



## **Leaching and recovery of rare-earth elements from neodymium magnet waste using organic acids**

Downloaded from: <https://research.chalmers.se>, 2024-09-20 10:26 UTC


Citation for the original published paper (version of record):

Gergoric, M., Ravaux, C., Steenari, B. et al (2018). Leaching and recovery of rare-earth elements from neodymium magnet waste using organic acids. *Metals*, 8(9).  
<http://dx.doi.org/10.3390/met8090721>

N.B. When citing this work, cite the original published paper.

## Article

# Leaching and Recovery of Rare-Earth Elements from Neodymium Magnet Waste Using Organic Acids

Marino Gergoric <sup>1,\*</sup> , Christophe Ravaux <sup>2</sup>, Britt-Marie Steenari <sup>1</sup>, Fredrik Espegren <sup>1</sup> and Teodora Retegan <sup>1</sup>

<sup>1</sup> Nuclear Chemistry and Industrial Materials Recycling, Chemistry and Chemical Engineering, Chalmers University of Technology, 412 96 Göteborg, Sweden; bms@chalmers.se (B.-M.S.); espegren@chalmers.se (F.E.); tretegan@chalmers.se (T.R.)

<sup>2</sup> Decontamination and Environmental Management, National School of Chemistry Montpellier, 34090 Montpellier, France; christophe.ravaux@enscm.fr

\* Correspondence: marino@chalmers.se; Tel.: +46-(0)31-772-28-42

Received: 20 August 2018; Accepted: 11 September 2018; Published: 13 September 2018



**Abstract:** Over the last decade, rare-earth elements (REEs) have become critical in the European Union (EU) in terms of supply risk, and they remain critical to this day. End-of-life electronic scrap (e-scrap) recycling can provide a partial solution to the supply of REEs in the EU. One such product is end-of-life neodymium (NdFeB) magnets, which can be a feasible source of Nd, Dy, and Pr. REEs are normally leached out of NdFeB magnet waste using strong mineral acids, which can have an adverse impact on the environment in case of accidental release. Organic acids can be a solution to this problem due to easier handling, degradability, and less poisonous gas evolution during leaching. However, the literature on leaching NdFeB magnets waste with organic acids is very scarce and poorly investigated. This paper investigates the recovery of Nd, Pr, and Dy from NdFeB magnets waste powder using leaching and solvent extraction. The goal was to determine potential selectivity between the recovery of REEs and other impurities in the material. Citric acid and acetic acid were used as leaching agents, while di-(2-ethylhexyl) phosphoric acid (D2EHPA) was used for preliminary solvent extraction tests. The highest leaching efficiencies were achieved with 1 mol/L citric acid (where almost 100% of the REEs were leached after 24 h) and 1 mol/L acetic acid (where >95% of the REEs were leached). Fe and Co—two major impurities—were co-leached into the solution, and no leaching selectivity was achieved between the impurities and the REEs. The solvent extraction experiments with D2EHPA in Solvent 70 on 1 mol/L leachates of both acetic acid and citric acid showed much higher affinity for Nd than Fe, with better extraction properties observed in acetic acid leachate. The results showed that acetic acid and citric acid are feasible for the recovery of REEs out of NdFeB waste under certain conditions.

**Keywords:** rare earths; neodymium magnets; solvent extraction; leaching; citric acid; acetic acid

## 1. Introduction

Rare-earth elements (REEs) possess excellent physical and chemical properties, which is why they are used on a large scale in permanent magnets, lamp phosphors, NiMH batteries, catalysts, various mechanical and electric devices as well as electric motors and generators, which are important for transition to a greener economy. Their demand in industry is thus growing rapidly today [1]. Mined mostly in China (over 95% of global supply), REEs are still considered the most critical raw materials in the European Union (EU) in terms of supply risk [2–4]. Due to the geopolitical situation, even the most optimistic predictions cannot rule out a REE market crisis on a global level, similar to the one that occurred in 2011 [5]. However, an imminent crisis in REEs supply in the EU is not expected.

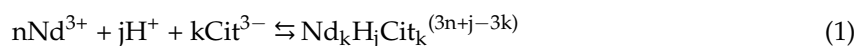
The processes for the production of pure REEs out of ores use highly concentrated mineral acids, which take a toll on the environment, including acids leakage and release of toxic gasses generated during leaching [6]. Furthermore, large amounts of solvents are used for the recovery of REEs out of the obtained leachates. Despite the environmental issues, there are very few ongoing large-scale processes for recycling REEs from end-of-life products, mainly due to price stabilization since the crisis in 2011 and due to varying environmental legislation across the globe [7]. Development of a sustainable and economically feasible recycling process for the recovery of the REEs out of secondary sources is needed in order to decrease the dependence of the industry on mining. As of today, the recycling of REEs in the EU is still in its early stages, with only 7% of the light REEs and 6% of the heavy REEs recovered from secondary sources to meet the EU's demand for REEs [2]. NdFeB scrap magnets are a viable source of some REEs. They consist mainly of Nd (around 30%) and Fe (around 64%), with trace amounts of B (around 0.5%) [6]. Small admixtures of Pr and Dy are also often present [3], with Dy being especially important because it is added to increase the temperature stability against demagnetization. Furthermore, according to predicted growth [8], REE magnets and dysprosium are expected to be the most in-demand materials (in tons) due to the development of green technologies, with an average annual growth of 5.3% between 2010 and 2035 [7]. Electronic devices, such as speakers, mobile devices, and hard disk drives, are available as waste today and can be readily recycled unlike large magnets found in wind turbines and electric cars that have a long life span [3].

Hydrometallurgical methods, such as leaching, solvent extraction, and precipitation, are attractive and efficient methods for recovery of REEs out of NdFeB magnets [3]. The elements contained in the magnet are normally dissolved/leached into an aqueous solution, followed by solvent extraction (occasionally ion-exchange) from the leachate and back-extraction into a new aqueous solution for further reprocessing. Various leaching processes for recovery of REEs out of NdFeB magnets have been developed. In 2016, Önal et al. [9] developed a selective leaching process for REEs by leaching Fe in the solid residue. The NdFeB magnet powder sample was turned into a sulfate mixture by mixing with concentrated  $\text{H}_2\text{SO}_4$  (12–16 mol/L) in crucibles. After drying and high-temperature treatment, the powder was leached in demineralized water for 15 min to 24 h, which led to >95% recovery of REEs while Fe remained in the solid residue in the form of a sulfate. In 2014, Yoon et al. [10] studied the leaching of NdFeB magnet scrap using  $\text{H}_2\text{SO}_4$  at different temperatures and concentrations. The optimal leaching conditions were determined to be 70 °C and 3 mol/L  $\text{H}_2\text{SO}_4$  with a leaching time of 4 h. In 2013, Lee et al. [11] carried out an investigation on leaching of NdFeB magnets using  $\text{H}_2\text{SO}_4$ , HCl,  $\text{HNO}_3$ , and NaOH. Out of the four leaching agents, HCl and  $\text{H}_2\text{SO}_4$  showed the best leaching performance. Optimum conditions for this process were S:L (solid-to-liquid ratio) ratio of 20 g/L, leaching time of 15 min, and concentrations of 3 mol/L HCl and 1.5 mol/L  $\text{H}_2\text{SO}_4$ . The vast majority of research so far has been conducted using strong mineral acids for leaching [12–15]. The extraction of the metals of interest after leaching is most commonly done using solvent extraction agents like di-(2-ethylhexyl) phosphoric acid (D2EHPA), tributyl phosphate (TBP) and 2-ethylhexyl phosphonic acid (HEHEHP) [16], although a lot of research in recent years has been focused on the investigation of solvent extraction using ionic liquids as promising new, environmentally friendly extractants [3,17]. Even though efficient, hydrometallurgical methods have drawbacks. As already mentioned, large amount of waste is generated during the processes and toxic chemicals are often used. This has to be mitigated using more environmentally friendly chemicals and decreasing the quantities of both the aqueous and the organic waste produced.

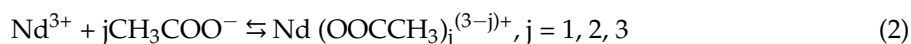
Despite possessing excellent properties for leaching REEs out of NdFeB magnets, strong mineral acids such as HCl,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  pose the risk of adverse impact on the environment [6,18,19] because of issues with regeneration of the used acids, while handling can also pose a great challenge in some situations. In cases where highly concentrated acids are released to the environment, they could acidify the soil and would require further soil treatment to neutralize the acidified soil [20]. Moreover, when using strong mineral acids, evolution of poisonous gasses is often a problem. Using organic acids or significantly more diluted mineral acids [21] could have advantages in this regard because of

easier handling, less poisonous gas evolution due to lower acidities, and much easier degradability. Some researchers even claim that a more sustainable REE-leaching process could be achieved using some bacteria like *Shewanella putrefaciens* [22].

