentration in the solutions, formed as a result of the leaching processes, was calculated by the ICP-OES (Spectro Genesis) analysis. Based on the ICP results, the percent resolution efficiencies of the metals in the initial powder are explained using Equation (2) [26].

$$\text{Recovery}(\%) = \frac{\left(\text{Metal solution ICP}\left(\frac{\text{g}}{\text{L}}\right)\right) * (\text{Leach volume}(\text{L}))}{(\text{Metal amount in Fe} - \text{Nd}(\%)\text{from XRF}) * (\text{Initial Fe} - \text{Nd amount}(\text{g}))} * 100 \tag{2}$$

3. Result and discussion

3.1. Characterisation results of NdFeB permanent magnets

The NdFeB magnets with Ni-coating were supplied from Arçelik A.Ş. The supplied magnets were first demagnetised. The demagnetised NdFeB permanent magnet samples were cut into two pieces to determine the coating thickness of Ni by the SEM analysis. About 9–10 µm Ni coating was observed *via* the SEM analysis. Cross-sectional SEM images of waste NdFeB magnets are shown in Figure 3(a), and also, bulk waste magnet's SEM images are presented in Figure 3(b). As seen in the SEM images, the darker phases are $Nd_2Fe_{14}B$, while the light colour regions are Nd-rich phases [27]. The demagnetisation process was applied to bulk magnets. The high contact surface area with the acid solution increases the leaching efficiency. The demagnetised magnets were milled to increase the surface area. It was determined by the DLS analysis that the particle size of the milled powders was approximately 27 µm. The particle size distribution of demagnetised and milled waste NdFeB magnet powders is shown in Figure 4. After the grinding process of the demagnetised waste NdFeB magnet, the composition and main phases of the powder sample were determined by the XRD-XRF analyses. Nd and Fe present in the waste NdFeB magnet is 20.46% wt. and 70.21% wt. (see Table 2), respectively, and the main phase in the waste NdFeB magnet powder obtained as $Nd_2Fe_{14}B$ is presented in Figure 5.

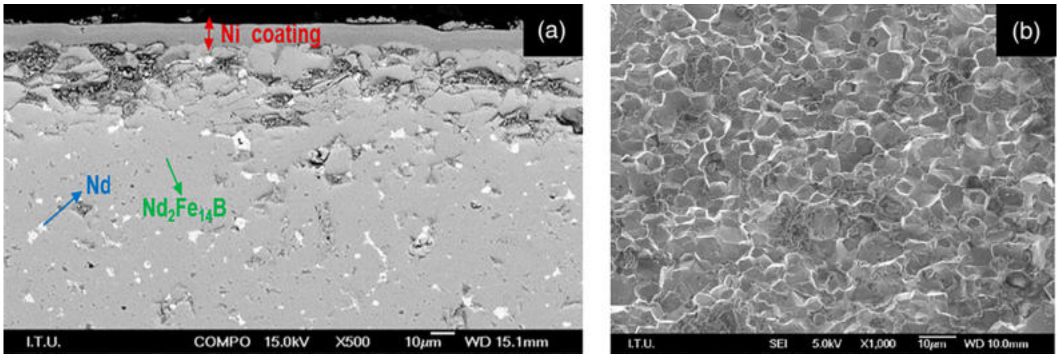

Figure 3. (a) Cross-sectional SEM images of the waste NdFeB magnet (×500 magnification) and (b) longitudinal section SEM images of the waste NdFeB magnet (×1000 magnification).

