BAUXITE RESIDUE VALORISATION AND BEST PRACTICES CONFERENCE
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Recovery of scandium from leachates of Greek bauxite residue by adsorption on functionalized chitosan-silica hybrid materials

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Use of **biomaterials** for selective adsorption

* Chitosan from seafood waste
* Alginate from brown algae

**Valorization** of **waste** streams by recovery of **critical metals**

* Rare-earth elements
* Gallium and indium
• Production rate of bauxite residue = 120 million tons per year, with currently no large-scale industrial applications → large amounts have been stockpiled already

• “The” solution to the red mud problem should consist of a combination of applications in different fields (iron & steel, building & construction, REE, …)

• Inclusion of critical metal recovery in the flow sheet of alumina refineries could help
  1) to guarantee a stable supply of these critical metals
  2) to meet the high processing/disposal costs of bauxite residue

• 90% of the economical value of bauxite residue arises from the presence of scandium
  o Price of Sc₂O₃ (99.99%) > 5000 US$/kg (2013)
  o Upcoming market because of promising applications (Al-Sc alloys, SOFC’s, …)

• Promising trials already showed that ion-exchange adsorption is the most suitable technique to recover small amounts of valuable elements from high amounts of diluted waste streams
**Introduction**

1. **Project outline**
2. **Valorization of bauxite residue**
3. **APPROACH**

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**1. Biosorbent hybridization with silica**

- Hybridization of chitosan and silica results in a superior material with combined benefits: high adsorption capacity, porosity, stability and chemical (acid) resistance
- The material becomes industrially applicable in chromatography set-ups

**2. Immobilization of proper functional groups**

- Sorbent selectivity can be improved by easy functionalization on chitosan NH$_2$ groups
- Affinity of a certain organic group for specific metal ions can be predicted by considering the corresponding stability constants between free ligand and metal ion:

<table>
<thead>
<tr>
<th>log K values</th>
<th>Sc(III)</th>
<th>Fe(III)</th>
<th>Nd(III)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IDA</td>
<td>9.9</td>
<td>11.1</td>
<td>6.5</td>
</tr>
<tr>
<td>NTA</td>
<td>12.70</td>
<td>15.87</td>
<td>11.26</td>
</tr>
<tr>
<td>DTPA</td>
<td>26.3</td>
<td>27.3</td>
<td>21.6</td>
</tr>
<tr>
<td>EGTA</td>
<td><strong>25.4</strong></td>
<td><strong>20.5</strong></td>
<td><strong>16.3</strong></td>
</tr>
</tbody>
</table>
1. **Hybridization** of chitosan with silica by sol-gel chemistry

![Chemical structure of hybridized chitosan and silica](image)

2. **Functionalization** by immobilization of organic ligands (via formation of a stable amide bond)

![Chemical structures of functionalized materials](image)
• Greek bauxite residue (AoG)
• Leaching was done with a 0.20 M HNO₃ solution (L:S ratio = 50:1)
  ➢ constant agitation for 24 h at 160 rpm and 25 °C
• Leachates were filtrated to remove solid particles
• **Composition of the leachates:**

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>106 ppm</td>
</tr>
<tr>
<td>Al</td>
<td>670 ppm</td>
</tr>
<tr>
<td>Na</td>
<td>1104 ppm</td>
</tr>
<tr>
<td>Ca</td>
<td>939 ppm</td>
</tr>
<tr>
<td>Si</td>
<td>558 ppm</td>
</tr>
<tr>
<td>Ti</td>
<td>106 ppm</td>
</tr>
<tr>
<td>Sc</td>
<td>2.1 ppm</td>
</tr>
<tr>
<td>Y</td>
<td>0.4 ppm</td>
</tr>
<tr>
<td>La</td>
<td>0.6 ppm</td>
</tr>
<tr>
<td>Nd</td>
<td>0.8 ppm</td>
</tr>
<tr>
<td>Dy</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>Σ Ln</td>
<td>6.0 ppm</td>
</tr>
</tbody>
</table>
Investigation of Fe(OH)$_3$ and Sc(OH)$_3$ precipitation as a consequence of hydrolysis. **Experimental conditions:** $V = 10.0$ mL, $c_i = 0.50$ mM.

**Co-precipitation** of Sc(III) with Fe(III) is observed in a binary, equimolar solution of Fe(III) and Sc(III) with increasing pH. **Not possible** to separate Fe(III) and Sc(III) by variation of the pH, certainly not at higher (relative) concentrations of Fe(III).
Standard adsorption experiment:

- 10 mL of aq. solution
- 25 mg of adsorbent
- magnetically stirred (300 rpm)

Adsorption amount:

\[ q_{eq} = \frac{c_i - c_e}{m_{ads}} V \]

Sc(III) adsorption with DTPA-chitosan-silica and EGTA-chitosan-silica as a function of the contact time. **Experimental conditions:** \( m_{ads} = 25.0 \) mg, \( V = 10.0 \) mL, \( c_i = 0.50 \) mM, \( pH_{eq} = 2.02 \).
Functionalization with two different organic ligands \( \Rightarrow \) opposite affinities in single-element solutions of Sc(III)/Fe(III) as a consequence of different stability constants \( \Rightarrow \) selectivity observed for Sc(III) with EGTA-chitosan-silica in an equimolar, binary solution of Fe(III) and Sc(III)
Reusability of **EGTA-chitosan-silica**. Adsorption from an aqueous solution of Sc(NO₃)₃. Stripping with 1.0 M HNO₃ (10 mL). **Experimental conditions:** \( m_{ads} = 25.0 \text{ mg} \); \( V = 10 \text{ mL} \); \( c_i = 0.50 \text{ mM} \); adsorption time = 4 h; stripping time = 1 h.
Chelating ion exchange: formation of a coordinate bond between the metal cation and the surface functional group

- Selectivity depends on $\neq$ in stability constants
- A higher affinity for the resin results in slower migration through the column
- **Breakthrough** of the different elements in the leachate is initiated by applying a decreasing pH gradient with diluted solutions of HNO$_3$. 

(1) = bauxite residue leachate
(2) = HNO$_3$ solution
(3) = column filled with EGTA-chitosan-silica
(4) = fraction collector
Optimized isolation of scandium from a bauxite residue leachate by ion-exchange column chromatography with EGTA-chitosan-silica as resin material and a decreasing pH gradient.
CONCLUSIONS

- **Metal-ion recovery** is considered as an important aspect in the valorization of bauxite residue, in order to solve the red mud problem in combination with applications in other fields.

- Functionalization 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, functionalized with DTPA-groups.

- A **high selectivity** was observed compared to the other components (mainly iron, titanium and silicon) present in a **HNO₃ leachate of Greek bauxite residue**.

- Scandium was isolated from the other elements by **ion-exchange column chromatography**, by applying a decreasing pH gradient with aqueous solutions of HNO₃. Scandium broke through the column at a **pH of 0.50**, a much lower value than the ones observed for the other metal ions present in the leachate.
Other work

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