Citric acid is an organic acid that contains three carboxylic groups, with the three hydrogen dissociation constants being  $pK_{a1} = 3.13$ ,  $pK_{a2} = 4.76$ , and  $pK_{a3} = 6.40$  at 25 °C [23]. It is naturally found in citrus fruits but is usually produced through a cheaper process by fermentation of sugars using *Aspergillus niger* bacteria [24]. As citric acid is in high demand both in chemical and food industry, the price is comparable to that of mineral acids. Two possible mechanisms of dissolution with citric acid include metal ion displacement with hydronium ions and formation of soluble metal–ligand complexes by metal chelation [25]. In a study by Brown et al. [26], it was shown that  $Nd^{3+}$  complex with citrate counterion is formed according to the following equilibrium:



The existence of  $NdCit$ ,  $NdHCit$ ,  $NdHCit_2$ , and  $NdCit_2$  was confirmed by the solution in the pH range 2–5, which proved that citric acid could be used for the leaching of Nd and other REEs out of e-scrap. Acetic acid is an organic acid containing one carboxylic group with  $pK_a = 4.76$ . It is largely produced by methanol carbonylation [27], and the price is comparable with that of mineral acids, making it attractive for usage as a leaching agent. In the work of Zanonato et al. [28], it was shown that  $Nd^{3+}$  forms at least successive mononuclear complexes according to the following equilibrium:



This indicates that acetic acid could be used for the recovery of Nd and possibly other REEs from electronic waste.

Carboxylic acids have been previously used for actinide and lanthanide separations [29,30] and could be suitable for the recovery of REEs out of NdFeB magnet waste as they can form soluble complexes with REEs. However, the leaching of neodymium magnets with organic acids is very scarcely investigated. In 2016, Behera et al. [6] investigated in detail the kinetics of extraction of Nd out of NdFeB waste using acetic acid. The study showed that acetic acid in concentrations higher than 0.4 mol/L at 800 rpm, 1% (*w/v*) and 308 K was effective at leaching Nd and Fe out of the waste. However, in this study—as well as in other works—little attention was paid to the recovery of other REEs, meaning no detailed kinetic or temperature gradient study was performed for vital REEs like Dy and Pr in the waste; the behavior of other impurities such as Fe, B and Co during the leaching process was not completely addressed either. The feasibility of further extraction of REEs out of leachates of organic acids was also not addressed.

In this study, leaching of a high-temperature-treated neodymium magnet powder was investigated using diluted citric acid and acetic acid. The leaching process was optimized in order to achieve the maximum REEs recovery by varying leaching time, acids concentration, and S:L ratio. Before the leaching experiments, the powder before and after roasting treatment was analyzed using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDX) analysis, X-ray diffraction (XRD), and total dissolution using aqua regia. Solvent extraction with D2EHPA was performed on the obtained leachates to test the feasibility of REEs recovery from such leachates using conventional methods.

## 2. Materials and Methods

### 2.1. Material Characterization

The hydrogen decrepitated (HD) NdFeB powder was used in both original and pretreated form. Pretreating was done by roasting at 400 °C for 1.5 h in an Entech muffle furnace (LF2) in a ceramic crucible. After roasting, the powder was sieved to a particle size of <355 µm using a Retsch AS

200 (Retsch, Haan, Germany) vibratory sieve shaker. Throughout this research, these two forms of powder used will be referred to as HD NdFeB powder and roasted NdFeB powder. To determine the elemental composition, 0.5 g of the powder was dissolved in 25 mL aqua regia (V (conc. HCl): V (conc. HNO<sub>3</sub>) = 3:1) at  $23 \pm 1$  °C for 6 hours and filtered with Whatman microfiber filters (GF/A 125 and 65 mm diameter). After filtration, the solution was diluted using 0.5 mol/L HNO<sub>3</sub> (suprapur<sup>®</sup> 65%, Merck, Kenilworth, NJ, USA). No residues were observed on the filter paper after filtration. The composition of the prepared solution was measured using ICP-OES (inductively coupled plasma optical emission spectroscopy, Thermo Scientific iCAP 600 Series ICP Spectrometer, Thermo Fisher, Cambridge, UK) and recalculated into weight percentages of the elements in the roasted powder. The same procedure was performed on the nonroasted HD NdFeB powder. The same measuring method was used throughout this paper. All experiments were done in triplicate to ensure statistical reliability of the results. SEM/EDX analysis was carried out on the HD NdFeB before and after roasting using a Phenom ProX (Thermo Fisher Scientific, Phenom-World B.V., Eindhoven, The Netherlands) scanning electron microscope with Phenom ProSuite (Thermo Fisher Scientific, Phenom-World B.V., Eindhoven, The Netherlands) software and Element Identification module in order to determine whether any surface modifications might have occurred during roasting or if there was any elemental redistribution in the particles. The chemical composition of both the HD and roasted NdFeB powders were further ascertained using XRD Bruker D8 Advance (Bruker Corporation, Billerica, MA, USA) with Cu K $\alpha$  used to examine the phase content. The  $2\theta$  range was 20–80° and step size 0.04°/s.

## 2.2. Leaching Kinetics

Acetic acid (Sigma-Aldrich,  $\geq 99.5\%$ ) and citric acid (Sigma-Aldrich,  $\geq 99.5\%$ ) were used as leaching agents, prepared by diluting the concentrated acids with MiliQ water (Merck Millipore Q-POD) to a desired concentration. In order to choose the optimal leaching conditions, the first variables investigated were time and concentration. Each sample was reacting in a closed 100 mL PP plastic cup. Solid to liquid ratio was kept at 0.5 g of magnet powder per 25 mL of acid, the temperature at  $23 \pm 1$  °C, and stirring speed at 400 rpm. The samples were leached for 100, 200, 300 min, and 24 h. The starting concentrations of the organic acids used were 0.1, 0.2, 0.4, 0.8, and 1 mol/L. Each experiment was done in triplicate. The heating and stirring plate used was an IKA<sup>®</sup> RT15. Powder was weighed on a Fisher MH-214 Analytical scale before the reaction and was used in leaching efficiency calculation. The sampled leachates were diluted in 1 mol/L HNO<sub>3</sub> (suprapur<sup>®</sup> 65%, Merck, Kenilworth, NJ, USA), and the metal concentrations were measured using ICP-OES. The pH values of the acids before leaching and leachates after 24 h leaching time was measured using MeterLab<sup>™</sup> PHM 240 pH/ion Meter pH electrode (Radiometer, Copenhagen, Denmark).

## 2.3. Solid to Liquid Ratio Study

After the determination of the optimal leaching time and acid concentration, the solid to liquid ratio for leaching was investigated. For this study 1/30, 1/50, and 1/80 g/mL S:L ratio was chosen. The volume of the leaching agent was kept at 25 mL in all cases, and the mass of the NdFeB powder was varied. The samples were reacted with 1 mol/L citric and 1 mol/L acetic acid for 300 min in PP plastic cups. The rotation speed was kept constant at 400 rpm, and the temperature was kept at  $23 \pm 1$  °C. After the reaction, the leachates were sampled, diluted in 1 mol/L nitric acid, and the metal concentrations were measured using ICP-OES.

## 2.4. Solvent Extraction

To extract metals from the aqueous leachate, D2EHPA (Sigma-Aldrich 97%) in Solvent 70 was used. D2EHPA is a widely used industrial extracting agent, which was used in the case of 1 mol/L citric acid and acetic acid leachates to determine the possible use for the recovery of REEs and other

elements out of organic acids leachates using solvent extraction. The usual extraction reaction of lanthanides using acidic extractants like D2EHPA [31] is of ion-exchange character:



where  $Ln$  represents the lanthanide ion and  $HX$  represents a molecule of D2EHPA. The experiments were performed on the Ika Vibrax Vxr basic shaking machine in 3.5 mL glass shaking vials, for 1 h and the  $V_{org}: V_{aq} = 1$ . After the extraction, the aqueous phase was sampled, diluted in 1 mol/L  $HNO_3$ , and measured using the ICP-OES. The distribution ratios ( $D$ ) were calculated as the mass balance in the aqueous phase before and after the extraction. Distribution ratios were calculated according to the following equation:

$$D_A = \frac{[A]_{org}}{[A]_{aq}} \quad (4)$$

where  $[A]_{org}$  and  $[A]_{aq}$  are the equilibrium concentration of the metal of interest in all its existing species in the organic and aqueous phase, respectively. Separation factor represents the degree of separation between species A and B in the extraction system and is calculated according to the following equation.

$$SF = \frac{D_A}{D_B} \quad (5)$$

The equilibrium pH values in the aqueous phase were measured using MeterLab™ PHM 240 pH/ion Meter pH electrode.

### 3. Results and Discussion

#### 3.1. Material Characterization

The composition of the HD NdFeB powder used in this research was determined in a previous work performed by our group [13], where  $HNO_3$  was used to leach the HD NdFeB and TODGA (N, N, N', N'-tetraoctyl diglycolamide) was used to extract the REEs from the acquired leachate. The results were in accordance with the composition of neodymium magnets found on the market [3,7,32]. Preliminary leaching tests were performed on the HD NdFeB powder using 0.4–1.6 mol/L citric acid and acetic acid at S:L ratio 1/50 g/mL and  $25 \pm 1$  °C. REEs exhibited very slow leaching kinetics (less than 20% REEs leached after 8 hours, even at concentrations above 1.2 mol/L, while it took roughly five days to leach 80% of Nd and 60% of Pr and a mere 20% of Dy). Thus, the HD NdFeB powder was roasted and demagnetized to potentially increase its leaching properties. Roasting was used to change the powder chemically and demagnetization to minimize the amount of powder clinging to the stirring magnet. After roasting, the composition of the roasted powder was determined by dissolving it in aqua regia (results shown in Table 1).

