# FUNCTIONALISED ACTIVATED CARBON FOR THE ADSORPTION OF RARE-EARTH ELEMENTS FROM AQUEOUS SOLUTIONS

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## Abstract

The Flemish Strategic Initiative Materials (SIM) "MaRes" programme is about recycling of "Materials from solid and liquid industrial process Residues", and aims at creating and demonstrating an operational, flexible toolbox of different concentration, extraction and valorisation technologies. Within the "Get-A-Met" project, part of the SIM MaRes programme, a 'Groundbreaking Extraction Technology for critical Metals and Metalloids from industrial waste waters' is developed through electrometallurgical approach. The core technology is capacitive an electroprecipitation, which involves the development of a gas-diffusion electrode material from activated carbon. This is combined with advanced speciation knowledge, pre-treatment with membrane electrolysis and surface-functionalised carbon materials, to achieve high selectivity and performance. In this paper, we discuss the functionalisation of AC with the chelating agent ethylenediamine tetraacetic acid for the selective adsorption of rare-earth elements from aqueous solutions.

### Introduction

Waste water is generated by a variety of industrial activities. Contamination of waste water with rare earths creates a serious threat to environment and human health because of their toxicity, non-biodegradability and accumulation in living organisms.<sup>1</sup> Moreover, since rare earths (and other critical metals) are required for a wide range of high-technological applications, research is becoming more and more focused on the selective recovery of these elements. This might allow turning (landfill disposal) costs into revenues. Among many techniques attempted to recover valuable metals from dilute waste waters, adsorption is generally considered the preferred technology, due to its combined simplicity, effectiveness and low cost.<sup>2</sup> Like many adsorbent materials, activated carbon (AC) is unlimitedly available, environmentally friendly and cheap.<sup>3</sup> AC has also interesting properties, such as a high specific surface area, a well-developed porous structure and tuneable surface chemistry.<sup>4</sup> In addition, AC is characterised by a high chemical resistance and conductive behaviour, so it can be used in a wide range of chemical environments, temperatures and pressures, in

different kinds of (electrochemical) processes.<sup>5</sup> It has been reported that surface functionalisation with ethylenediamine tetraacetic acid (EDTA) results in materials with a high selectivity for and amongst rare-earth elements (REEs) by the formation of stable coordination complexes.<sup>6</sup>

In this work, AC was oxidised to incorporate oxygen groups over the carbon matrix. These allowed subsequent functionalisation with the chelating agent EDTA on the AC surface. The obtained materials were extensively characterised by FTIR and Raman spectroscopy, TGA, N<sub>2</sub> physisorption, SEM and the Boehm titration method, the latter being used to determine the amount and type of oxygen functional groups present in carbon samples. Then, the adsorption of REEs from aqueous solutions with EDTA-functionalised AC was examined. Kinetic and thermodynamic adsorption data were fitted with common adsorption models. EDTA-AC appeared to have a high selectivity for the rare earths, so this adsorbent material could be used as well to separate these valuable metals from other metals (present, for instance, in electronic waste). Finally, was shown that the functionalised AC sample was well reusable. Hereby, it was demonstrated that EDTA-functionalised AC is highly suitable for the selective recovery of REEs from waste water.

### Experimental

Oxidation of AC powder (Norit SX1G, 5 g) was done with concentrated  $HNO_3$  (15 M, 50 mL). The reaction mixture was refluxed at 85°C for 6 h. Note that the combination of fine AC powder (with a high specific surface area) and strong acids or oxidising agents can be explosive. The residue was filtered, washed several times with deionised water until neutral pH and dried under vacuum at 50°C. The optimised immobilisation of N-[(3-trimethoxysilyl)propyl]ethylenediamine triacetic acid (TMS-EDTA) over oxidised AC was performed in a solvent mixture of isopropanol and water.<sup>7</sup> AC (1 g) was added to an isopropanol–water mixture (85:15 volume ratio) and the pH was adjusted to a value of 4 to 5 with HCl. The mixture was ultrasonicated for 2 h to get a uniform dispersion. Then, the beaker was set in stirring mode and TMS-EDTA (5 mL) was added dropwise to the solution. Acetic acid (1 mL) was added to the solution to increase the amount of condensation reactions between the -OH groups of AC and the hydrolysed silanol groups in TMS-EDTA. The reaction mixture was stirred for 24 h at room temperature. After functionalisation, the particles were filtrated and washed with water and acetone. Finally, the EDTA-functionalised AC particles (EDTA-AC) were dried under vacuum at 50°C. The overall synthesis procedure of EDTA-AC is depicted in Figure 1.



