Removal of toxic metals from sewage sludge by EDTA in a closed-loop washing process

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Problem

- More than 50,000 wastewater treatment plants are operating in the European Union, producing more than 10 million tons of dry solids per year.
- Nitrogen and P are abundant in sewage sludge, reaching concentrations ranging from 1.5 to 6.0% and from 0.8 to 11.0% of total solids, respectively.

Wastewater treatment plant in Slovenia
Current sludge treatments techniques

**Physical**
- Heat (300-400 °C), Electroremediation
  - Short time
  - Elimination of potential organic pollutants
  - Some authors suggest the use of low pH for Electroremediation
  - +
  - -

**Biological**
- Vermicomposting, Bioleaching, Biosurfactant application
  - Low risk of secondary pollution
  - Efficient
  - Long time
  - Efficiency changes according substrate composition
  - +
  - -

**Chemical treatment**
- Acidification, Ion Exchange, Chelating, etc.
  - +
  - -

- Short time
- Simple
- Efficient
- Could change properties
- Could be expensive
Why EDTA?

- Can be recycled
- Economically feasible
- Efficient
- Not harmful in low concentrations
- Simultaneous metals removal

Resoil

- Soil EDTA + Oxalic acid + Dithionite washing
  - 60% As removal
  - 76% Pb removal
  - 29% Zn removal
  - 53% Cd removal
How does EDTA washing process works?

Toxic metals in Sewage Sludge (SS)

- Organic matter
- Exchangeable
- Carbonates
- Fe and Mn oxides
- Residual

SS EDTA washing

Rinsing 1

Rinsing 2

Rinsing 3

Washed SS

Used washing and rinsing solutions
Used washing and rinsing solutions (RS1, RS3) + Lime (CaO) solid = Treated washing solutions + Metals hydroxides (solid)

RS1 + H₂SO₄ = Acid rinsing solution (pH2) + Acidic EDTA (solid) to be recycled for next batch

Me-EDTA + Ca²⁺ + 2(OH)⁻ ⇌ Ca-EDTA + Me (OH)₂
Pre-experiments

SS coming from WTP of Slovenia metals concentration (mg kg⁻¹)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>EDTA (mM)</th>
<th>Oxalic Acid (mM)</th>
<th>Dithionite (mM)</th>
<th>H₂SO₄ (mM)</th>
<th>Ratio (w/V)</th>
<th>Time (h)</th>
<th>Pb rem. (%)</th>
<th>Zn rem. (%)</th>
<th>Fe rem. (%)</th>
<th>Cu rem. (%)</th>
<th>Mn rem. (%)</th>
<th>Cr rem. (%)</th>
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<tbody>
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<td>64</td>
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Process

Sludge conditioning
- Drying
- Grinding

Sludge washing
- 1 h
- EDTA and $\text{H}_2\text{SO}_4$

Sludge rinsing
- Fresh water
- 3 times

Products
- EDTA washing solution
- 3 Rinsing solutions
- Washed sludge

Treatment of Processing solutions
- CaO
- RS1 EDTA

Sludge washing
- 68% of EDTA are recovered
## Table 2: The efficiency of removal of toxic metals from sewage sludge in a series of 10 consecutive washing batches.

<table>
<thead>
<tr>
<th>Batch number</th>
<th>Pb</th>
<th>Zn</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
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<td>58</td>
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</table>

*SS washed in batch 5 was externally contaminated with Pb and Mn after grinding/sieving.
Fig. 2. The properties of used washing, first, second and third rinsing solution (uWS, uRS1, uRS2, and uRS3, respectively) over the 10 consecutive remediation batches.

Fig. 3. The properties of the recycled washing, first and third rinse solutions (WS, RS1, and RS3, respectively) over the 10 consecutive remediation batches.
Fig. 4. Fractionation of Pb, Zn, Cu, Mn, Cr, and Fe in original and washed SS. Data are given as averages of 3 subsamples obtained from the homogenized bulk of orig. SS and a combined sample of washed SS from batches 1-10 (except batch 5, which was excluded due to external contamination with Pb and Mn).
Table 3. Leaching of metals from original and washed SS. Data are given as average ± SD of 3 subsamples taken from the homogenized bulk of orig. SS and from a combined sample of washed SS from batches 1-10 (except batch 5, which was excluded due to external contamination with Pb and Mn). Different letters indicate significant differences between treatments according to Duncan's test (P < 0.05).

<table>
<thead>
<tr>
<th>Metals (mg kg⁻¹)</th>
<th>Orig. SS</th>
<th>Washed SS</th>
<th>DIN 3814-S4*</th>
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</thead>
<tbody>
<tr>
<td>Pb</td>
<td>0.63 ± 0.04b</td>
<td>1.59 ± 0.05a</td>
<td>10</td>
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<tr>
<td>Zn</td>
<td>11.50 ± 0.02b</td>
<td>43.73 ± 0.07a</td>
<td>50</td>
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<tr>
<td>Cu</td>
<td>41.02 ± 0.47a</td>
<td>3.05 ± 0.05b</td>
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<tr>
<td>Cr</td>
<td>0.59 ± 0.02a</td>
<td>0.17 ± 0.01b</td>
<td>10</td>
</tr>
<tr>
<td>Mn</td>
<td>1.67 ± 0.05b</td>
<td>3.25 ± 0.05a</td>
<td>/</td>
</tr>
<tr>
<td>Fe</td>
<td>34.52 ± 0.53b</td>
<td>54.43 ± 1.02a</td>
<td>/</td>
</tr>
</tbody>
</table>

*Concentrations stipulated as hazardous (DIN 38414-S4, Council Decision 2003/33/EC)
Table 1. Metal concentrations and properties of original and washed SS. Data for metal concentrations in orig. SS are given as average ± SD of 3 subsamples taken from the homogenized bulk, and for washed SS as the calculated average from batches 1-10 (except for batch 5, which was excluded because of external contamination with Pb and Mn). The properties of orig. SS refer to the homogenized bulk, and washed SS of the combined sample from batches 1-10, batch 5 was excluded.
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Labwork team

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Fig. 1. The flowchart of the process with material balance. Process steps: (1) SS washing, (2) solid-liquid separation and SS rinsing, (3) compensation of water losses, (4) alkalization of uWS, (5) alkalization/acidification of uRS1, (6) alkalization of uRS3. (7) Addition of other solutions and fresh water to each of the process solutions to reach the final volume.

WS, uWS denotes washing and used washing solution, RS1 and uRS1 represent first rinsing and used rinsing solution, RS2 and uRS2 represent second rinsing and used rinsing solution, RS3 and uRS3 third rinsing and used rinsing solution. Blue lines denote flow of solutions, dashed blue lines denote flow of solutions from previous batch, black lines denote flow of solids.