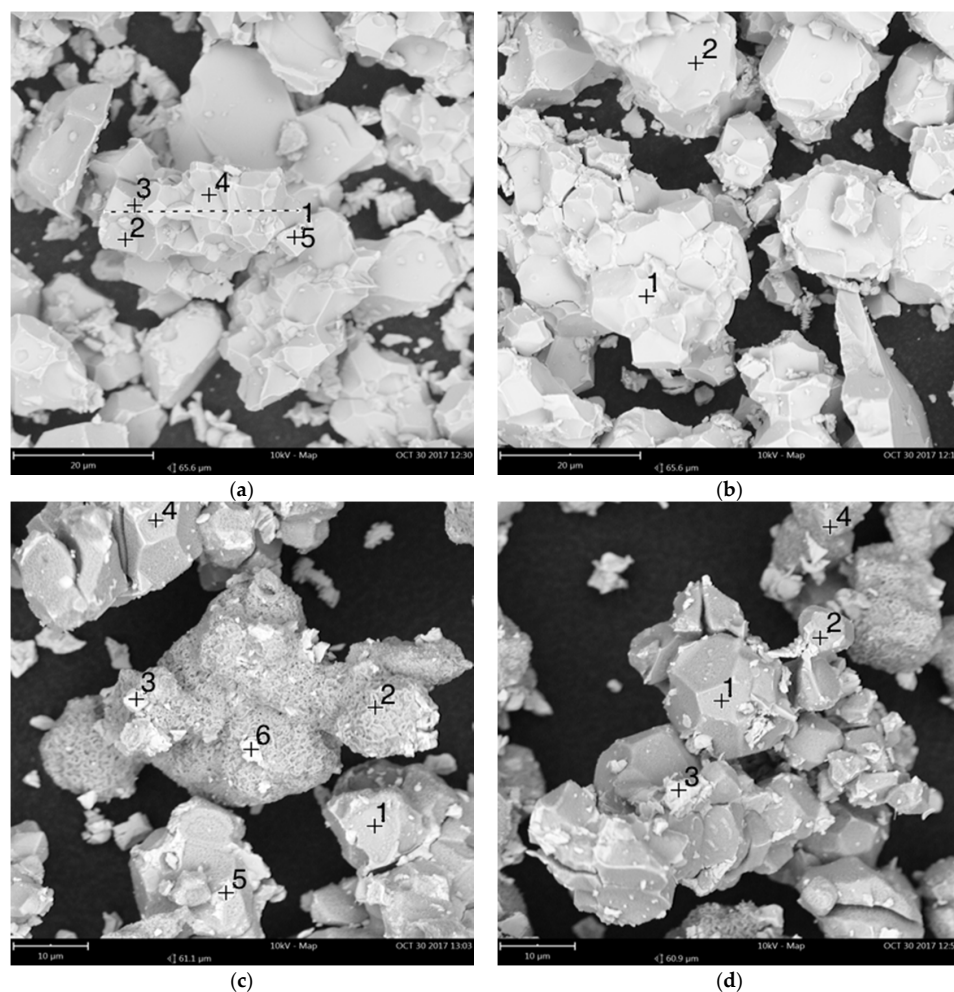
**Table 1.** Elemental composition, in wt %, of the (a) hydrogen decrepitated (HD) NdFeB totally dissolved in aqua regia for 1 h at  $80 \pm 1$  °C and S:L = 1/10 g/mL and (b) roasted NdFeB powder dissolved in aqua regia for approximately six hours at temperature  $23 \pm 1$  °C and S:L = 0.1/5 g/mL. No residues were left after filtration.

Element	(a) Mass Fraction in HD NdFeB Magnet Powder/wt % [13]	(b) Mass Fraction in Roasted NdFeB Magnet Powder/wt %
Fe	$61.1 \pm 1.0$	$56.4 \pm 0.3$
Nd	$25.3 \pm 0.7$	$22.7 \pm 0.0$
Pr	$2.62 \pm 0.17$	$2.73 \pm 0.05$
Dy	$1.08 \pm 0.27$	$0.77 \pm 0.01$
Co	$1.42 \pm 0.07$	$1.25 \pm 0.03$
B	$1.00 \pm 0.02$	$0.74 \pm 0.01$



Over one quarter of the roasted NdFeB powder weight fraction consists of REEs, which makes it a feasible source for REEs recovery. As expected, the two major components of the roasted neodymium magnet powder were Fe and Nd, making up  $56.4 \pm 0.3\%$  and  $22.7 \pm 0.0\%$  of the powder, respectively. Pr made up  $2.73 \pm 0.05\%$  and Dy  $0.77 \pm 0.01\%$  of the overall composition—percentages that are similar to the ones in the HD NdFeB powder. Some impurities present in the NdFeB magnet structure, such as Co and B, were also present, but in percentages lower than 2%. Fe and Nd were represented in slightly lower percentages than expected, which can be attributed to the reaction of oxygen and other atmospheric gases with the original powder during roasting as the oven did not have a controlled atmosphere. Due to the inability to measure the content of oxygen and other air components using the ICP-OES, the composition of these could not be reported by aqua regia dissolution. Some percentages of Fe and Ni (normally present in the magnet coating) might have been lost during the sieving of the roasted powder as larger chunk-like chips from the protective coating of the original magnet were removed. The protective coating is not, however, of interest here from a recycling standpoint as it does not contain REEs. Lastly, the difference from 100% can be attributed to the experimental errors while performing the experiments.

To further characterize the waste, SEM/EDX analysis was performed. This was done in order to determine the surface changes that occurred in the HD NdFeB powder during roasting and to examine possible redistributions of elements during roasting and sieving. Figure 1 shows the SEM and EDX of the HD NdFeB powder (a and b) and the roasted NdFeB powder (c and d).



**Figure 1.** Four different SEM magnifications (4100 $\times$ , 10 kV-Map) HD NdFeB powder in two different locations (a,b) and roasted neodymium magnet powder sample in two locations (c,d). The crosses and lines on the SEM pictures show the locations where the EDX analysis was performed.

In Figure 1a,b, it can be observed that the morphology of the powder looked even except for the particle size, which varied and ranged from 2–20  $\mu\text{m}$ . EDX analysis was also performed on the same powder shown in Figure 1. The EDX results suggested that the HD NdFeB powder elemental composition correlated to the composition of NdFeB magnets found in the market [7]. No clusters with higher concentration of certain elements than in the bulk material were found. Some locations on the powder—like the one represented by Line 1 in Figure 1a and point 2 in Figure 1b—showed higher amounts of oxygen, which can be attributed to the fact that the REE-rich grain boundary phase oxidizes fast when exposed to air during the HD process [33].

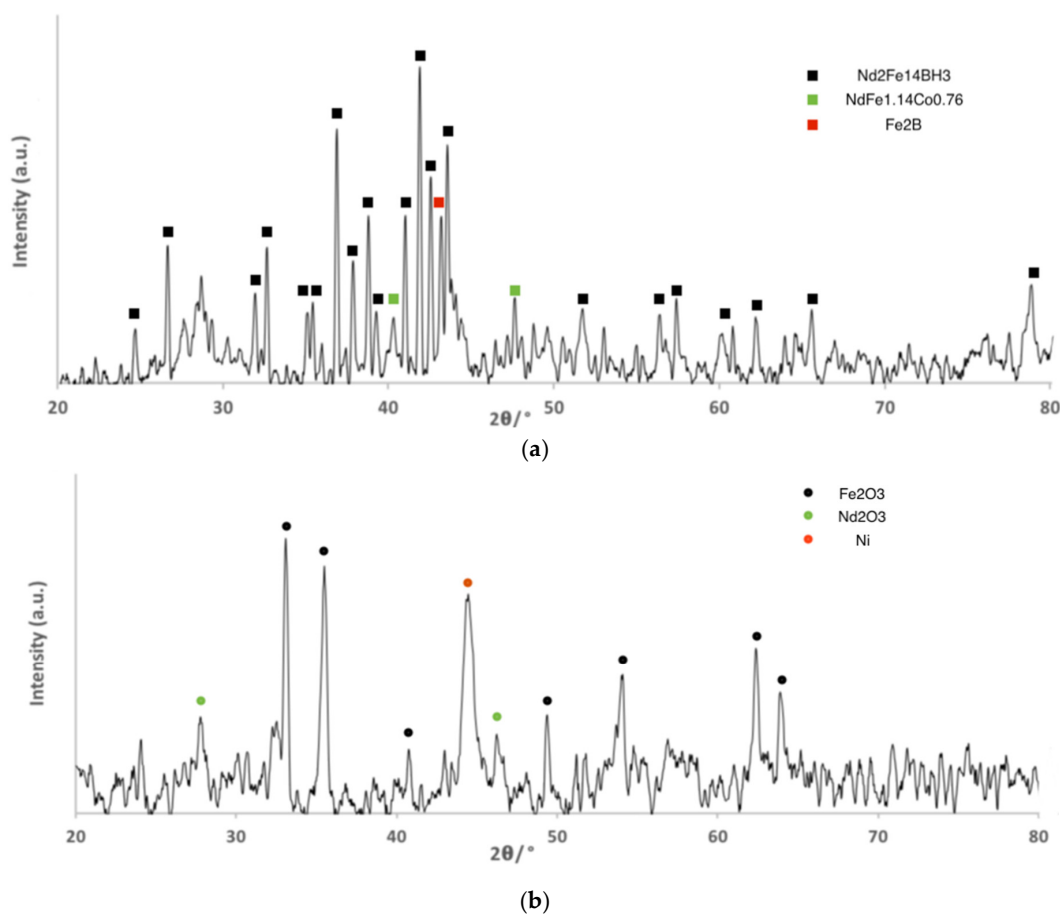
The results of the SEM/EDX analysis of the roasted NdFeB powder showed different results. In Figure 1c,d, it can be observed that the morphology of the powder was significantly more diverse now than it was before the roasting treatment. Three types of particles could be observed: the flat surface particles sized around 10  $\mu\text{m}$  in diameter, the bulkier particles with a distinct rugged morphology with the diameter size of around 10–20  $\mu\text{m}$ , and the small white specs less than 5  $\mu\text{m}$  in diameter. EDX was performed in order to determine the elemental composition of the various particle types.