Figure 1: Schematic diagram for the synthesis of EDTA-functionalised AC

In adsorption experiments, functionalised particles (20 mg) were added to a rareearth solution (10 mL). Unless stated otherwise, a 1 mM Nd(III) solution was used. The adsorption experiments were maintained for 4 h by shaking the solutions at 250 rpm and 20°C. After adsorption, the solid AC particles were separated from the liquid by centrifugation. Aqueous metal concentrations were analysed by TXRF. The equilibrium adsorption capacity ( $q_e$ ) was then calculated by Equation 1:

$$q_e = \frac{V(C_0 - C_e)}{M} \tag{1}$$

where  $C_o$  and  $C_e$  are the initial and equilibrium concentration (mg L<sup>-1</sup>) of the metal ion in solution, V the aqueous volume (L) and M the mass of the adsorbent (g).

#### **Results and discussion**

#### Synthesis and characterisation

Oxygen surface groups on AC were identified and quantified by the Boehm titration method. For the subsequent functionalisation step, especially the amount of –OH (phenolic) groups was targeted, being 117, 252 and 981  $\mu$ mol g<sup>-1</sup> for HNO<sub>3</sub> concentrations of 5, 10 and 15 M, respectively. Since the highest number of phenolic groups was created through oxidation with 15 M HNO<sub>3</sub>, this oxidation treatment was used for the preparation of AC particles for further functionalisation with EDTA.

FTIR measurements were performed to identify the surface functional groups in the synthesised materials. Immobilisation of EDTA was evident from the peaks at 1350 and 1600 cm<sup>-1</sup>, which can be attributed to, respectively, symmetrical and asymmetrical stretching modes of carboxylate groups. The intense peak around 1100 cm<sup>-1</sup> originated from the stretching vibration of Si-O bonds.

Measurement of the particle size distribution elucidated an increase in the particle size when going from oxidised AC to functionalised AC, up to a maximum value of 18.50  $\mu$ m for the 90% smallest particles. This can be explained by the immobilisation

of EDTA-groups on the AC particles. SEM analysis of EDTA-AC revealed particles of varying size and no distinct morphology (Figure 2). The functionalised particles showed some aggregation and coating of lighter particles over the carbon particles. Evidently, these originate from the immobilisation of the EDTA-ligand on the AC support through silica linkers, as originating from TMS-EDTA. Textural properties of AC materials were thoroughly examined by N<sub>2</sub> physisorption measurements. EDTA-functionalised AC had a specific surface area of 741 m<sup>2</sup> g<sup>-1</sup>, a total pore volume of 0.41 cm<sup>3</sup> g<sup>-1</sup> and an average pore diameter of 1.54 nm.



Figure 2: SEM-image of Norit AC (a) and EDTA-AC (b)

From CHN analysis, the incorporation of oxygen and nitrogen atoms in the respective materials became clear. From the mass percentages given in Table 1, the amount of functionalisation could be calculated to be 264 mg g<sup>-1</sup> of TMS-EDTA per gram of AC. Together with the data from TGA measurements, these results showed that the oxidation and the functionalisation procedure proceeded successfully.