3.2. Leaching of Fe and Nd with sulphuric acid

The H_2SO_4, HCl and HNO_3 mineral acids are commonly used in the leaching process of the NdFeB magnets [20–22]. Mineral acid leaching is an exothermic process and allows trivalent REE's to dissolve into solution [8]. Neodymium metal dissolves in sulphuric acid and forms Nd (III) ion with the hydrogen gas release [28]. Depending on the type of acid used, iron dissolves into the solution as Fe^{2+} or Fe^{3+} ions. H_2SO_4 was found to be the most effective mineral acid for dissolving Nd out of the three widely used mineral acids [29]. For a solvent extraction method, nitric or hydrochloric acid is favoured, whereas sulphuric acid might be utilised for selective precipitation [1]. Considering the environmental factors, maximum leaching efficiency was aimed with minimum acid consumption for the design of leaching experiments. Reactions for Nd and Fe (main components in waste NdFeB magnet) dissolution in H_2SO_4 are given in Equations 3 and 4. Gibbs free energy changes of the reactions given in Equations (3) and (4) were calculated using the FactSage [30] software and are presented in Figure 6. It has been observed that the efficiency of the reactions at low temperatures is higher. Therefore, leaching processes were carried out at room temperature without external heat. Although no external heat was given, the leaching temperature increased spontaneously, as the reactions were exothermic. The maximum temperature values reached by the experimental sets are given in Table 3. München et al. studied sulphuric acid leaching for the most efficient recovery rate of Nd and Pr from waste secondary sources [31]. They examined the effects of different temperatures and times on recovery rates. They determined that 30 min leaching time is optimum for 25°C. So, in this study, we worked for 30 min. Furthermore, they used 2 M acid concentration and 1/20–1/40 solid-to-liquid ratios [31]. We used lower acid concentrations; and also, we increased the solid-to-liquid ratio. Our solid-to-liquid ratios are 1/20, 1/15 and 1/10.

$$2Nd(s) + 3H_2SO_4(aq) \rightarrow 2Nd^{3+}(aq) + 3SO_4^{-2}(aq) + 3H_2(g) \quad (3)$$

$$Fe(s) + H_2SO_4(aq) \rightarrow Fe^{2+}/Fe^{3+}(aq) + SO_4^{-2}(aq) + H_2(g) \quad (4)$$

The leaching efficiencies of each experiment were calculated using Equation (1) and are given in Table 4. According to the overall metal dissolution experiment 7 (acid concentration: 1 M, solid-to-liquid ratio: 1/20, and stirring speed: 500 rev min^{-1}) gives the most efficient result, while experiment 1 (acid concentration: 0,25 M, solid-to-liquid ratio: 1/20, and stirring speed: 200 rev min^{-1}) gives least efficiency. The concentration of metal ions taken into the leaching solution was determined by the ICP analysis, and their efficiencies were

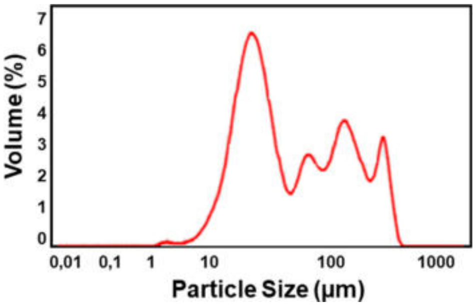

Figure 4. Particle size distribution of demagnetised and milled waste NdFeB magnet powders.

Table 2. XRF results of NdFeB magnet powders.

Element	Fe	Nd	Pr	Co	Ni	Mn
%	70.21	20.46	5.63	1.26	1.03	0.30
Element	Zr	Nb	Sn	V	Ba	Ag
%	0.09	0.05	0.04	0.03	0.02	0.01
Element	Cd	Sb	As	Cu	Mo	Ga
%	0.007	0.007	0.005	0.66	0.01	0.14