The flat surface particles were largely composed of iron and oxygen (spots 1 and 2 in Figure 1d). EDX analysis of the white specs showed that these consisted mainly of Nd, Pr, and O, pointing to the creation of clusters of REE oxides during the roasting treatment. The large particles with the rugged surface consisted mostly of Fe and O and smaller amounts of REEs. The weight percentage fluctuations were probably due to variations in the penetration depth of the electrons during the EDX analysis, which can vary depending on the surface topography and composition. Because the electrons penetrate at an approximately constant mass, spatial resolution is a function of density.

From the SEM images, it can be observed that the morphology of the hydrogen decrepitated and roasted powder differed significantly, which was expected. In the case of the HD NdFeB powder, the surfaces of the particles were relatively similar, with most of the particles looking homogeneous and having sharp edges. On the other hand, the roasted powder was heterogeneous. It was confirmed using the EDX analysis that the heterogeneity was also present from a particle composition point of view as it was shown that the composition varied significantly across the particle size and shape in the roasted NdFeB powder.

To determine the chemical species that can be found in the powder before and after treatment, as well as the changes that occurred in the HD NdFeB powder during the roasting process, both powders were analyzed using XRD. The XRD pattern of the HD NdFeB powder (Figure 2a) showed the presence of  $\text{Nd}_2\text{Fe}_{14}\text{BH}_3$ , a hydride formed during the hydrogen decrepitation process. Apart from the main  $\text{Nd}_2\text{Fe}_{14}\text{BH}_3$ , the presence of  $\text{Fe}_2\text{B}$  and  $\text{NdFe}_{1.14}\text{Co}_{0.76}$  was observed. The XRD pattern also showed the presence of traces of Ni. The XRD pattern of the roasted NdFeB powder (Figure 2b) showed the presence of  $\text{Fe}_2\text{O}_3$  and  $\text{Nd}_2\text{O}_3$ , which were formed during the roasting process in the presence of air atmosphere. Ni was also present in higher amounts in elemental form. Apart from these main components there were also present traces of  $\text{Pr}_2\text{O}_3$  and Fe in elemental form. The results of the XRD correlated with the results of the SEM-EDX analysis.

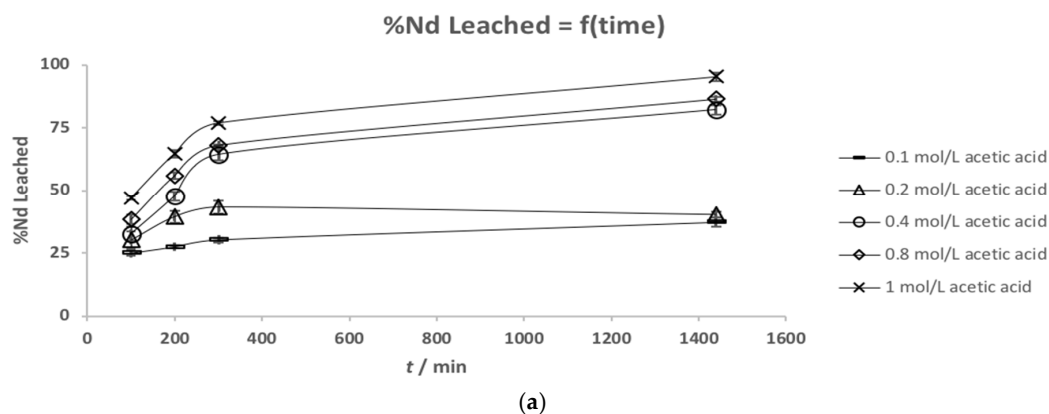




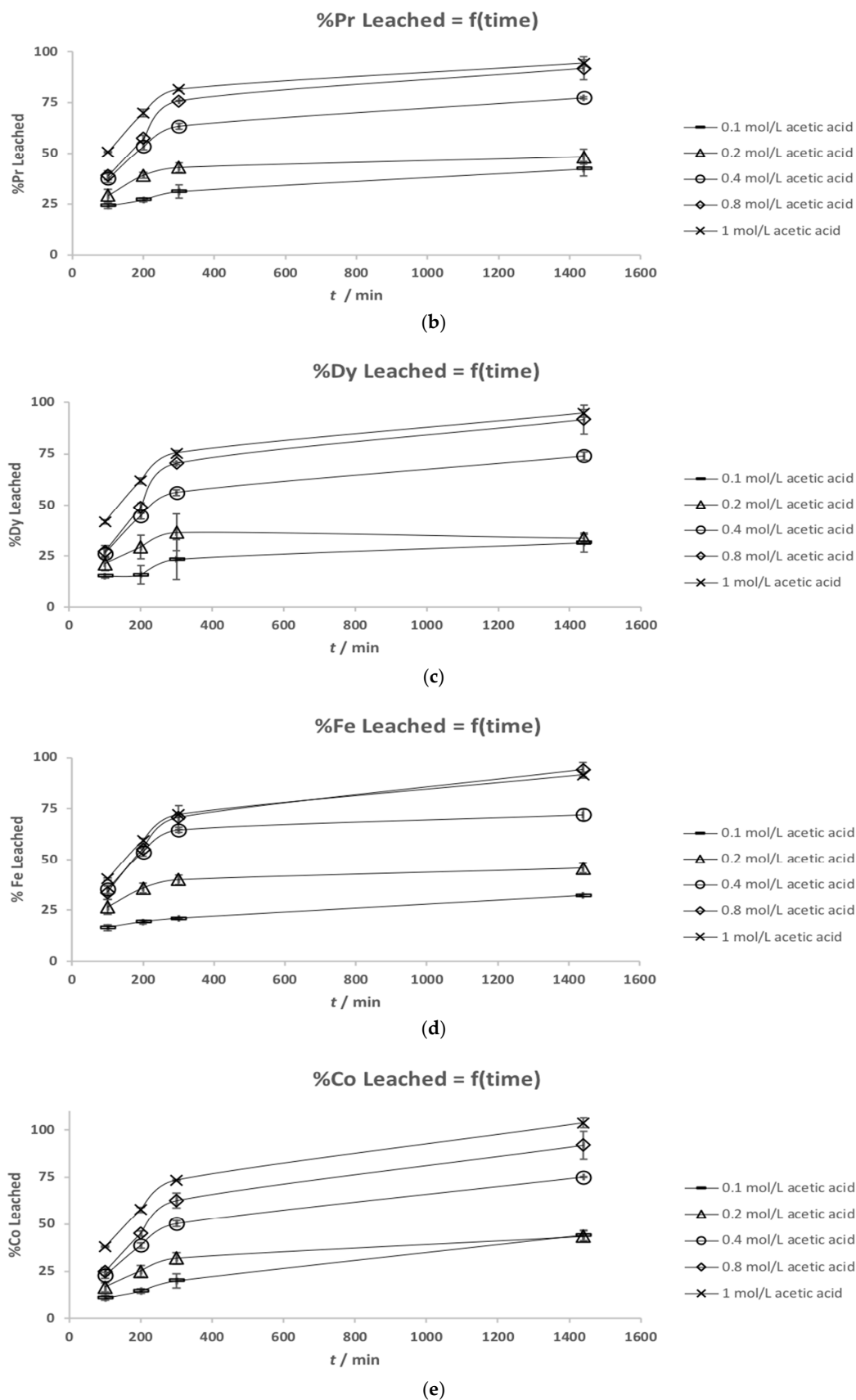
**Figure 2.** XRD pattern of the (a) hydrogen decrepitated NdFeB powder and (b) roasted NdFeB powder.

