New bench scale plant for biosorption

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Biosorption – new trends

Biosorption process

Focus on:
- sorbate removal
  - Wastewater treatment
    - (11,993 papers)

Focus on:
- biosorbent enrichment
  - Biological feed supplements with micronutrients
    - (30 papers)
  - Micronutrients fertilizer components
    - (29 papers)

Webofknowledge.com - keywords: biosorption and wastewater, biosorption and feed supplements, biosorption and fertilizer
Potential biosorbents

**Plants**
- Leaves
- Seeds

**Algae**
- Microalgae
- Macroalgae

**Microbes**
- Bacteria
- Archea

**Fungi**
- Micromycetes
- Macromycetes

**Animal**
- Bones
- Eggshells

**Waste**
- Manure
- Agricultural waste

Micronutrient fertilizer additives

Raspberry

Leaves, buds, branches

Product: tea, dried, spices, herbal medicines

DRYING

PRESSING

Residue

Product: dried residues, food dyes, substrates for plastics, phenolic extracts, bakery substrates, dietary fibers, moldings, lecithin

Fruit pomace

Supercritical CO₂ extraction

Postextraction residue 15-30% of all by products

Waste

Various technologies

Oils - pharmacy and dietary supplements

Micronutrient fertilizer additives

Non-toxic, easy dosing, competitive for commercial products

Biosorption + Zn, Mn, Cu

Installation - stirred tank mode

Fig. 3. Simplified scheme of the process in stirred tank mode - a system of two stirred tank reactors.

Streams:
B - Biomass,
M - Micronutrients,
W - Deionized water.

Equipment: 1 - Biomass homogenizer; 2 - Micronutrient solution tank; 3, 5, 6 - Stirrers; 4, 9, 12 - Peristaltic pumps; 7, 8 - Stirred tank reactors tank (equipped with pH regulator); 10, 13 - Biomass sedimentators; 11, 14 - Post-process tanks.
**Installation - fixed bed mode**

Fig. 4. Simplified scheme of the process in fixed bed mode - a system of two column reactors.

Streams: B – Biomass, M – Micronutrients, W- Deionized water.

Equipment: 1 – Biomass homogenizer; 2 – Micronutrient solution tank; 3 – Stirrer; 4, 8, 10, 12, 14 – Peristaltic pumps; 5, 6 - Reactor tanks; 7, 11 – Sieve; 9, 13 – Recirculated solution tanks (equipped with pH regulator).
### Process parameters

<table>
<thead>
<tr>
<th>Mode</th>
<th>Stirred tank</th>
<th>Fixed bed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorbate</td>
<td>Cu(II) (CuSO₄·5H₂O)</td>
<td></td>
</tr>
<tr>
<td>Sorbate concentration</td>
<td>300 mg/L</td>
<td></td>
</tr>
<tr>
<td>Reactor volume</td>
<td>70L</td>
<td></td>
</tr>
<tr>
<td>Solution volume</td>
<td>50L</td>
<td>200L</td>
</tr>
<tr>
<td>pH</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>25°C</td>
<td></td>
</tr>
<tr>
<td>Material losses</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Volumetric flow rate</td>
<td>-</td>
<td>1L/min</td>
</tr>
<tr>
<td>Process time</td>
<td>2.5h</td>
<td>6h</td>
</tr>
<tr>
<td>Drying</td>
<td>24 h, 50°C</td>
<td></td>
</tr>
</tbody>
</table>
Final product

R

R + Cu(II)
Results

Daily productivity
• 300–400 g at stirred tank mode
• 10–16 kg at fixed bed mode

Material loses
• 10% in both cases

Estimated 100 kg production costs
• 419$ at stirred tank mode
• 48.1$ at fixed bed mode
### Multielemental content of product

<table>
<thead>
<tr>
<th>Element (mg/kg)</th>
<th>R - natural</th>
<th>R + Cu – stirred tank mode</th>
<th>R + Cu – fixed bed mode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Micronutrients</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>8.96±1.79</td>
<td>12611±2522 <strong>EC=1407</strong></td>
<td>12808±2562 <strong>EC=1429</strong></td>
</tr>
<tr>
<td>Zn</td>
<td>34.6±6.9</td>
<td>171±34</td>
<td>58.2±11.6</td>
</tr>
<tr>
<td>Mn</td>
<td>75.9±15.2</td>
<td>14±3</td>
<td>13.3±2.660</td>
</tr>
<tr>
<td>Fe</td>
<td>122±24</td>
<td>184±37</td>
<td>77±15.4</td>
</tr>
<tr>
<td>Mo</td>
<td>6.54±1.31</td>
<td>4.41±0.88</td>
<td>0.247±0.049</td>
</tr>
<tr>
<td><strong>Macronutrients</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>1551±310</td>
<td>797±159</td>
<td>1839±368</td>
</tr>
<tr>
<td>K</td>
<td>2767±553</td>
<td>156±31 <strong>(-94.4%)</strong></td>
<td>140±28 <strong>(-94.9%)</strong></td>
</tr>
<tr>
<td>S</td>
<td>1407±281</td>
<td>1370±274 <strong>(-2.63%)</strong></td>
<td>925±185 <strong>(-34.3%)</strong></td>
</tr>
<tr>
<td>Ca</td>
<td>2502±500</td>
<td>585±117 <strong>(-76.6%)</strong></td>
<td>188±38 <strong>(-92.5%)</strong></td>
</tr>
<tr>
<td>Mg</td>
<td>1802±360</td>
<td>170±34 <strong>(-90.6%)</strong></td>
<td>209±42 <strong>(-88.4%)</strong></td>
</tr>
<tr>
<td>Na</td>
<td>472±94</td>
<td>630±126</td>
<td>72.8±14.6</td>
</tr>
<tr>
<td><strong>Toxic elements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd (5)*</td>
<td>0.83±0.17</td>
<td>0.532±0.106</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>Ni (60)*</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
<td>&lt;0.03</td>
</tr>
<tr>
<td>As (50)*</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>10.2±2.0</td>
</tr>
<tr>
<td>Pb (140)*</td>
<td>&lt;0.5</td>
<td>19±4</td>
<td>7.99±1.60</td>
</tr>
<tr>
<td>Cr (100)*</td>
<td>0.117±0.023</td>
<td>0.616±0.123</td>
<td>0.655±0.131</td>
</tr>
</tbody>
</table>