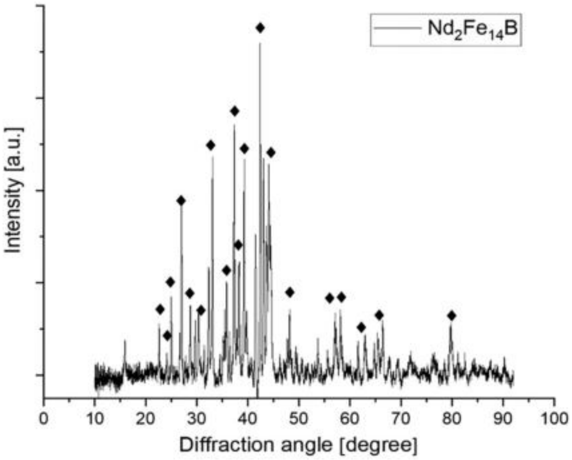

Figure 5. XRD pattern of waste NdFeB magnet powders.

calculated using Equation (2) (results are given in Table 3). The maximum leaching efficiency for Fe and Nd ions were obtained with experiment 7 (acid concentration: 1 M, solid-to-liquid ratio: 1/20, and stirring speed: 500 rev min^{-1}) and experiment 8 (acid concentration: 1 M, solid-to-liquid ratio: 1/15, and stirring speed: 200 rev min^{-1}), respectively. Decreasing the solid-to-liquid ratio affects Nd leaching positively, nevertheless, decreasing string speed affects negatively. Furthermore, as shown in Figure 6, the dissolution of Nd is higher than Fe in each experiment. Although the Nd leaching efficiency reached 98.79%, the Fe leaching efficiency remained at 60.63. As can be seen from thermodynamic studies, the Gibbs free energy of Nd dissolution is more negative. Therefore, Nd dissolution in the leaching system occurs more easily than Fe dissolution. When working at low concentrations and acid amounts, the Nd leaching efficiency is higher than the Fe leaching efficiency as in this study, even leaching is not selective. As can be seen from thermodynamic studies, the Gibbs free energy of Nd dissolution is more negative. Therefore, Nd dissolution in the leaching system occurs more easily than Fe dissolution.

Table 3. Maximum temperatures reached in each set of experiments.

Experiment number	Achieved max. temperature (°C)
1	25
2	35
3	34
4	44
5	35
6	32
7	41
8	43
9	51

3.3. Taguchi experimental analysis of leaching process

The Taguchi experimental design, which is of $L_9(3^3)$ orthogonal arrangement and Nd-Fe ions, and obtained

Table 4. Leaching efficiencies of each experiment.

Experiment Code	% The leaching efficiency	% Efficiency for Fe [ICP]	% Efficiency for Nd [ICP]
1	4.00	4.442	11.55
2	24.98	24.82	28.83
3	5.60	9.00	8.97
4	73.20	55.72	70.40
5	34.28	33.03	62.72
6	20.15	17.90	19.87
7	98.50	60.63	95.7
8	89.87	45.45	98.79
9	49.90	30.46	48.41

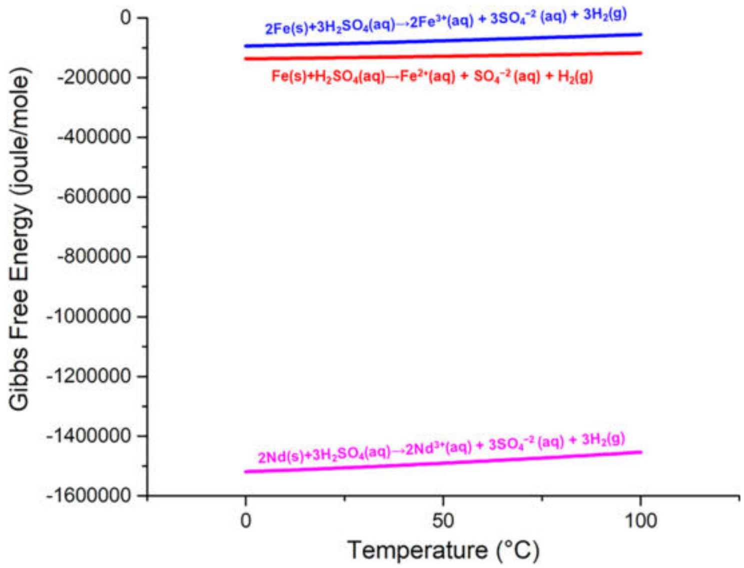

Figure 6. Graph of Gibbs free energy changes of resolution reactions for Fe and Nd.