### 3.2. Leaching Kinetics

Apart from the REEs, Fe and Co leaching efficiencies were also monitored as they make up a sufficient percentage of the material to compromise the leaching process. Citric acid and acetic acid showed good leaching properties for REEs out of the roasted magnet powder waste. The results from leaching of roasted neodymium magnet powder with acetic acid and citric acid are shown in Figures 3 and 4, respectively. The leaching kinetics of the REEs, Fe, and Co are represented as an average of a triplicate experiment.



**Figure 3.** Cont.



**Figure 3.** Effect of the concentration of acetic acid (0.1, 0.2, 0.4, 0.8 and 1 mol/L) and leaching time (100 min, 200 min, 300 min and 24 h) on the leaching efficiency of (a) Nd, (b) Pr, (c) Dy, (d) Fe, and (e) Co. The temperature was kept at  $25 \pm 1$  °C, magnetic stirring at 400 rpm, and S:L ratio at 1/50 g/mL.

Leaching of Nd, Pr, Dy, Fe, Co, and B at varying concentrations of acetic acid were studied. Leaching time varied from 0–24 h, while the temperature and S:L ratio were kept constant. The leaching efficiency was found to be significantly dependent on the acetic acid concentration as well as the leaching time. It can be observed that changing the acetic acid concentration from 0.05 to 1 mol/L and using a 24 h leaching time increased the leaching efficiency from <20% to >95% for all REEs. Thus, acetic acid in concentrations higher than 1 mol/L is recommended for the efficient recovery of REEs from roasted neodymium magnet powder. After 24 h of leaching with 1 mol/L acetic acid, almost all of Dy, Pr, Fe, Co, and B were leached into the solution, while over 95% of Nd was recovered. Diluting acetic acid from 1 mol/L to 0.1 mol/L decreased the pH value from 2.2 to 2.8. The pH values of the leachates after 24 h leaching were 4.1, 4.2, 4.6, 5.2, 5.6, and 5.9 for 1 mol/L, 0.8 mol/L, 0.6 mol/L, 0.4 mol/L, 0.2 mol/L, and 0.1 mol/L leachates, respectively, pointing at proton starvation during leaching.

Fe, B, and Co showed similar trends and no selectivity for REEs was observed, meaning that the increase in leaching of the REEs was also followed by the co-leaching of Fe, B, and Co into the solution. As 1 mol/L acetic acid was needed for quantitative leaching of REEs, this concentration was used for further experiments.

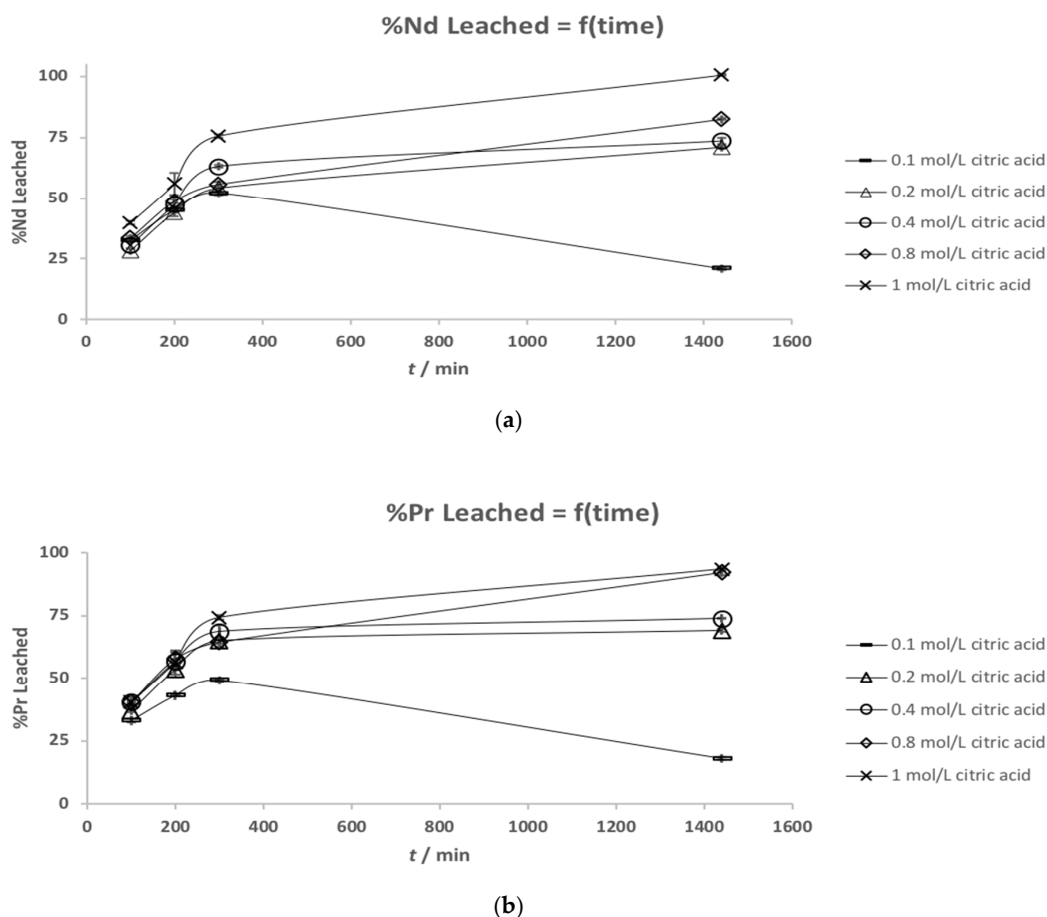
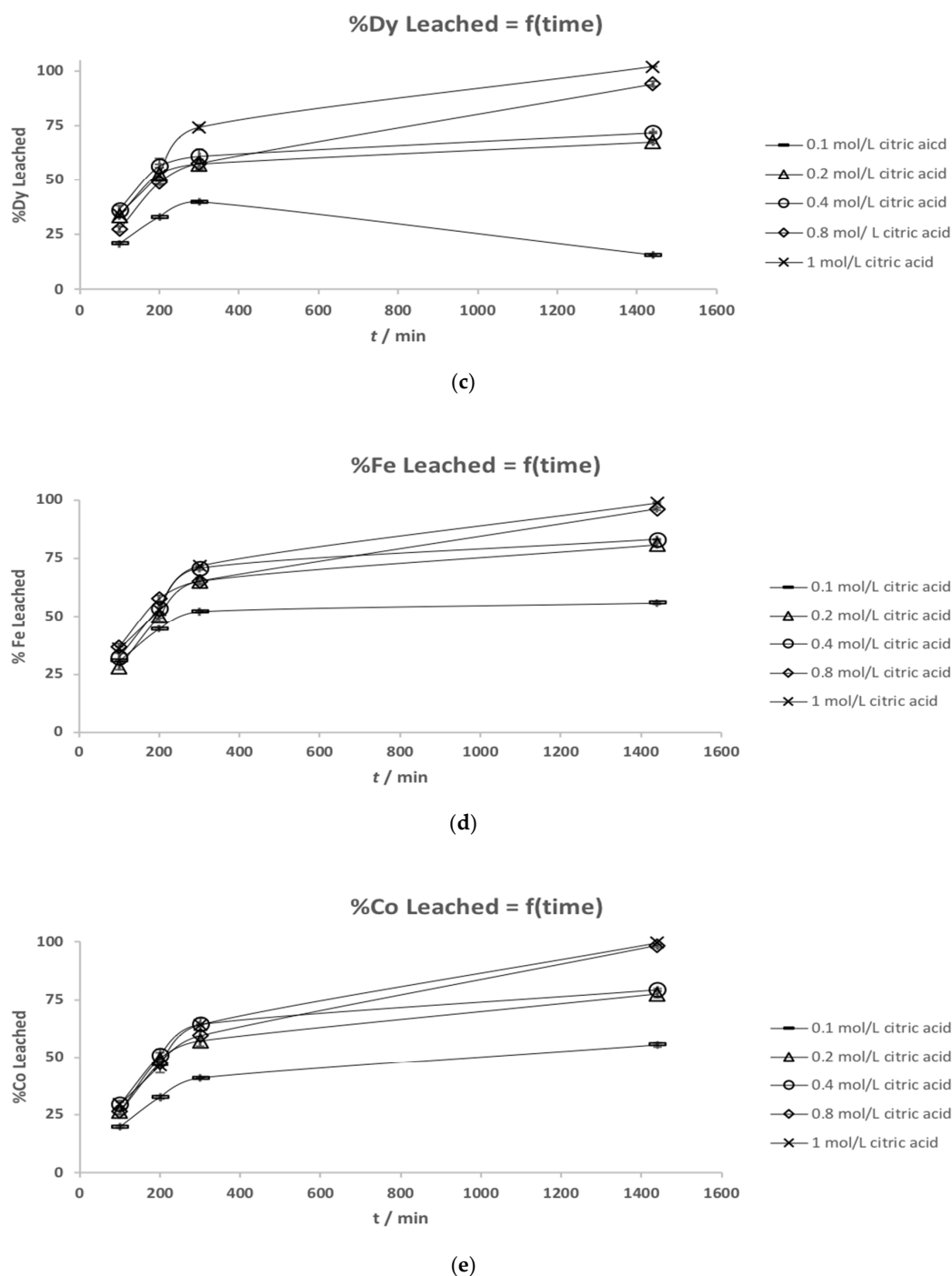


Figure 4. Cont.



