BIORECOVERY OF SCANDIUM FROM BAUXITE RESIDUE


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Introduction

- The bauxite residue (BR), is a highly alkaline waste by-product.
- 3.5 billion tons of BR have been stockpiled globally in storage areas.
- The disposal of BR is a universal environmental concern.
- BR contains valuable metals, such as rare earth elements (REEs), in particular, Scandium (Sc).
- Higher demand for critical raw materials (CRMs).
- The most senior supply risk of CRMs corresponds to REEs.

Filter-pressed (dry) bauxite residue being stockpiled in Greece, at Mytilneos S.A. (former Aluminum of Greece)

Scandium crystals
Bioleaching

- Biotechnologies Essential role in metal recovery
- Sustainable technology for waste
- Eco-friendly “Green technology”
- Operational flexibility
- Low energy requirements

Bioleaching of Red Mud
Materials and methods

Batch experiments

Microbial sources:

1. Digestate (anaerobic digestion effluent) collected from a pilot-scale anaerobic digester

2. Chemoheterotrophic Bacterium, *Acetobacter tropicalis* (Pure Culture)

3. Chemoheterotrophic Fungus, *Aspergillus niger* (Pure Culture)

- Bauxite Residue (BR) provided by Mytilineos S.A. (ferroalumina 12/2016) – Sc content: 100±5 mg/kg
- The initial pH of the BR was 11.3.
Materials and methods

1. Digestate

- AMPTS' bottles (500 ml total volume; 400 ml working volume and 100 ml headspace)
- Bench-scale anaerobic bioreactor
- Subculturing (8 months period)

Materials and methods

2. *Acetobacter tropicalis* (1/2)

*Bacterial growth*

- Inoculation into leaching medium and incubated at 30°C and 80 rpm in an shaking incubator for 1 month for activation.
Materials and methods

2. *Acetobacter tropicalis* (2/2)

**Bioleaching experiments**

- 10% and 20% v/v of bacterium suspension was inoculated into 150 mL of leaching medium in 250 mL Erlenmeyer flask

- 120 RPM

  - pH adjustment to 7 with HCl
  - BIOMASS 10% and 20% v/v
  - 1%, 2%, 10%, 20% and 30% w/v BR pulp density
  - Incubation time 0-30 days
  - T= 20 and 30 °C

*Aerobic conical flasks*
Materials and methods

3. *Aspergillus niger* (Pure culture)

**Bioleaching experiments**

- 2, 4 6 % v/v of fungus suspension was inoculated into 120 mL of leaching medium in 250 mL Erlenmeyer flask

- 100 RPM

- **NO pH adjustment to 7**

- Incubation time 20 days

- 1%, 5% and 10% w/v BR pulp density

- BIOMASS 2, 4, 6% v/v

- **T=30°C**

- 40, 90 and 140 g/L Sucrose

*Aspergillus niger culture from Institute Leibniz, DSMZ, Germany*

*Incubation in an orbital shaking incubator*
pH monitoring
Sc % Recovery

Digestate and subculturing

 Longer enrichment

Stimulation of Bioleaching!
Sc % Recovery

Acetobacter Tropicalis
Bioleaching Experiments

Aspergillus Niger

- **Bioleaching Conditions**: 30 °C, 120 rpm
- **Time**: 20 days
- **Optimization of scandium extraction using Taguchi methodology**

<table>
<thead>
<tr>
<th>Parameters Taguchi</th>
<th>Sucrose (g/L)</th>
<th>S/L BR (%)</th>
<th>A. Niger (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Π1</td>
<td>40</td>
<td>1</td>
<td>2</td>
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<td>Π9</td>
<td>140</td>
<td>10</td>
<td>4</td>
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</tbody>
</table>
Sc % Recovery

