Recovery of Rare Earth Elements (Nd^{3+} and Dy^{3+}) by Using Waste-Derived Carbon Adsorbents

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The growth of advanced technological applications in the day-life is related to the increasing demand for Rare Earth Elements (REEs). The scarcity and supply risk of REEs from primary resources have stimulated the development of pathways to treat and valorise secondary resources, such as end-of-life products and wastes of electric and electronic equipment (WEEEs) which are often rich in REEs (Rademaker, Kleijn and Yang, 2013).

WEEEs are a rising problem in technological societies. The current recycling paths are characterised by technological difficulties and economical constraints. Nevertheless, they are a source of REEs, which are critical raw materials for the technological industry in Europe and worldwide (European Commission, 2017). REEs show excellent physical and chemical properties, playing an important role on todays' high technologies.

As a result, the recovery and recycling of REEs is significant and requires the appropriate attention. Although several methods have been proposed, they are generally characterized by high economic and environmental restrictions. Amongst the available processes, adsorption has recently gained wider consideration for this purpose due to its simplicity, high efficiency, and low cost.

Although adsorption processes can be considered a sustainable and "green" process, the type and nature of the used adsorbent play an important role in the economic and environmental feasibility of this technology (Anastopoulos, Bhatnagar and Lima, 2016).

This work will report the adsorption of Nd^{3+} and Dy^{3+} onto spent tire waste-derived chars, in order to maintain a sustainable approach to tackle the problem at hand, while promoting circular economy.

The precursors used in this work were two types of spent tire rubber: a) sample A, which was obtained via cryogenic recycling of rubber from passenger car tires (particle size: 0.18 - 0.60 mm); b) sample B, attained from mechanically recycled rubber from a mixture of passenger car and heavy truck tires (particle size: 0.6 - 0.8 mm). Two types of pyrolysis processes were applied: a) batch pyrolysis at 405 ºC for 30 minutes, in nitrogen (N_2) atmosphere; b) semi-continuous pyrolysis in a fixed-bed reactor at 900 ºC for 30 minutes and 0.1 $L.min^{-1}$ N_2 flow. The chars resulting from the former pyrolytic process were extracted from the liquid products with hexane and acetone, and then washed with water. These chars were coded as A405 and B405. The chars produced in the latter pyrolytic process were not extracted and were coded as A900 and B900.

The chars were characterized for elemental analysis and pH_{PZC} (Table 1), N_2 adsorption-desorption isotherms at 77 K (Table 2), thermogravimetric analysis (TGA) (not shown), mineral content (not shown), x-ray powder diffraction (XRPD) (not shown), Fourier-transform infrared spectroscopy (FTIR) (not shown) and particle size distribution (not shown).

Table 1. Elemental analysis (as-received basis) and pH_{PZC} .

Sample	C (w/w %)	H (w/w %)	N (w/w %)	S (w/w %)	Ashes (w/w %)	pH_{PZC}
ST rubber A	79.20	7.07	0.40	1.64	9.16	n.d.
ST Rubber B	83.39	7.60	0.40	2.04	3.92	n.d.
Char A405	71.33	0.71	0.28	2.51	36.20	7.4
Char A900	80.05	0.13	0.13	2.97	42.00	under analysis
Char B405	79.06	0.86	0.33	3.94	31.40	6.7
Char B900	75.59	0.13	0.15	3.96	34.60	under analysis

n.d. – not determined; ST – Spent Tire

Comparing the chars obtained from both types of pyrolysis processes, it is possible to observe that the samples resulting from semi-continuous pyrolysis and higher temperature exhibit lower hydrogen and nitrogen contents, therefore lower organic compounds leftover from the rubber of the precursors. Conversely, these samples present higher ash and sulphur contents when compared to their counterparts produced by batch pyrolysis and lower temperature.

Table 2. Textural parameters of carbon samples obtained from N_2 adsorption-desorption isotherms.

Char	A_{BET} ($m^2.g^{-1}$)	V_{total} ($cm^3.g^{-1}$)	V_{micro} ($cm^3.g^{-1}$)	V_{meso} ($cm^3.g^{-1}$)
A405	73	0.133	0.008	0.125
A900	75	0.195	0.004	0.191
B405	90	0.125	0.016	0.109
B900	73	0.191	0.003	0.188

All chars presented low total pore volume as well as surface area, which is characteristic of this type of adsorbent (Antoniou, Stavropoulos and Zabaniotou, 2014). Nevertheless, the chars A900 and B900 (obtained from the semi-continuous pyrolysis) presented higher total pore volume and a higher fraction of mesoporous volume when compared to their batch pyrolysis counterparts.

Afterwards, the chars were applied as adsorbent agents of Nd^{3+} and Dy^{3+} from aqueous solutions. Batch adsorption assays were performed with a S/L ratio of 1 $g.L^{-1}$ and initial adsorbate concentration of 100 $mg.L^{-1}$. After 48 h under continuous stirring, the solutions were filtered and the final REEs' concentration determined by ICP-AES. Adsorption kinetics were studied up to 48 h and adsorption isotherms were obtained for a concentration range of 10-100 $mg.L^{-1}$.

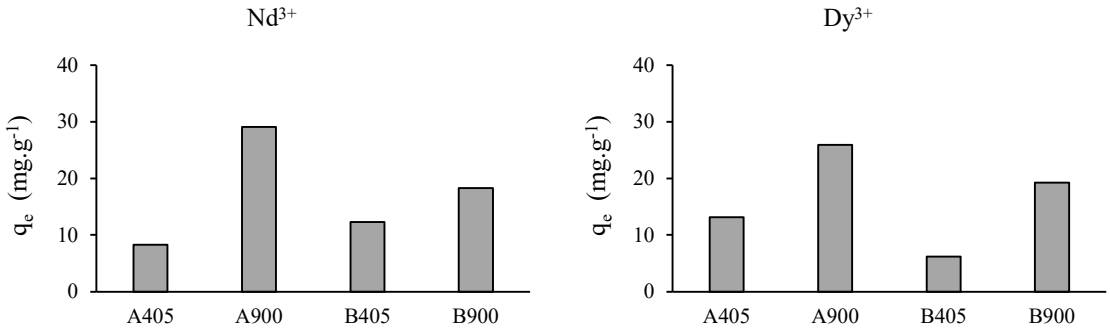

Figure 1. Chars' uptake capacity of Nd^{3+} (left-hand side) and Dy^{3+} (right-hand side)

The highest uptake capacity for both Nd^{3+} and Dy^{3+} was obtained by the sample A900 with values of 29.1 and 25.9 $mg.g^{-1}$, respectively. It was also possible to observe that the chars obtained by semi-continuous pyrolysis revealed higher uptake capacities for both REEs when compared to the batch pyrolysis chars, possibly due to the higher removal of volatile matter at higher pyrolysis temperatures providing higher porosity development.

These results make possible to conclude that using waste derived carbon-based adsorbents produced from used tires to recover and recycle REEs show promising outcomes. Further research is needed to improve the properties of these chars, aiming to improve the adsorption and recovery of REEs.

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