**Figure 4.** Effect of the concentration of citric acid (0.1, 0.2, 0.4, 0.8 and 1 mol/L) and leaching time (100 min, 200 min, 300 min and 24 h) on the leaching efficiency of (a) Nd, (b) Pr, (c) Dy, (d) Fe, and (e) Co. The temperature was kept at  $25 \pm 1$  °C by magnetic stirring at 400 rpm, and S:L ratio at 1/50 g/mL.

As in the case of acetic acid, the effect of variation in the concentration of citric acid was observed to influence the leaching efficiency of the components of the roasted neodymium powder (Figure 4). Increasing the concentration of citric acid from 0.1 mol/L to 1 mol/L increased the leaching efficiency for the REEs from <20% to >95%, reaching the highest leaching efficiency after 24 h. The increase in the leaching efficiency of REEs was accompanied by the co-leaching of Fe, B, and Co into the solution. The pH value of the leaching acid measured increased from 1.23 to 2.5 from 1 mol/L to 0.1 mol/L, while the values after 24 h leaching were 2.3, 2.6, 3.4, 4.5, and 5.3 for 1 mol/L, 0.8 mol/L, 0.6 mol/L,

0.4 mol/L, 0.2 mol/L, and 0.1 mol/L of citric acid, respectively. An interesting observation here is the decrease in leaching efficiency of the Nd, Pr, and Dy that occurred after 24 h leaching with 0.1 mol/L citric acid. Fe and Co did not exhibit the same behavior—the leaching efficiency reached equilibrium after 300 min for Fe, while the leaching efficiency for Co increased another 10% after 24 h. This can be explained by the pH increase up to 5.3 in the 0.1 mol/L, which led to the precipitation of the REEs, most likely as citrates as citrates of REEs are known to be soluble in aqueous solutions around pH 2–5 [26].

Both acetic acid and citric acid showed much better leaching properties when the roasted and sieved NdFeB powder was used than was the case for the HD NdFeB magnet. It was shown that roasting and the elemental redistributions that occurred during the process (molar volume changes during the oxidation and pore formation that make the inner surfaces of the powder more available for leaching) benefited the leaching properties. Sieving the powder into smaller particles also improved the leaching process, which was also shown in a previous work by Behera et al. [6]. The ideal conditions for the leaching of Nd were determined to be 1 mol/L of either citric or acetic acid, and further experiments were conducted with these concentrations.

### 3.3. Solid to Liquid Ratio Study

The leaching efficiencies of Nd, Pr, Dy, Fe, and Co in 1 mol/L citric acid and acetic acid as a function of solid to liquid ratio are shown in Figure 5a,b. The S:L ratios used were 1/30, 1/50, and 1/80 g/mL. In the case of 1 mol/L citric acid, changing the S:L ratio from 1/30 to 1/80 g/mL had negligible effects on the leaching efficiencies of all the elements present. Dy showed slightly higher leaching efficiency at 1/80 S:L ratio, but all within the statistical error. On the other hand, in the case of 1 mol/L acetic acid, the change of S:L ratio from 1/30 to 1/80 g/mL had a significant effect on the leaching of Fe, which was leached at  $61.69 \pm 6.58\%$  at 1/30 g/mL and  $79.30 \pm 2.28\%$  at 1/80 g/mL. This can be attributed to the strength of the acids. Acetic acid is a monoprotic acid with  $pK_a = 4.76$ , while citric acid is a triprotic acid with  $pK_{a1} = 3.13$ ,  $pK_{a2} = 4.76$  and  $pK_{a3} = 6.39$ , which can explain why the leaching efficiency of Fe was lower due to proton starvation in the leachate. Exact amounts of  $H^+$  were not recalculated from the  $pK_a$  values as activity coefficients would need to be determined in that case. The leaching efficiency of Co was also slightly affected by increasing the S:L ratio; it increased from  $86.11 \pm 0.38\%$  at 1/30 g/mL to  $93.92 \pm 1.70\%$  at 1/80 g/mL. For industrial purposes, it can be extracted from the leachate using Cyanex 272 (di-(2,4,4-trimethylpentyl) phosphinic acid) at equilibrium pH 4–5 [34]. Changing the S:L ratio from 1/30 to 1/80 g/mL did not, however, affect the leaching efficiency of Nd, Pr, and Dy, which stayed the same across the S:L ratio. B was found to be leached quantitatively at all S/L ratios investigated. For complete extraction of B from the leachate, aliphatic 1,3-diols can be used [35].

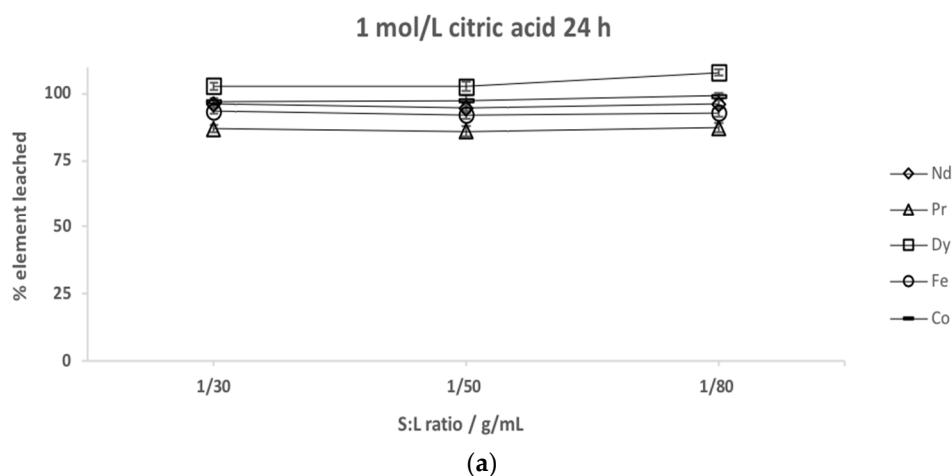
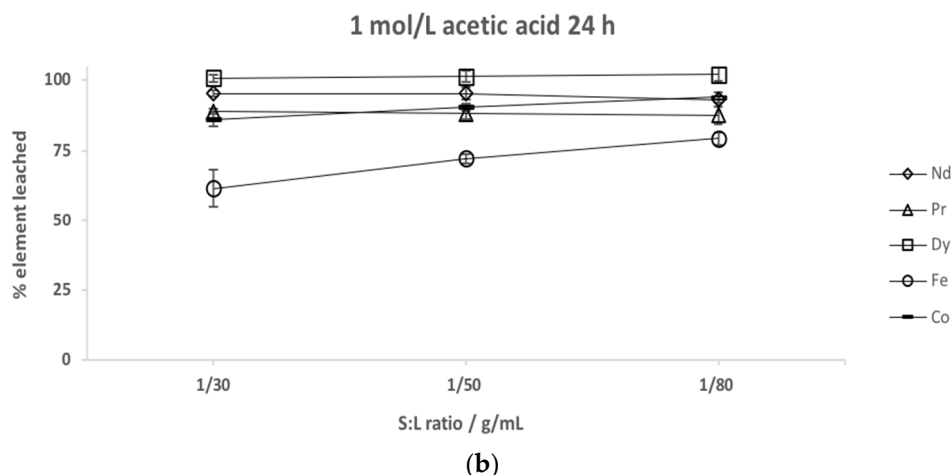


Figure 5. Cont.

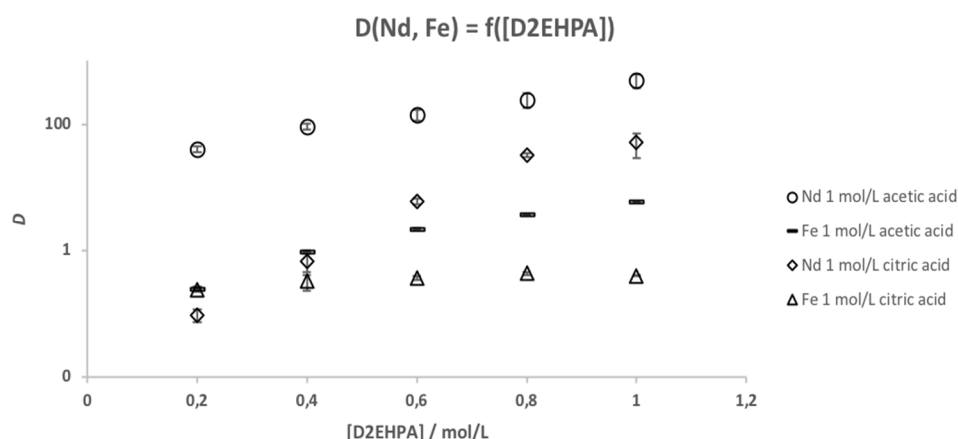


**Figure 5.** The dependence of the amount of Nd leached on the S:L ratio at  $25 \pm 1$  °C using (a) 1 mol/L citric acid and (b) 1 mol/L acetic acid with 400 rpm stirring for 24 h in both cases.

