THE EFFECT OF LEAD AND ZINC CONCENTRATION RATIO IN AQUEOUS SOLUTIONS ON THEIR REMOVAL ON FIXED BED OF ZEOLITE CLINOPTILOLITE

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Examinations of natural zeolites on Faculty of Chemistry and Technology University of Split

- removal of Cu, Zn and Pb on natural and pre-treated zeolite using batch method
- study of kinetic and thermodynamic of Zn on natural zeolite
- removal of Pb or Zn on natural and pre-treated zeolite using column method
- removal Pb and Zn from binary solution on natural and pre-treated zeolite using column method
- recent examinations are directed on removal of metal ions on iron coated zeolite
EXPERIMENT

SERVICE CYCLE
-experiments were performed in glass columns, d=12mm
-fixed bed depth, H=40mm
-binary aqueous solutions of total initial concentration 1 mmol/l lead and zinc ions have been prepared by dissolving of Pb(NO$_3$)$_2$ and Zn(NO$_3$)$_2$ in doubly distilled water
-flowrate was 1 ml/min

REGENERATION CYCLE
-regeneration solution NaNO$_3$, 15 g/l
-flowrate was 1 ml/min
Concentrations of metal ions in binary solutions for each service cycle.

<table>
<thead>
<tr>
<th>Concentration ratio $c_o$(Pb)/$c_o$(Zn)</th>
<th>$c_o$(Pb+Zn) mmol/l</th>
<th>$c_o$(Pb) mmol/l</th>
<th>$c_o$(Zn) mmol/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>1.031</td>
<td>0.165</td>
<td>0.866</td>
</tr>
<tr>
<td>0.71</td>
<td>1.149</td>
<td>0.478</td>
<td>0.671</td>
</tr>
<tr>
<td>0.95</td>
<td>1.062</td>
<td>0.516</td>
<td>0.546</td>
</tr>
<tr>
<td>1.37</td>
<td>1.060</td>
<td>0.612</td>
<td>0.448</td>
</tr>
</tbody>
</table>
Removal Pb and Zn from binary solution on zeolite-clinoptilolite using column method

\[ \frac{c}{c_0} = \frac{c(Pb+Zn)}{c_0(Pb+Zn)} \quad \text{Pb/Zn} = \frac{c_0(Pb)}{c_0(Zn)} \]

\[ BV = \frac{V}{V_s} \]
$c/c_0 = \frac{c(\text{Pb or Zn})}{c_0(\text{Pb or Zn})}$
Calculation of experimental parameters

\[ h_Z = H \cdot \left[ \frac{V_E - V_B}{V_E - (1 - F) \cdot (V_E - V_B)} \right] \]

height of mass transfer zone

\[ q_B = \int_{0}^{V_B} (c_0 - c) dV = \frac{c_0 \cdot V_B}{\rho \cdot H \cdot A} \]

breakthrough capacity

\[ q_E = \int_{0}^{V_E} (c_0 - c) dV = \frac{n_E}{\rho \cdot H \cdot A} \]

exhaustion capacity
<table>
<thead>
<tr>
<th>Concentration ratio Pb/Zn in influent</th>
<th>$V_{B'}$ BV</th>
<th>$V_{E'}$ BV</th>
<th>$q_{B'}$ mmol/g</th>
<th>$q_{B}(Pb)/q_{B}(Zn)$</th>
<th>$q_{E'}$ mmol/g</th>
<th>$q_{E}(Pb)/q_{E}(Zn)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19</td>
<td>218.9</td>
<td>564.0</td>
<td>0.336</td>
<td>0.545</td>
<td>0.189</td>
<td>0.080</td>
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<tr>
<td></td>
<td>0.053</td>
<td>Zn</td>
<td>0.281</td>
<td></td>
<td></td>
<td>0.460</td>
</tr>
<tr>
<td></td>
<td>Pb+Zn</td>
<td>Pb</td>
<td>0.189</td>
<td>0.174</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.71</td>
<td>206.8</td>
<td>583.9</td>
<td>0.337</td>
<td>0.521</td>
<td>0.714</td>
<td>0.260</td>
</tr>
<tr>
<td></td>
<td>0.140</td>
<td>Zn</td>
<td>0.196</td>
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<td>0.257</td>
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<tr>
<td></td>
<td>Pb+Zn</td>
<td>Pb</td>
<td>1.012</td>
<td></td>
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<tr>
<td>0.95</td>
<td>221.2</td>
<td>614.8</td>
<td>0.336</td>
<td>0.509</td>
<td>0.942</td>
<td>1.980</td>
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<tr>
<td></td>
<td>0.163</td>
<td>Zn</td>
<td>0.173</td>
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<tr>
<td></td>
<td>Pb+Zn</td>
<td>Pb</td>
<td>0.396</td>
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<tr>
<td>1.37</td>
<td>209.0</td>
<td>572.8</td>
<td>0.312</td>
<td>0.581</td>
<td>1.364</td>
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<tr>
<td></td>
<td>0.180</td>
<td>Zn</td>
<td>0.132</td>
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</tr>
<tr>
<td></td>
<td>Pb+Zn</td>
<td>Pb</td>
<td>0.388</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.193</td>
<td>Zn</td>
<td>0.193</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Removal Pb and Zn from binary solution on zeolite-clinoptilolite using column method

**REGENERATION CYCLE**
- experiments were performed in glass columns, d=12mm, H=40mm
- regeneration solution has been prepared by dissolving of NaNO₃ in doubly distilled water
- flowrate was 1 ml/min
REGENERATION CURVES for particular ions

Regeneration was completed with 100 BV of solution.
n_S - the quantity of ion loaded to the fixed bed
n_B - the quantity of ion bound onto the fixed bed until the breakthrough point
n_E - the quantity of ion bound onto the fixed bed until the exhaustion point
n_R - the quantity of each metal ion eluted during the regeneration
CONCLUSIONS

Removal of lead and zinc on zeolite using column method is applicable in practice.

CEC of zeolite doesn't depend on concentration ratio in feeding solution.

The quantity of regenerated zinc is significantly lower compared to the lead. The only exception is the binary solution with a small Pb/Zn ratio.

This confirms that lead was mostly bound onto zeolite, possible due to replacement of zinc ions with lead ions during the service cycle.

This replacement is due to higher selectivity of natural zeolite for lead ions. Lower radius of the hydrated Pb$^{2+}$ ion in comparison to Zn$^{2+}$ provides for its better mobility through the framework structure.

Advantage of column method is regeneration of zeolite what enables use of the same bed in many cycles.
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Ivona Nuić - assistant

Marin Ugrina - assistant
Thank you!