Recovery of Rare Earth Elements from E-Waste using Tire Rubber-Derived Carbon Adsorbents

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Introduction

Neodymium (Nd) and Dysprosium (Dy) integrate the group of Rare Earth Elements (REE). These metals are considered Critical Raw Materials (CRM) by the European Union (EU) and the US Department of Energy, due to their economic and strategic implications, as well as the risks associated with their supply chain (European Commission, 2021). REEs play a vital role in the transition to a sustainable, low-carbon, and low-environmental impact economy, due to their unique magnetic and catalytic properties. Neodymium and dysprosium face an increasing demand due to their indispensable role in the production of high-performance permanent magnets, which further highlights the importance of sustainable strategies for their recovery (Binnemans et al., 2013).

E-waste is the fastest-growing waste stream, which demands sustainable valorization pathways for CRM recovery, reducing the EU's dependency on external sources. REE-containing permanent magnets, particularly NdFeB magnets, stand out as a promising candidate for e-waste recycling. These magnets represent a key waste flow with a high potential for recovering Nd and Dy. Despite their potential, current recycling methods face technological and economic challenges, resulting in an urgent need to develop strategies for managing this complex waste flow in a sustainable and environmentally friendly manner.

Spent tire rubber (STR) poses a significant global environmental threat, with its disposal escalating due to the rising production of new tires, particularly in developing countries. Approximately 17 million tons of STR are discarded annually, predominantly through landfilling and, to a lesser extent, energetic valorization via combustion. These disposal methods not only lead to material loss but also generate highly toxic compounds and greenhouse gas emissions. To address these challenges, enhancing STR recycling and valorization through innovative solutions and optimizing current management policies is imperative. Pyrolysis emerges as a promising avenue for STR valorization, converting waste into high-value products, including porous carbon materials with applications in diverse industries, notably as efficient adsorbents and catalyst supports (Nogueira et al., 2024).

In the pursuit of sustainable and circular approaches, this research focuses on utilizing activated carbons derived from the rubber of spent tires. The incorporation of spent tires as precursors for adsorbents not only addresses the issue of waste management but also aligns with circular economy principles. This innovative approach aims to transform a discarded resource into a valuable component for the recovery of Nd and Dy from end-of-life NdFeB magnets. Adsorption, a fundamental process in this study, serves as the key mechanism for the recovery of Nd and Dy.

Materials and Methods

The STR used in this work was provided by a company that performs cryogenic recycling of light vehicle tires. The rubber sample consisted of only the rubber fraction of the spent tires, after the removal of the metal support frame as well as of the fabric present in the tires. This precursor was named Rubber B.

Batch pyrolysis was performed in a 5 L reactor with continuous stirring. After loading the rubber, the reactor was sealed and purged with N_2 and pressurized at 0.6 MPa. A heating rate of 5 ºC.min^{-1} was applied to a maximum temperature of 405 ºC with a hold time of 30 minutes. After cooling, the solid fraction (char) was separated from the liquid fraction (pyrolysis oil) by soxhlet extraction using hexane, acetone, and water sequentially. The obtained char was denominated B405.

Activation of the char was performed in a bench-scale fluidized bed reactor under CO_2. A selected amount of the char was loaded onto the reactor which was then purged with N_2. A heating step with a rate of 5 ºC.min^{-1} was applied until 800 ºC. At this point, the N_2 flow was changed to CO_2, and the sample was activated for 8 hours. The resulting Activated Carbon (AC) was coded B405-CO2.

The textural and morphological properties of the STR char and AC were evaluated by adsorption of N_2 at 77 K, and SEM-EDS. Thermal stability was investigated by TGA. The chemical characterization comprised the following analysis: XPS, FT-IR, Proximate Analysis, Elemental Analysis, pH_{PZC}, mineral content, and XRPD. Bulk density and particle size distribution were also characterized.

End-of-life NdFeB magnets were sourced from end-of-life computer hard disk drives. The dissolution and leaching of the magnets were performed using *aqua regia* (nitric acid/hydrochloric acid = 1/3) (nitric acid

65% and hydrochloric acid 37%) or only nitric acid under the following conditions: Solid/Liquid ratio = 6, contact time = 6 hours, and temperature = 60 °C.