### 3.4. Solvent Extraction

A screening investigation regarding the possible separation of the leached metal ions by solvent extraction was made on the leachates obtained after 24 h leaching of the roasted magnet powder using 1 mol/L citric acid and acetic acid. D2EHPA dissolved in Solvent 70 in concentrations of 0.2, 0.4, 0.6, 0.8, and 1 mol/L was used as the organic phase for the extraction of the REEs out of the leachates. Figure 6 represents the D values for Fe and Nd as they are the major components of the leachate. The distribution ratios of other REEs were shown to behave very similarly to the distribution ratios of Nd, and these metals were completely extracted at higher D2EHPA concentrations. The distribution ratios of REEs increased with increasing D2EHPA concentration in the organic phase, as expected. The distribution ratios of Fe were much lower compared to Nd, so high separation factors were expected to be found, the highest being the ones at 0.2 acetic acid extraction with 1 mol/L D2EHPA, which reached the value of  $161.9 \pm 21.0$ . The distribution ratios were one order of magnitude higher in the acetic acid media than in the citric acid solutions. This can be attributed to the equilibrium pH values, which were around 3.5 after the extraction from 1 mol/L acetic acid leachate and slowly increased with the decreasing D2EHPA concentration but stayed around 1.5 after the extraction from 1 mol/L citric acid leachate. As shown in a previous study [36], higher equilibrium pH values gave higher distribution ratios for REEs due to REE–D2EHPA complex formation, which is favored in higher equilibrium pH media as D2EHPA is an acidic extractant that exhibits the ion-exchange mechanism, with release of  $H^+$  ions after the complex has been formed (Equation (3)). The behavior of B and Co was also monitored in the extraction process. It was found that at investigated conditions (0.2–1 M D2EHPA in Solvent 70), less than 1% of both the B and Co were extracted from the leachates, which makes this system even more attractive in terms of selective REEs recovery. According to Table 2, separation factors between Nd and Fe were generally higher in the case of 1 M acetic acid leachate but had reached a value of  $129 \pm 55$  in extraction from 1 M citric acid leachate, making these systems promising in separating valuable elements like Nd from large amounts of Fe usually contained in NdFeB magnets.





**Figure 6.** Distribution ratio of Nd and Fe as a function of the concentration of D2EHPA in a small-scale solvent extraction set-up ( $V_{org}/V_{aq} = 1$ ; 1 h shaking at 1500 rpm on an adaptable vortex mixer). The aqueous phase was a leachate (citric acid and acetic acid 1 M; S:L 1g /50 mL; 25 °C; 24 h; 400 rpm stirring) using D2EHPA in Solvent 70 solutions as extracting agents, while temperature was thermostatically kept at  $25 \pm 1$  °C.

**Table 2.** Separation factors between Nd and Fe after extraction with 0.2, 0.4, 0.6, 0.8, and 1 mol/L D2EHPA in Solvent 70. The aqueous phases used were 1 mol/L citric acid and acetic acid leachates previously obtained. Phase ratios were kept at  $V_{org}/V_{aq} = 1$  during 30 min shaking at 1500 rpm on the custom-made shaking machine. Temperature was thermostatically kept at  $25 \pm 1$  °C.

c (D2EHPA)/mol/L	SF <sub>Nd/Fe</sub> (1 mol/L Acetic Acid)	SF <sub>Nd/Fe</sub> (1 mol/L Citric Acid)
0.2	161.9 ± 21.0	0.39 ± 0.10
0.4	94.9 ± 9.4	2.07 ± 0.86
0.6	64.5 ± 13.4	17.0 ± 2.4
0.8	64.1 ± 16.0	76.7 ± 5.9
1	82.2 ± 21.0	129 ± 55

#### 4. Conclusions

In the present work, the leaching of REEs, Fe, and Co from roasted NdFeB magnet powder was studied using citric acid and acetic acid. The treated NdFeB powder was characterized prior to the leaching experiments by total dissolution with aqua regia and SEM/EDX analysis. Kinetics of the leaching process at different concentrations of acids and S:L ratios were studied. After the leaching experiments, solvent extraction was performed using D2EHPA in Solvent 70 as the organic phase and the leachates of citric acid and acetic acid to determine the feasibility of the extraction of REEs from such leachates as well as possible further developments of the process.

By total dissolution of the roasted NdFeB magnet powder in aqua regia, the composition of the magnet was determined to be consistent with that found in the market. Lower percentages of some elements, such as Fe, pointed towards the presence of oxygen due to air contact during roasting. SEM analysis of the neodymium magnet powder before and after roasting showed significant changes in the morphology of the powder. EDX showed the composition of the powder was composed of NdFeB matrix and further confirmed the redistribution of the elemental composition that ensued after roasting. In the HD NdFeB magnet powder, the elemental composition was even throughout the particles observed before roasting. By contrast, in the roasted NdFeB magnet powder, elemental composition was significantly more uneven, with some parts containing significantly higher amounts of REEs, while others contained higher amounts of Fe. Faster leaching kinetics observed in the case of acetic acid and citric acid can be attributed to the elemental redistribution during roasting and sieving.

Acetic acid and citric acid showed good leaching properties for REEs, Fe, and Co. Of all the concentrations studied, 1 mol/L citric acid and 1 mol/L acetic acid exhibited the best leaching

properties. Over 95% of REEs were leached after 24 h with 1 mol/L acetic acid, while REEs were leached almost quantitatively after 24 h with 1 mol/L citric acid. Co-leaching of Fe and Co into the solution could not be avoided due to similar dissolution properties as the REEs, and both were leached >95% in both 1 mol/L citric acid and 1 mol/L acetic acid after 24 h.

Changing the S:L ratio from 1/30 to 1/80 g/mL in 1 mol/L citric acid after 24 h showed no difference in leaching efficiency, while 1 mol/L acetic acid after 24 h showed significantly less Fe leached with a S:L ratio 1/30 g/mL. When making preliminary solvent extraction tests with 1 mol/L D2EHPA in Solvent 70 on the leachates in 1 mol/L citric acid and acetic acid, the REEs distribution ratios increased with increasing D2EHPA concentration from 0.2 mol/L to 1 mol/L. Higher distribution ratios were achieved in acetic acid with higher SF between Nd and Fe, but good separation between Nd and Fe was achieved in extraction from 1 M citric acid leachate. The study showed significant results with respect to organic acids leaching and further extraction of REEs from the leachate using D2EHPA. A further development in this direction would be beneficial, especially using mixer-settler bench scale systems, to further determine the process parameters for efficient separation of REEs from Fe.

**Author Contributions:** Conceptualization: M.G., C.R.; Methodology: M.G., C.R.; Software: F.E., B.-M.S.; Validation: M.G., T.R.; Formal analysis: M.G., C.R., F.E.; Investigation: M.G., C.R.; Resources: T.R., B.-M.S.; Data curation: M.G., C.R., F.E.; Writing—original draft preparation: M.G.; Writing—review and editing: M.G., B.-M.S., T.R.; Visualization: M.G., C.R.; Supervision: T.R.; Project administration: B.-M.S.; Funding acquisition: T.R., B.-M.S.

**Funding:** The research leading to these results has received funding from the European Community's Seventh Framework Programme ([FP7/2007–2013]) under grant number No. 607411 (MC-ITN EREAN: European Rare Earth Magnet Recycling Network). This publication reflects only the authors' views, exempting the Community from any liability. Project website: <http://www.erean.eu>. The authors would like to extend special thanks to the ENVIREE project (Environmentally friendly and efficient methods for extraction of rare-earth elements (REE) from secondary sources-ERA-MIN project 2015–2017) contribution with additional funding.