Table 5. The parameters and the results of experiments based on L_9 Taguchi's orthogonal arrays.

Acid Concentration (M)	Solid-to-Liquid Ratio (g l^{-1})	Stirring Speed (rev min^{-1})	ICP Fe (g l^{-1})	ICP Nd (g l^{-1})	S/N for Fe (db)	S/N for Nd (db)
0.25	1/20	200	0.31052	0.23724	−10.15820845	−12.49624169
0.25	1/15	350	2.32322	0.78738	7.321806755	−2.076312416
0.25	1/10	500	1.26410	0.36764	2.035628627	−8.691544851
0.5	1/20	350	3.91196	1.44358	11.84788811	3.18881713
0.5	1/15	500	3.09104	1.71290	9.802092503	4.674640187
0.5	1/10	200	2.51346	0.81412	8.005439562	−1.786231521
1	1/20	500	4.25730	1.96062	12.5826851	5.84786857
1	1/15	200	4.25348	2.69790	12.5748879	8.620516963
1	1/10	350	4.27712	1.98350	12.6230287	5.948644096

as a result of each experiment *via* the ICP analysis, is presented in Table 5. Since the leaching efficiency is directly proportional to the amount of ions obtained, the larger is better approach was used to determine the signal-noise (S/N) ratios of each parameter [20]. Equation (5) was used to calculate the S/N ratios. In this equation, '*n*' represents the total number of repetitions of each experiment, and '*y*' represents the concentration of metal ions [24]. The effect parameters were calculated by using the S/N ratios in Equations (6–8) [32]. The obtained parameters graphs are given in Figure 7(a–c) for Fe and in Figure 8(a–c) for Nd. The highest value of the S/N ratio for each factor is the optimum level for the experimental design with defined limits [33]. About 1 M H_2SO_4, 1/15 solid-to-liquid ratio and 350 rev min^{-1} stirring speed are obtained at optimum levels to achieve maximum Fe and Nd leaching efficiency at working ranges.

$$S/N = -10* \log\left(\frac{1}{n} * \sum_{n}^{i=0}\left[\frac{1}{y_i^2}\right]\right) \tag{5}$$

