

# SEPARATION OF SCANDIUM FROM LEACHATES OF GREEK BAUXITE RESIDUE BY ADSORPTION WITH FUNCTIONALISED CHITOSAN-SILICA HYBRID MATERIALS

Joris ROOSEN<sup>1,3</sup>, Stijn VAN ROOSENDAEL<sup>1</sup>, Chenna RAO BORRA<sup>2</sup>, Tom VAN GERVEN<sup>2</sup>, Steven MULLENS<sup>3</sup>, Koen BINNEMANS<sup>1</sup>

<sup>1</sup> KU Leuven, Department of Chemistry, B-3001 Heverlee, Belgium

<sup>2</sup> KU Leuven, Department of Chemical Engineering, B-3001 Heverlee, Belgium

<sup>3</sup> VITO, Sustainable Materials Management, B-2400 Mol (Belgium)

*Joris.Roosen@chem.kuleuven.be*

## Abstract

*Chitosan is one of the most interesting biosorbents, due to its high adsorption capacity, selectivity for certain metal ions and easy functionalisation. By incorporating chitosan in an inorganic silica matrix, a more rigid and porous hybrid material results, thus mitigating the shortcomings of pure chitosan. In the separation of valuable scandium from bauxite residue the highest challenge arises from the similar chemical behaviour between scandium(III) and iron(III). This hampers high selectivity for scandium, especially because iron, as one of the major elements in bauxite residue, is present in much higher concentrations than scandium. After an acidic, pre-selective leaching step for the dissolution of scandium, adsorption by DTPA- or EGTA-functionalised chitosan was found to be very useful for the effective separation of scandium from the other elements dissolved in the leachate.*

## Introduction

Recovery of valuable metals from industrial effluents would be beneficial for both economic and sustainable reasons.<sup>1</sup> Especially the winning of rare-earth elements from secondary resources has gained interest as an additional route to their primary mining, since they become indispensable in lots of modern high-tech and green applications.<sup>2-4</sup> Bauxite residue (also called red mud) is the waste product of the Bayer process, which is used for the production of alumina.<sup>5</sup> Bauxite residue is stockpiled in huge amounts, but it is harmful, largely due to its high pH (around 12).<sup>5</sup> With a production rate of 120 millions of tonnes a year, the valorisation of bauxite residue imposes itself. Indeed, besides its major components (iron oxides, quartz, sodium aluminosilicates, calcium carbonate/aluminate and titanium dioxide), bauxite residue also contains valuable minor elements, such as the rare earths.<sup>6</sup> Compared to global concentration levels, bauxite residue is especially rich in scandium. After leaching, ion exchange onto functionalised adsorbent materials is believed by the

authors to be the best method to separate scandium from the other elements. Chitosan is a linear polysaccharide which is mainly obtained by alkaline deacetylation of chitin, a naturally abundant organic material that can be found in the exo-skeleton of crustacea (such as lobsters and shrimps) and insects.<sup>1,7,8</sup> The low cost, the availability, the biocompatibility, the biodegradability, the non-toxicity, and its solubility at acidic pH values (in contrast to chitin) make chitosan an interesting material.<sup>7,8</sup> Chitosan shows excellent adsorption characteristics because of its high hydrophilicity (hydroxyl groups), high activity for the chelation of metal ions (primary amino groups), and a flexible structure which enables to adopt the suitable configuration for complexation with metal ions.<sup>9</sup> Also, the large number of highly reactive amino and hydroxyl groups allows to easily adjust the selectivity for specifically targeted metal ions by immobilisation of the proper functional group.<sup>10,11</sup> Since pure chitosan suffers from poor mechanical properties and low porosity, it was decided to hybridise it with silica. Organic-silica hybrid materials combine the functional properties of the polymer with the robustness of silica.<sup>12,13</sup> Thereby, these hybrid chitosan-silica sorbents become useful as functional resin materials in chromatography separation columns on an industrial scale.<sup>12,14,15</sup>

In this work, hybrid chitosan-silica hybrid materials were synthesised and functionalised with both diethylenetriamine pentaacetic acid (DTPA) and ethyleneglycol tetraacetic acid (EGTA). Selectivity for the uptake of scandium(III) from nitrate leachates was investigated in binary, equimolar solutions of scandium(III) and iron(III) with respect to the functional group immobilised on the polymer matrix. Optimisation on real leachates of Greek bauxite residue eventually led to the effective separation of scandium from bauxite residue in a column chromatography set-up.