* Act of fertilizer and fertilization, 18 June 2008, approved by Polish Ministry of Agriculture and Rural Development.
Stirred tank mode modelling

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Linear form</th>
<th>Parameters</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pseudo-1st order</strong></td>
<td>$\frac{dq_t}{dt} = k_1(q_{eq1} - q_t)$</td>
<td>$\ln(q_{eq} - q_t) = \ln(q_{eq1}) - k_1 \cdot t$</td>
<td>$k_1=0.0235 \text{ (1/min)}$</td>
<td>0.997</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$q_{eq1}=12.7 \text{ (mg/g)}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$q_{ICP-OES}=12.6 \text{ (mg/g)}$</td>
<td></td>
</tr>
<tr>
<td><strong>Pseudo-2nd order</strong></td>
<td>$\frac{dq_t}{dt} = k_2(q_{eq2} - q_t)^2$</td>
<td>$t = \frac{1}{q_{eq2}} + \frac{1}{q_{eq2} \cdot k_2} \cdot t$</td>
<td>$k_2=0.00426 \text{ (g/mg·min)}$</td>
<td>0.913</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$q_{eq2}=15.3 \text{ (mg/g)}$</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Pseudo-1st order model linear plot

Fig. 6. Pseudo-2nd order model linear plot

## Fixed bed mode modelling

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Linear form</th>
<th>Parameters</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yoon-Nelson</td>
<td>( \frac{c_t}{c_0 - c_t} = \exp(k_{YN}t - \tau k_{YN}) )</td>
<td>( \ln \frac{c_t}{c_0 - c_t} = k_{YN}t - \tau k_{YN} )</td>
<td>( T=105 \text{ (min)} ) ( k_{YN}=0.0078 \text{ (1/min)} )</td>
<td>0.996</td>
</tr>
<tr>
<td>Thomas</td>
<td>( \frac{c_t}{c_0} = \frac{1}{1+ \exp\left(\frac{k_{TH}q_{eq}x}{q} - k_{TH}c_0 t\right)} )</td>
<td>( \ln \left( \frac{c_0}{c_t} - 1 \right) = \frac{k_{TH}q_{eq}x}{q} - k_{TH}c_0 t )</td>
<td>( k_{TH}=0.0260 \text{ (mL/min mg)} ) ( q_{eq}=13.5 \text{ (mg/g)} ) ( q_{ICP-OES}=12.8 \text{ (mg/g)} )</td>
<td>0.996</td>
</tr>
<tr>
<td>Walborska</td>
<td>( \partial \frac{\partial c_b}{\partial t} + \nu \partial \frac{\partial c_b}{\partial H} + \partial \frac{\partial q}{\partial t} = D_{ax} \frac{\partial^2 c_b}{\partial H^2} )</td>
<td>( \ln \left( \frac{c}{c_0} \right) = \frac{\beta_a c_0 t}{q} - \frac{\beta_a H}{\nu} )</td>
<td>( \beta_a=0.181 \text{ (1/min)} ) ( q=17.5 \text{ (mg/g)} )</td>
<td>0.935</td>
</tr>
<tr>
<td>Adams-Bohart</td>
<td>( \frac{c_t}{c_0} = \exp \left( k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{U_0} \right) )</td>
<td>( \ln \left( \frac{c_t}{c_0} \right) = k_{AB} C_0 t - k_{AB} N_0 \frac{Z}{U_0} )</td>
<td>( N_0 = 17500 \text{ (mg/L)} ) ( k_{AB} = 0.0103 \text{ (mL/min mg)} )</td>
<td>0.935</td>
</tr>
</tbody>
</table>

**Fig. 7.** Yoon-Nelson model linear plot vs. experimental data.

**Fig. 8.** Thomas model linear plot vs. experimental data.

**Fig. 9.** Adams-Bohard, Walborska model linear plot.
Conclusions

- New bench scale installation for biosorption and comparison of two possible process mode was presented with kinetics description.

- New eco-friendly micronutrient fertilizer additives with copper based on raspberry seeds were produced and multielemental content was determined after sample mineralization.

- The material losses in the process were about 10% for fixed bed and stirred tank reactors.

- The cost of the utilization of berries seeds to micronutrient fertilizer components in fixed bed mode was much lower (48.1 $/100 kg) than in stirred tank mode (419 $/100 kg).

- New installation is an efficient tool in biosorption studies and enables investigation of parameter influence in a wide range.
Perspectives

Selection of the process parameters (and minor modifications of installation)

Vegetation tests of new product (TF determination and comparison with commercial products)

Scale up to pilot plant scale (transfer proven solutions)
The work was supported by Polish National Science Centre, project no. 2012/05/E/ST8/03055 entitled: Biosorption of metal ions to the biomass of seeds of berries

Thank you for your attention!

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