$$a_{(1,2,3)} = \frac{db_{(1,2,3)} + db_{(1,2,3)} + db_{(1,2,3)}}{3} \tag{6}$$

$$b_{(1,2,3)} = \frac{db_{(1,2,3)} + db_{(1,2,3)} + db_{(1,2,3)}}{3} \tag{7}$$

$$c_{(1,2,3)} = \frac{db_{(1,2,3)} + db_{(1,2,3)} + db_{(1,2,3)}}{3} \tag{8}$$

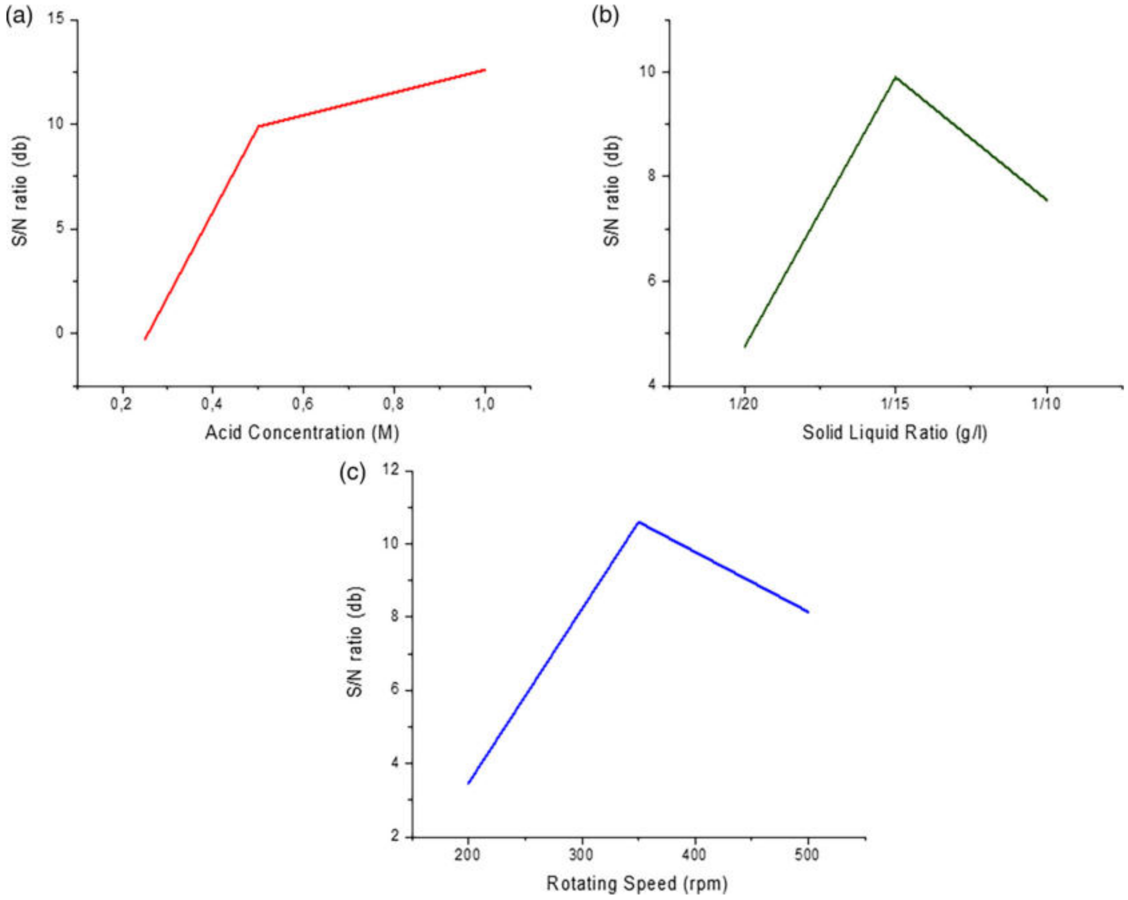

Figure 7. S/N ratio graphics for Fe (a) acid concentration, (b) solid-to-liquid ratio and (c) stirring speed.