Dynamic adsorption studies were carried out with a sample of B405-CO2 using a fixed-bed column device, with 100 mg of adsorbent, 1.5 $mL.min^{-1}$ flow rate, initial concentrations of 1.25 to 10 $mg.L^{-1}$ Nd and Dy, and running time of 180 minutes. Firstly, pure synthetic solutions of either Nd^{3+} or Dy^{3+} were used, then binary solutions containing both metals were tested, and lastly, the magnet leachates were used. The obtained experimental data were fitted to the Thomas model. A commercially available activated carbon (CAC) was used for benchmarking purposes.

Results and Discussion

By analyzing the data from the single-component dynamic adsorption studies, it was possible to conclude that the AC B405-CO2 had similar behavior for the adsorption of both metals. The maximum uptake capacity was 3.48 $mg.g^{-1}$ for Nd^{3+} and 3.69 $mg.g^{-1}$ for Dy^{3+}, with saturation times, t_s (C_t/C_0 = 0.95), of 180 and 150 minutes, respectively. When compared with CAC, this represents an improvement of 130% in saturation times and 371% in maximum uptake capacities, in favor of B405-CO2.

In the multi-component adsorption studies (where both metals were in solution), it was possible to see that both B405-CO2 and CAC were able to recover both metals from the solution. Mirroring the behaviors in single component studies, B405-CO2 had better performances, with a maximum uptake capacity of 1.57 $mg.g^{-1}$ and saturation time of 142 minutes, which represent a twofold increase over the CAC.

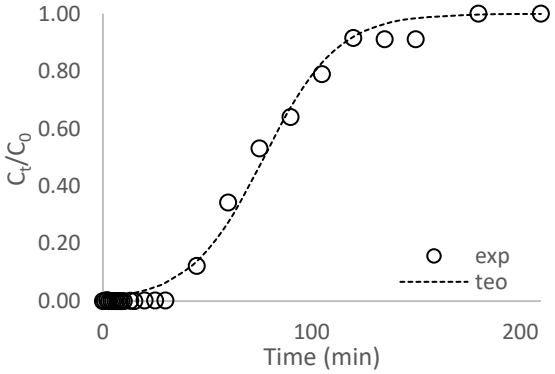

Figure 1 - Breakthrough curve for Nd^{3+} using real magnet leachates. Dots – experimental data; line- theoretic data

Looking at the data from the magnet dissolution, both acids (*aqua regia* and nitric acid alone) were able to solubilize the totality of REEs present on the magnets, but nitric acid did not extract the total solubility of the iron present. The nitric acid leachates were then used in the adsorption study using the adsorbent B405-CO2. Beforehand, the pH of the solution was raised to 5.5 using NaOH 6M to precipitate all the iron out of the solution, The precipitate was then filtered, and the solution was diluted in water until the initial concentration of REEs was desired (Nd^{3+} = 1.25 $mg.L^{-1}$) for the adsorption assays. Analyzing the breakthrough curve for Nd^{3+} in the real magnet leachates (Figure 1), it was possible to see that B405-CO2 was able to recover the REE from solution and maintained the performances displayed in the synthetic solution assays, with maximum uptake capacities of 1.36 $mg.g^{-1}$ and saturation times of 162 minutes.

Conclusions

This research pioneers a sustainable approach to recover Nd and Dy from end-of-life NdFeB magnets, addressing critical raw material challenges in the e-waste landscape. Using an activated carbon produced from STR pyrolysis, the study aligns with circular economy principles. The activated carbon, B405-CO2, exhibited remarkable adsorption capabilities, outperforming commercial alternatives in both single-component and multi-component studies. The breakthrough performance in real magnet leachates further underscores the efficacy of B405-CO2 in an environmentally friendly REE recovery. This innovative method not only contributes to sustainable waste management, but also exemplifies the transformative potential of circular economy practices in resource recovery.

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