## Experimental

A chitosan-silica hybrid material was made according to the *in-situ* Stöber based method as described previously.<sup>14</sup> In this work, also the consecutive functionalisation with DTPA from its anhydride was described. The immobilisation of EGTA proceeded differently, according to the method described by Repo et al.<sup>16</sup> In this procedure, EGTA and chitosan-silica were combined with 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) at 40 °C. EDC is a water soluble cross-linking agent that activates carboxyl groups for the coupling of primary amines.<sup>17</sup> The leaching of bauxite residue was carried out by constant agitation for 24 h at 160 rpm and 25 °C. The leaching experiments were carried out with a 0.20 N HNO<sub>3</sub> solution with a liquid to solid ratio of 50:1.<sup>6</sup>

Selectivity experiments were conducted by adsorption in batch mode, in aliquots of a properly diluted stock solution. Stock solutions were kept at pH 1.0. To adjust the experimental pH, 1.0 M HCl or 0.1 M NaOH was added to decrease or increase the pH, respectively. Functionalised particles were then added to the vials. Solutions were stirred at room temperature with a magnetic stirring bar at 300 rpm for 4 h. Next, the particles were separated from the aqueous solution by filtration, making use of a regenerated cellulose syringe filter with a pore size of 0.45  $\mu\text{m}$ . The remaining metal ion concentration of the aqueous solution was measured by TXRF (Bruker S2 Picofox). The amount of metal ions adsorbed onto the chitosan-silica particles was then determined using the following formula:

$$q_e = \frac{(c_i - c_e) V}{m_{ads}} \quad (1)$$

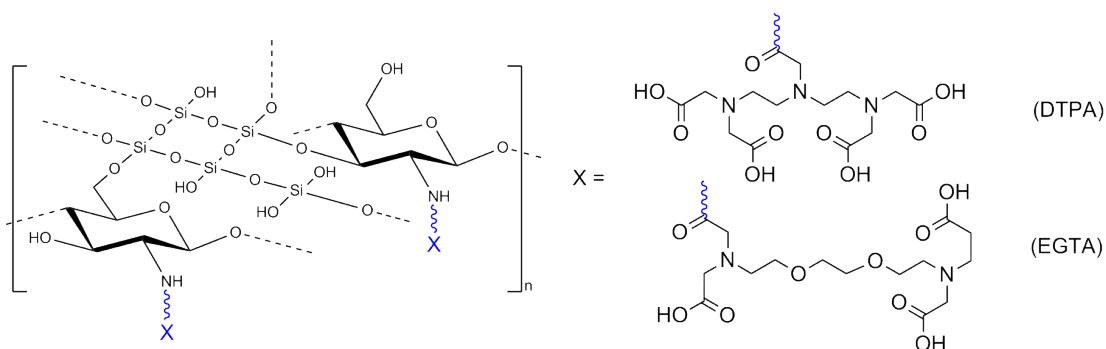
In this formula,  $q_e$  is the amount of adsorbed metal ions at equilibrium ( $\text{mmol g}^{-1}$  adsorbent),  $c_i$  is the initial metal ion concentration in aqueous solution ( $\text{mmol l}^{-1}$ ),  $c_e$  is the equilibrium metal ion concentration in aqueous solution ( $\text{mmol l}^{-1}$ ),  $V$  is the volume of the solution (0.010 l) and  $m_{ads}$  is the mass of the adsorbent (0.025 g).