Adsorbent	C (wt%)	H (wt%)	N (wt%)	O (wt%)
Norit AC	91.70	0.87	0.57	6.86
Oxidised AC	74.59	1.18	0.52	23.71
EDTA-AC	65.64	2.08	1.60	30.68

Table 1: Elemental analysis of the adsorbent materials

#### Adsorption performance

Adsorption isotherms were constructed for AC, oxidised AC and EDTA-AC by varying the Nd(III) concentration (10 to 300 mg  $L^{-1}$ ) and fitting with the Langmuir and Freundlich adsorption models. The maximum adsorption capacity of EDTA-AC was determined to be 71.42 mg g<sup>-1</sup>, whereas a value of only 19.08 mg g<sup>-1</sup> was derived for the original AC. From these results, we can conclude that the immobilisation of EDTA over AC significantly enhanced the adsorption capacity for Nd(III). Kinetic adsorption data were modelled with the pseudo-second order rate equation. Nd(III) was

completely removed from the aqueous solution within 15 min of contact time. The rapid adsorption may be attributed to the textural properties of EDTA-AC. The amount of Nd(III) adsorption increased sigmoidally with an increasing pH, until a maximal plateau value was obtained around pH 5. This can be explained by (de)protonation of the functional groups immobilised on the AC surface. In addition, increasing temperatures resulted in enhanced Nd(III) adsorption. Thermodynamic data were modelled with the Van 't Hoff equation. Since reusability plays a vital role in bulk-scale production processes, regeneration of the adsorbent was tested over five consecutive adsorption-desorption cycles. The adsorption efficiency remained 90% after the fifth regeneration cycle, revealing the potential of EDTA-AC for industrial applications.

Affinity for and selectivity between REEs was investigated for EDTA-functionalised AC (Figure 3). High adsorption values were observed for all lanthanide ions. Moreover, adsorption increased gradually with the atomic mass of the respective lanthanide ions, probably a consequence of the *"lanthanide contraction"*.<sup>8</sup> These differences in selectivity between distinct rare-earth ions may eventually be exploited to separate them from each other. Adsorption tests were as well performed from binary mixtures of several metal-ion pairs: La(III)/Ni(II), Sm(III)/Co(II), Eu(III)/Y(III) and Dy(III)/Nd(III). These were chosen because of their occurrence in End-of-Life waste sources, like batteries, magnets and lamp phosphors.<sup>9</sup> The adsorption of La(III), Sm(III), Eu(III), Sm(III), From the considerable differences in uptake percentage (up to a difference of 70 to 17% for the Sm(III)/Co(II) pair), the separation capability of this low-cost EDTA-AC adsorbent material becomes evident.



**Figure 3:** EDTA-AC equilibrium adsorption capacity from single-element lanthanide solutions (a) and equimolar, binary metal-pair mixtures (b)

## Conclusions

By immobilisation of the chelating agent EDTA on AC, an adsorbent material with an excellent capability of recovering REEs from aqueous solutions was obtained. Characterisation of the functionalised AC particles elucidated a high specific surface area (740 m<sup>2</sup> g<sup>-1</sup>) and micropores with a volume of 0.41 cm<sup>3</sup> g<sup>-1</sup>, enabling a high accessibility of the functional groups and avoiding any kind of diffusion problem. The amount of functionalisation was determined to be 264 mg g<sup>-1</sup>. Adsorption was fast: equilibrium was reached within 15 min. The adsorption capacity of EDTA-AC was found to be 71.42 mg g<sup>-1</sup>, which was almost 4 times higher than that of pure AC. A high selectivity was achieved towards the (heavier) REEs. Separations were studied for the binary mixtures La(III)/Ni(II), Sm(III)/Co(II), Eu(III)/Y(III) and Dy(III)/Nd(III), all commonly present in electronic waste. The regeneration efficiency remained higher than 90% after five consecutive adsorption-desorption cycles. Because the EDTA-functionalised AC is cheap, easily synthesised, chemically stable and highly efficient, application can be found for the recovery of REEs from industrial waste water streams.

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