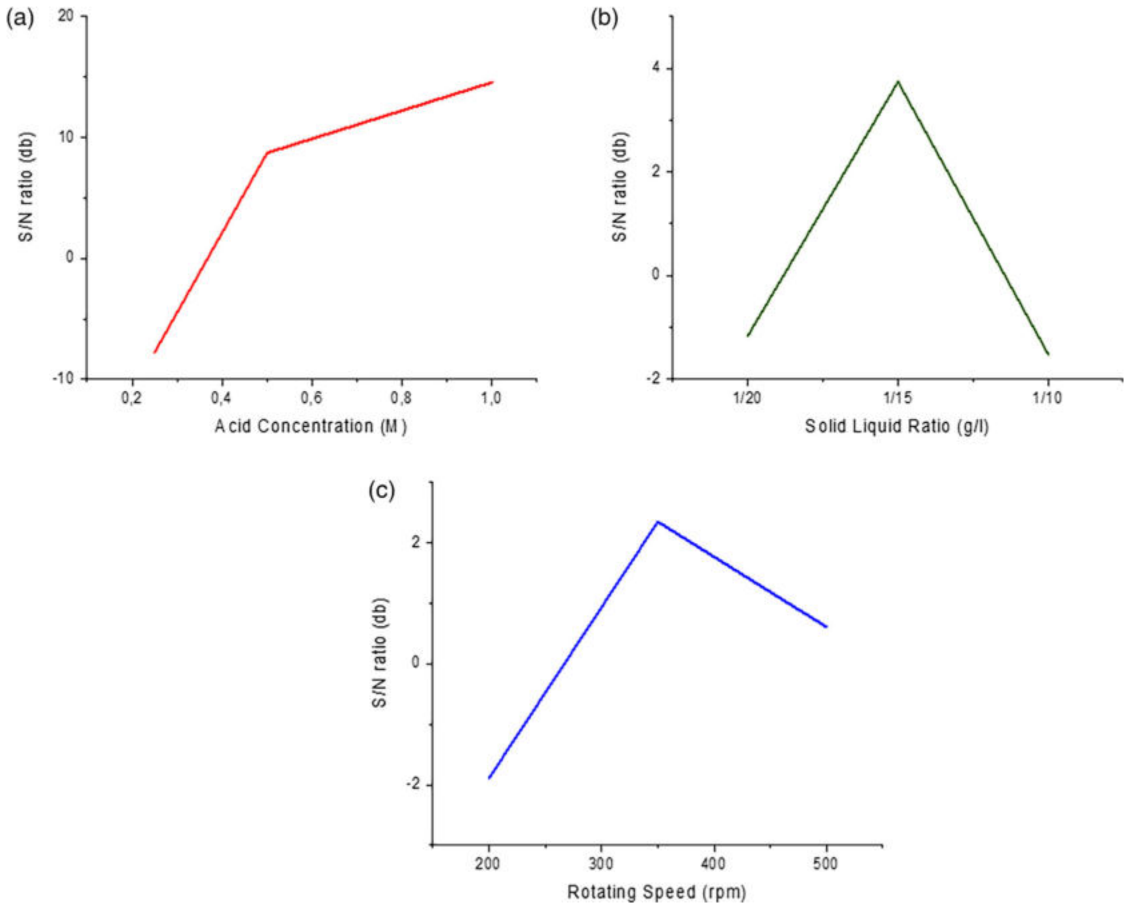

Figure 8. S/N ratio graphics for Nd (a) acid concentration, (b) solid-to-liquid ratio and (c) stirring speed.

Table 6. ANOVA analysis of Fe leaching from the NdFeB waste magnets.

Source	Degrees of Freedom	Seq SS	Adj SS	Adj MS	F	*P*
Sulphuric acid Concentration(M)	2	13.4783	13.4783	6.7391	23.41	0.041
Solid-to-liquid ratio (g l^{-1})	2	0.466	0.466	0.233	0.81	0.553
Stirring speed (rev min^{-1})	2	1.9738	1.9738	0.9869	3.43	0.226
Error	2	0.5757	0.5757	0.2878		
Total	8	16.4937				

The effects of parameters on the leaching efficiency were obtained by the analysis of variance (ANOVA). The most effective parameter for Fe and Nd leaching efficiencies is the acid concentration (Tables 6 and 7). The F and *P* values of each factor are calculated and presented in Tables 6 and 7. This study was tested at the 95% confidence interval. If the *P* value is less than 0.05, it indicates that that parameter is effective on the system within the selected levels [34]. Acid concentration is effective, although the solid-to-liquid ratio and stirring speed are not effective on this process within working ranges, according to the *P* values of the parameters. The ANOVA results of this process presented that the most effective parameter on the system is

Table 7. ANOVA analysis of Nd leaching from the NdFeB waste magnets.