A column experiment was performed with a leachate of Greek bauxite residue. The column (bed volume = 8.3 ml) was packed with EGTA-chitosan-silica and connected to a chromatography pump to control the pressure (max. 10 bar) and the eluent flow (37 ml/h). The experiment was preceded by thorough washing of the column with demi-water, followed by conditioning of the column with a solution of  $\text{HNO}_3$ , set at pH 1.25 (same as leachate). After addition of the sample to the column, a decreasing pH gradient was applied. The distinct fractions (5 ml) were monitored by *ex situ* analysis of the fractions by ICP-MS (Thermo Electron X Series) to determine the respective metal concentrations.

## Results and Discussion

### Synthesis

DTPA-chitosan-silica and EGTA-chitosan-silica were successfully synthesised. Immobilisation of the functional group proceeded by an amide reaction with the free available amino groups on the chitosan moieties of the hybrid particles. The resulting structure is shown in Figure 1. The sorbents appeared as white powders and are characterised by a 1:4 chitosan-silica ratio.

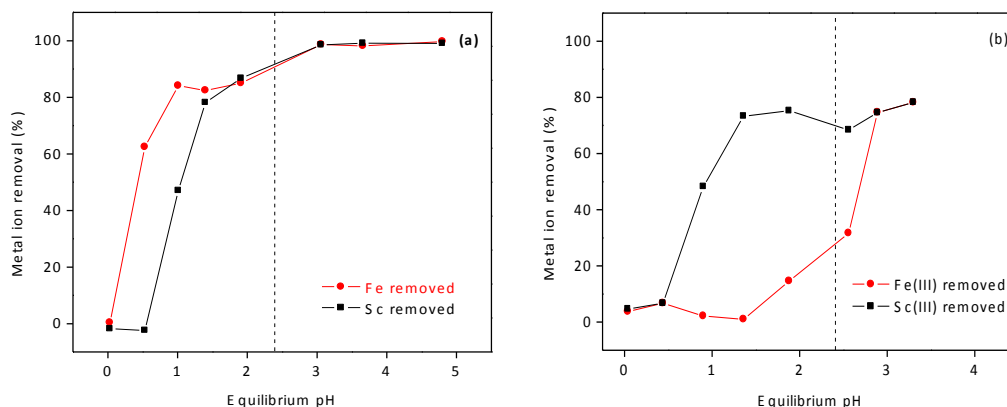


**Figure 1:** Chemical structure of chitosan-silica, functionalised with DTPA or EGTA

### Selectivity experiment

The main challenge for the isolation of pure scandium from leachates of bauxite residue is to obtain selectivity for Sc(III) compared to Fe(III). Both elements behave chemically very similarly and it is therefore difficult to separate them. Moreover, the concentration of iron in the leachates is usually about 100 times higher than that of scandium. One could think of pH variation as a way to separate iron and scandium since hydrolysis occurs at lower pH values for Fe(III) in comparison with Sc(III).<sup>18</sup> However, co-precipitation of scandium was observed in an equimolar ( $c_{\text{aq}} = 0.50 \text{ mM}$ ) binary solution of Fe(III) and Sc(III) at pH values higher than 2.4. In solutions with much higher concentrations of iron compared to scandium, this method is therefore not considered appropriate. Also the addition of reducing agents (like zinc powder or sodium sulphite), or the variation of the counter anion (like sulphate or chloride), was investigated but none of them was proven to be appropriate.