**Acknowledgments:** The authors would like to extend special thanks to Burçak Ebin for the help with XRD measurements.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References

1. Firdaus, M.; Rhamdhani, M.A.; Durand, Y.; Rankin, W.J.; McGregor, K. Review of High-Temperature Recovery of Rare Earth (Nd/Dy) from Magnet Waste. *J. Sustain. Metall.* **2016**, *2*, 276–295. [[CrossRef](#)]
2. European Commission. *Critical Raw Materials for the EU*; Report of the Ad-hoc Working Group on Defining Critical Raw Materials: Brussels, Belgium, 2018.
3. Binnemans, K.; Jones, P.T.; Blanpain, B.; Van Gerven, T.; Yang, Y.; Walton, A.; Buchert, M. Recycling of rare earths: A critical review. *J. Clean. Prod.* **2013**, *51*, 1–22. [[CrossRef](#)]
4. Guyonnet, D.; Planchon, M.; Rollat, A.; Escalon, V.; Tuduri, J.; Charles, N.; Vaxelaire, S.; Dubois, D.; Fargier, H. Material flow analysis applied to rare earth elements in Europe. *J. Clean. Prod.* **2015**, *107*, 215–228. [[CrossRef](#)]
5. Rollat, A.; Guyonnet, D.; Planchon, M.; Tuduri, J. Prospective analysis of the flows of certain rare earths in Europe at the 2020 horizon. *Waste Manag.* **2016**, *49*, 427–436. [[CrossRef](#)] [[PubMed](#)]
6. Behera, S.S.; Parhi, P.K. Leaching kinetics study of neodymium from the scrap magnet using acetic acid. *Sep. Purif. Technol.* **2016**, *160*, 59–66. [[CrossRef](#)]
7. Yang, Y.; Walton, A.; Sheridan, R.; Güth, K.; Gauß, R.; Gutfleisch, O.; Buchert, M.; Steenari, B.M.; Gerven, T.V.; Jones, P.T.; et al. REE Recovery from End-of-Life NdFeB Permanent Magnet Scrap: A Critical Review. *J. Sustain. Metall.* **2017**, *3*, 122–149. [[CrossRef](#)]
8. Alonso, E.; Sherman, A.M.; Wallington, T.J.; Everson, M.P.; Field, F.R.; Roth, R.; Kirchain, R.E. Evaluating Rare Earth Element Availability: A Case with Revolutionary Demand from Clean Technologies. *Environ. Sci. Technol.* **2012**, *46*, 3406–3414. [[CrossRef](#)] [[PubMed](#)]
9. Önal, M.A.R.; Borra, C.R.; Guo, M.; Blanpain, B.; Van Gerven, T. Recycling of NdFeB Magnets Using Sulfation, Selective Roasting, and Water Leaching. *J. Sustain. Metall.* **2015**, *1*, 199–215. [[CrossRef](#)]

10. Yoon, H.-S.; Kim, C.; Chung, K.W.; Lee, S.-J.; Joe, A.-R.; Shin, Y.-H.; Lee, S.; Yoo, S.-J.; Kim, J.-G. Leaching kinetics of neodymium in sulfuric acid from E-scrap of NdFeB permanent magnet. *Korean J. Chem. Eng.* **2014**, *31*, 706–711. [\[CrossRef\]](#)
11. Lee, C.; Chen, Y.; Liao, C.; Popuri, S.R.; Tsai, S.; Hung, C. Selective Leaching Process for Neodymium Recovery from Scrap Nd-Fe-B Magnet. *Metall. Mater. Trans.* **2013**, *44*, 5825–5833. [\[CrossRef\]](#)
12. Lyman, J.W.; Palmer, G.R. Scrap Treatment Method for Rare Earth Transition Metal Alloys. U.S. Patent 5,129,945, 14 July 1992.
13. Gergoric, M.; Ekberg, C.; Foreman, M.R.J.; Steenari, B.M.; Retegan, T. Characterization and Leaching of Neodymium Magnet Waste and Solvent Extraction of the Rare-Earth Elements Using TODGA. *J. Sustain. Metall.* **2017**, *3*, 638–645. [\[CrossRef\]](#)
14. Parhi, P.K.; Sethy, T.R.; Rout, P.C.; Saranji, K. Separation and recovery of neodymium and praseodymium from permanent magnet scrap through the hydrometallurgical route. *Sep. Sci. Technol.* **2016**, *51*, 2232–2241. [\[CrossRef\]](#)
15. Önal, M.A.R.; Chenna, E.A.; Borra, R.; Blanpain, B.; Gerven, T.V.; Guo, M. Recycling of NdFeB magnets using nitration, calcination and water leaching for REE recovery. *Hydrometallurgy* **2017**, *167*, 115–123. [\[CrossRef\]](#)
16. Xie, F.; Zhang, T.A.; Dreisinger, D.; Doyle, F. A critical review on solvent extraction of rare earths from aqueous solutions. *Miner. Eng.* **2014**, *56*, 10–28. [\[CrossRef\]](#)
17. Riano, S.; Binnemans, K. Extration 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.* **2015**, *17*, 2931–2942. [\[CrossRef\]](#)
18. Shabani, M.A.; Irannajad, M.; Azadmehr, A.R. Investigation on leaching of malachite by citric acid. *Int. J. Miner. Metall. Mater.* **2012**, *19*, 782–786. [\[CrossRef\]](#)
19. Astuti, W.; Hirajima, T.H.; Sasaki, K.; Okibe, N. Comparison of effectiveness of citric acid and other acids in leaching of low-grade Indonesian saprolitic ores. *Miner. Eng.* **2016**, *85*, 1–16. [\[CrossRef\]](#)
20. Park, H.; Jung, K.; Alorro, R.D.; Yoo, K. Leaching Behavior of Copper, Zinc and Lead from Contaminated Soil with Citric Acid. *Mater. Trans.* **2013**, *54*, 1220–1223. [\[CrossRef\]](#)
21. Josso, P.; Roberts, S.; Teagle, D.A.H.; Pourret, O.; Herrington, R.; Albarran, P.L. Extraction and separation of rare earth elements from hydrothermal metalliferous sediments. *Miner. Eng.* **2018**, *118*, 106–121. [\[CrossRef\]](#)
22. Fujimoto, J.; Tanaka, K.; Watanabe, N.; Takahashi, Y. Simultaneous recovery and separation of rare earth elements in ferromanganese nodules by using *Shewanella putrefaciens*. *Hydrometallurgy* **2016**, *166*, 80–86. [\[CrossRef\]](#)
23. Astuti, W.; Hriajima, T.; Sasaki, K.; Okibe, N. Comparison of atmospheric citric acid leaching kinetics of nickel from different Indonesian saprolitic ores. *Hydrometallurgy* **2016**, *161*, 138–151. [\[CrossRef\]](#)
24. Vandenberghe, L.P.S.; Soccol, S.R.; Pandey, A.; Lebeault, J.M. Microbial production of citric acid. *Braz. Arch. Biol. Technol.* **1999**, *42*, 263–276. [\[CrossRef\]](#)
25. McDonald, R.G.; Whittington, B.I. Atmospheric acid leaching of nickel laterites review: Part I. Sulphuric acid technologies. *Hydrometallurgy* **2008**, *91*, 35–55. [\[CrossRef\]](#)
26. Brown, M.A.; Kropf, A.J.; Paulenova, A.; Gelis, A.V. Aqueous complexation of citrate with neodymium(iii) and americium(iii): A study by potentiometry, absorption spectrophotometry, microcalorimetry, and XAFS. *Dalton Trans.* **2014**, *43*, 6446–6454. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Nam, J.S.; Kim, A.R.; Kim, D.M.; Chang, T.S.; Kim, B.S.; Bae, J.W. Novel heterogeneous Rh-incorporated graphitic-carbon nitride for liquid-phase carbonylation of methanol to acetic acid. *Catal. Commun.* **2017**, *99*, 141–145. [\[CrossRef\]](#)
28. Zanonato, P.L.; Bernardo, P.; Bismondo, A.; Rao, L.; Choppin, G.R. Thermodynamic Studies of the Complexation between Neodymium and Acetate at Elevated Temperatures. *J. Solut. Chem.* **2001**, *30*, 1–18. [\[CrossRef\]](#)
29. Cotton, S. *Lanthanide and Actinide Chemistry*; John Wiley & Sons: Chichester, UK, 2006; ISBN 9780470010082.
30. Nash, K.L.; Jensen, M.P. Analytical-scale separations of the lanthanides: A review of techniques and fundamentals. *Separ. Sci. Technol.* **2001**, *36*, 1257–1282. [\[CrossRef\]](#)
31. Geist, A.; Nitsch, W.; Kim, J. On the kinetics of rare-earth extraction into D2EHPA. *Chem. Eng. Sci.* **1999**, *54*, 1903–1907. [\[CrossRef\]](#)

32. Tunsu, C.; Petranikova, M.; Gergorić, M.; Ekberg, C.; Retegan, T. Reclaiming rare earth elements from end-of-life products: A review of the perspectives for urban mining using hydrometallurgical unit operations. *Hydrometallurgy* **2015**, *156*, 239–258. [[CrossRef](#)]
33. Awais, M.; Coelho, F.; Degri, M.; Herraiz, E.; Walton, A.; Rowson, N. Hydrocyclone Separation of Hydrogen Decrepitated NdFeB. *Recycling* **2017**, *2*, 22. [[CrossRef](#)]
34. Swain, B.; Cho, S.S.; Lee, G.H.; Lee, C.G.; Uhm, S. Extraction/Separation of Cobalt by Solvent Extraction: A Review. *Korean Soc. Ind. Eng. Chem.* **2015**, *26*, 631–639.
35. Karakaplan, M.; Tural, S.; Tural, B.; Turgut, Y.; Hosgoren, H. The Solvent Extraction of Boron with Synthesized Aliphatic 1,3-Diols: Stripping and Extraction Behavior of Boron by 2,2,5-Trimethyl-1,3-hexanediol. *Solvent Extr. Ion Exch.* **2004**, *22*, 897–911. [[CrossRef](#)]
36. Gergoric, M.; Ekberg, C.; Steenari, B.M.; Retegan, T. Separation of Heavy Rare-Earth Elements from Light Rare-Earth Elements Via Solvent Extraction from a Neodymium Magnet Leachate and the Effects of Diluents. *J. Sustain. Metall.* **2017**, *3*, 601–610. [[CrossRef](#)]



© 2018 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).