Source	Degrees of freedom	Seq SS	Adj SS	Adj MS	F	*P*
Sulphuric acid concentration (M)	2	4.59381	4.59381	2.29691	30.27	0.032
Solid-to-liquid ratio (g l^{-1})	2	0.75366	0.75366	0.37683	4.97	0.168
Stirring speed (rev min^{-1})	2	0.03685	0.03685	0.01842	0.24	0.805
Error	2	0.15178	0.15178	0.07589		
Total	8	5.361				

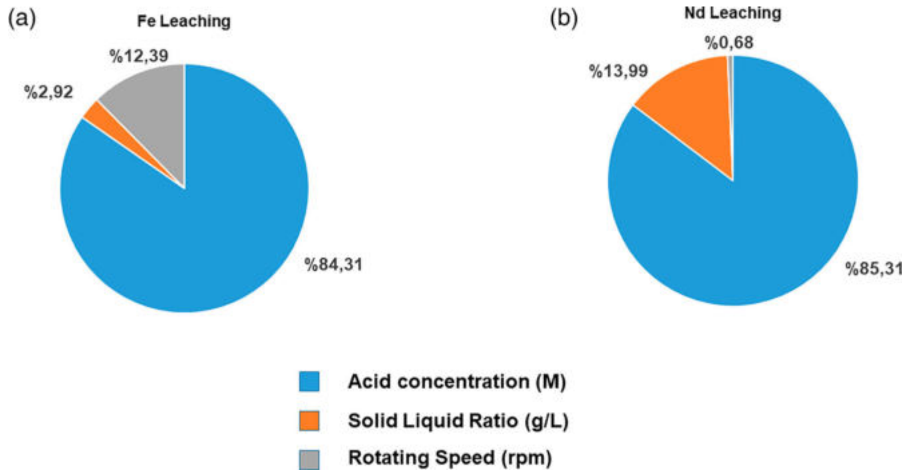

Figure 9. The effect of parameters on the system as a percentage: (a) Fe leaching and (b) Nd leaching.

the acid concentration (see Figure 8). R-Sq and R-Sq $_{\text{(Adj)}}$ values were calculated for both metal ions. R-Sq and R-Sq $_{\text{(Adj)}}$ were calculated as 96.51% and 86.04% for Fe leaching; 97.26% and 89.03% for Nd leaching, respectively.

The percentage effect of each parameter on this study was calculated by Equation (9) [35]. The acid concentration was the most effective factor for Fe and Nd leaching with 84.31% and 85.31%, respectively. Otherwise, the solid-to-liquid ratio was 2.92% for Fe and the stirring speed was the least effective factor for Nd with 0.68%. The percentage effect of the parameters is given in Figure 9.

$$\text{Effect of each factor } \% = \frac{\text{Seqss}}{\text{Seqss (Total)}} * 100 \tag{9}$$

Theoretically, maximum Nd and Fe resolution efficiency was calculated using Equation (10) [36,37]. In this equation, 'T' represents the mean of the S/N ratio in all experiments, and 'C' represents the optimum leaching conditions. For both metal ions, 1 M H_2SO_4 (a_3), 1/15 solid-to-liquid ratio (b_2) and 350 rev min^{-1} stirring speed (c_3) were chosen as they would give maximum results with the limited levels. Theoretically, the maximum leaching efficiency of Fe and Nd was calculated as 5.16660 and 2.68380 g l^{-1}, respectively. The control experiment was performed and the result of the performed experiment was consistent with the calculation result. The pH value of the control experiment was approximately 1,2 and it was found that the pH value was suitable for the Fe removal processes [38].

$$\boldsymbol{C} = \boldsymbol{T} + (\boldsymbol{a}_3 - \boldsymbol{T}) + (\boldsymbol{b}_2 - \boldsymbol{T}) + (\boldsymbol{c}_2 - \boldsymbol{T}) \tag{10}$$

3.3.1. Effect of acid concentration

The calculated S/N ratios of acid concentration for each level are presented in Figures 4(a) and Figure 5(a) for Fe/Nd leaching, respectively. In this study, 0.25, 0.5 and 1 M H_2SO_4 were used. The S/N ratios of 0.25, 0.5 and 1 M acid concentrations are calculated as −0.26692, 9.88514 and 12.59353 on Fe leaching, respectively. Also, the S/N ratios of acid concentration levels for Nd leaching are −7.7547, 8.736277 and 14.56916, respectively. The 1 M H_2SO_4's S/N ratio is the highest, so the most effective level was determined as 1 M. Manifestly, increasing the acid concentration allows the H^+ ion to increase in the leaching process and also allows more chances for the oxidation of metal atoms [39]. The 'p' values are 0.041 and 0.032 for Fe and Nd leaching, respectively. Therefore, the selected acid concentration range has an effect on the system when it is studied at the 95% confidence interval [40].