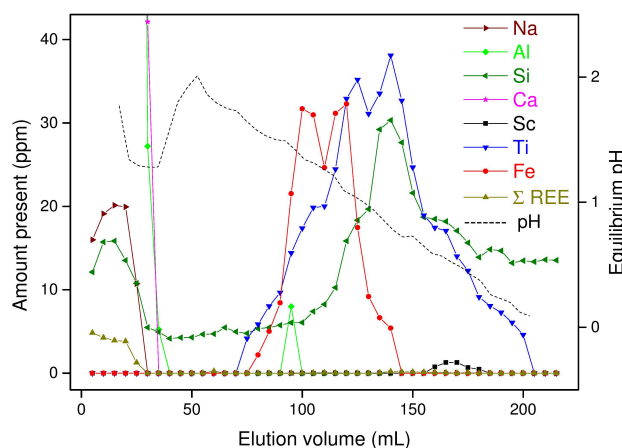
Variation of the functional group immobilised on the chitosan-silica particles was a more successful strategy. Since DTPA has been proven to be a very efficient chelating molecule for rare earths, it was tried first to immobilise this functional group to obtain selectivity for scandium.<sup>10</sup> However, as can be seen in Figure 2 (a), the affinity of DTPA-functionalised particles was higher for Fe(III) compared to Sc(III) in a binary, equimolar solution of both elements; a consequence of the corresponding stability constants between DTPA and Fe(III) or Sc(III), respectively. On the contrary, selectivity could be obtained for scandium in the presence of EGTA-chitosan-silica, as can be seen in Figure 2(b) This arises from the stability constant between EGTA and Sc(III) ( $\log K = 25.40$ ), which is significantly higher than that between EGTA and Fe(III) ( $\log K = 20.50$ ).<sup>19</sup> At pH 1.50, no Fe(III) is adsorbed, yet 80 % of the Sc(III) ions is adsorbed from the aqueous solution. This remarkably higher affinity for scandium can be exploited in a column chromatography set-up to separate scandium from the other components present in a leachate of bauxite residue.



**Figure 2:** Metal ion removal from a binary, equimolar solution of Fe(III) and Sc(III) in the presence of DTPA-chitosan-silica (a) or EGTA-chitosan-silica (b). The vertical dashed line indicates the pH at which precipitation of Fe(III) occurs because of hydrolysis. On the left side removal mainly occurs by adsorption, on the right side removal is also a consequence of precipitation. Experimental:  $m_{\text{ads}} = 25.0$  mg;  $V = 10$  ml;  $c_i = 0.50$  mM; adsorption time = 4 h

### Column separation experiment

The lower the affinity of a certain metal ion for a functionalised resin, the slower the migration through the chromatography column will be. A bauxite residue leachate sample was added on top of a column filled with EGTA-chitosan-silica. Elution with diluted  $\text{HNO}_3$  solutions then enabled to collect distinct fractions of metal ions in the order of affinity for the resin material. A decreasing pH gradient was applied (from pH 2.0 to pH 0.0), in order to induce consecutive desorption of the distinct complexed metal ions. The resulting chromatogram (metal ion concentration as a function of elution volume) is presented in Figure 3. Given the specifically high affinity for Sc(III), it is observed that the peak of Sc(III) is located at the highest elution volume, corresponding to an elution pH of 0.50, at which most other elements have eluted already. It has to be noted that the scandium containing fractions still contain contamination of titanium and silicon. However, the vast majorities of the corresponding ions have eluted earlier, as elution started at a pH value higher than pH 0.50. This indicates that even better separations could be obtained with a slower decreasing pH, a lower flow rate, a longer column or by considering other types of eluents, such as thiourea, which can serve as a source of sulphide with a preference for soft metal ions. Moreover, slightly contaminated scandium fractions can always be purified by selective precipitation of scandium with oxalic acid.<sup>20</sup> The formed scandium-oxalate precipitate can then immediately be converted to pure scandium oxide by heating up the sample to 1000 °C.



**Figure 3:** Chromatogram of scandium separation from a bauxite residue leachate by ion-exchange column chromatography with EGTA-chitosan-silica as resin material

## Conclusions

Functionalisation of chitosan-silica particles with EGTA groups resulted in a hybrid material with a remarkably high adsorption affinity for scandium, higher than that of a similar hybrid material, functionalised with DTPA groups. The affinity for valuable scandium was exploited to separate it from the other components (mainly iron) in a leachate of Greek bauxite residue by the principle of ion-exchange column chromatography.

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