Aspergillus Niger

Sucrose: 140 g/L
S/L: 1 %
As. Niger: 6 %
pH: 5.5
Effect of Taguchi Parameters

Main Effects Plot for Sc Concentration, Day 15
Data Means

Sucr (g/L) | S/L (%) | Asp Nig (%)
--- | --- | ---
| | | |

Mean

40 90 140 1 5 10 2 4 6
Estimated Sc Concentrations
Estimated Sc Recoveries
Effect of Subculturing

*Aspergillus Niger*

Sucrose: 90 g/L
S/L: 1%
As. Niger: 4%
Organic Acids Production

Digestate
Organic Acids Production

Digestate- Subculturing

[Bar chart showing concentrations of various organic acids (e.g., oxalic, citric, acetic, propionic, isobutyric, butyric, isoameric, and valeric) over different conditions and time periods.]

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Organic Acids Production

*Acetobacter tropicalis*
Organic acids standards
2 mg/L

90 g/L sucrose, 1 % S/L, 4 % As. niger
Day 4

Aspergillus Niger

90 g/L sucrose, 1 % S/L, 4 % As. niger
Day 18

Aspergillus Niger
Maximum Sc recoveries

- Aspergillus niger, 1% S/L, 6% fungus, pH 5.5, 30 oC, 20 days
- Acetobacter tropicalis, 1% S/L, 20% bacterium, pH 1.9, 30 oC, 20 days
- Inoculum digestate, 10% S/L, 35 oC, 10 days
- H2SO4, 5% S/L, pH 0.01, 25 oC, 60 min
- H3PO4, 2% S/L, pH 0.2, 25 oC, 60 min
Sc Recovery – S/L 10%

- Aspergillus niger, 10% S/L, 16 days
- Acetobacter tropicalis, 10% S/L, 20 days
- Inoculum digestate, 10% S/L, 10 days
- H2SO4, 10% S/L, 60 min
- H3PO4, 10% S/L, 60 min
Conclusions (1/2)

▪ After a longer acclimation the activated sludge inoculum (mixed culture) resulted in higher Sc recovery, equal to 33% (previous 20%) at 10% pulp density and shorter time.

▪ *Acetobacter tropicalis* resulted Sc recovery of 42% that was observed with 1% S/L- BR pulp density with 20% w/w of bacterium suspension, recorded after 20 days.

▪ *Aspergillus Niger* resulted in maximum Sc recovery: 46%

<table>
<thead>
<tr>
<th>S/L</th>
<th>Sucrose</th>
<th>As. niger</th>
<th>pH</th>
<th>Days</th>
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<tbody>
<tr>
<td>1%</td>
<td>140 g/L</td>
<td>6%</td>
<td>5.5</td>
<td>20</td>
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Conclusions (2/2)

▪ **Acetobacter Tropicalis** resulted in mainly acetic and oxalic acids with lower concentrations of citric acid, malic and succinic acid.

▪ **Aspergillus Niger** resulted also in mainly acetic and oxalic acids with lower concentrations of citric, malic, succinic, lactic, propionic and formic acid.

▪ Synergistic effect of the different organic acids produced by microorganisms.

▪ Factors affecting Sc recovery
  ▪ BR Solid to liquid ratios (S/L)
  ▪ Sucrose concentrations
  ▪ Subculturing
Future work

Optimization of the bioleaching process

- Different microorganisms – A fungus, *Penicillium oxalicum*
- Investigation of *biosorption*
- Incubation time minimization
- Maximize Sc recovery
References


THANK YOU FOR YOUR ATTENTION
Analytical Methods

- Chemical analysis of the leachate solutions after filtration for the identification of Sc was conducted by ICP-OES.

- The pH was measured using a digital pH-meter.

- The identification of organic acids was performed by HPLC and gas chromatograph.

- Volatile solids (VS) were carried out according to Standard Methods. VS determined as a measure of biomass production. By measuring VS, the organic portion of the total dry weight could be measured.

- The numbers of bacterial cell during bacterial growth was counted performed by standard plate count (SPC) method.

- Optical Density: Absorbance of the samples during time with a spectrophotometer at 600 nm.