3.3.2. Effect of solid-to-liquid ratio

In these experiments, the acid volume was preserved constant (200 ml) and the amount of powder was changed. The S/N ratios of 1/20, 1/15 and 1/10 solid-to-liquid ratios are as follows for Fe and Nd leaching processes, respectively: 4.757455, 9.899596 and 7.554699; −1,15318, 3,73961 and −1,50971. Increasing the S/L ratio from 1/20 to 1/15 increased the S/N ratio, while increasing the S/N ratio from 1/15 to 1/10 decreased the S/N ratio. Increasing the solid-to-liquid ratio up to a point increases the possibility of acid-powder interaction, and after a certain point, it causes the solution to be saturated [41] Furthermore, the 'P' values of the solid-to-liquid ratio are 0.553 and 0.168 for Fe and Nd. It was observed that the selected parameters do not have an intense effect on the system when studied at the 95% confidence interval [40].

3.3.3. Effect of stirring speed

Leaching experiments were performed using an overhead stirrer and operated at 200, 350 and 500 rev min^{-1} to examine the effect of stirrer speed on the leaching process. For 200, 350 and 500 rev min^{-1} stirring speed levels, the S/N ratios for Fe leaching were calculated as 3.4740, 10.5975 and 8.14013; it was calculated as −1.8873, 2.353716 and 0.61032 for the Nd leaching process. Stirring speed increasing to 350 rev min^{-1} from 200 rev min^{-1} positively affects the leaching process for both Fe and Nd dissolving. However, increasing the stirring speed to 500 rev min^{-1} from 350 rev min^{-1} decreases the leaching efficiency for both metal dissolving. At a low stirring speed, the powder is less dispersed in the leaching system, while high stirring speed increases the leaching efficiency by increasing the diffusion between the leach solution and the powder, because of the increase in the internal diffusion towards the unreacted particle surface [41]. As with the solid-to-liquid ratio, the calculated ‘P’ values of the stirring speed displayed that it has no significant effect on the system within the 95% confidence interval [40].

Conclusion

In this study, the dissolution of Fe and Nd metals from the NdFeB magnets with low concentration sulphuric acid leaching was studied. Before the leaching process, magnets were pre-treated and structural characterisation analyses were done. It was observed that the magnets consist of 70.21% Fe and 20.46% Nd, and the main phase was $Nd_2Fe_{14}B$. After the structural characterisation and chemical analysis of the magnet powders, the leaching process was employed. The leaching performed with a low acid concentration is both costly and environmentally important. Acid concentration, solid-to-liquid ratio and mixing speed were chosen as variable parameters. The effects of 0.25, 0.5 and 1 M of acid concentration, 1/20, 1/15 and 1/10 of solid-to-liquid ratios and stirring speeds of 200, 350 and 500 rev min^{-1} on the leaching efficiency were investigated. About 1 M of acid concentration, 1/15 of solid-to-liquid ratio and a stirring speed of 350 rev min^{-1} were found to be the optimum conditions for Nd and Fe. While the Fe extraction with 60.63% of efficiency was obtained, the extraction of Nd with 98.79% of efficiency was achieved. Investigations were made for the selected parameters and levels. Optimum conditions were determined within the studied parameters, and also constant parameters such as time and temperature. Furthermore, thermodynamic calculations are presented to reason that the Nd resolution efficiency is higher than the Fe resolution efficiency at low acid concentration and amount, even if the selective leaching is not performed.

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Disclosure statement

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