NATURAL ZEOLITE AS A PERMEABLE REACTIVE BARRIER

PREDICTION OF LEAD CONCENTRATION PROFILE THROUGH ZEOLITE BARRIER

N. Vukojević Medvidović, J. Perić, M. Trgo, M. Ugrina, I. Nuić

University of Split, Faculty of Chemistry and Technology, Teslina 10/V, 21000 Split, Croatia.
SOURCE AND TYPE OF GROUNDWATER CONTAMINATION

- Urban runoff
- Leaking sewers
- Industrial storage/contaminated land
- Landfills
- Petrol station
- Oil storage tanks
- Public water supply
- Pesticides and fertiliser application
- Transpiration
- Evaporation
- Manure spreading
- Uncovered road salt
- Ploughing
- Septic tank
- Unsaturated zone
- Saturated zone
- Impermeable layer

Groundwater flow
SCHEMATIC PRESENTATION OF PERMEABLE REACTIVE BARRIER
The reactive barrier materials are classified according to the target pollutant and the mechanism of removal:

- zero-valent iron (Fe$^0$) and iron based materials
- organic based material (activated carbon, peat, sewage sludge, sawdust, etc.)
- alkaline materials such as hydrated lime, ferrous sulphate
- phosphate minerals such as hydroxyapatite and biogenic apatite (e.g. fish bone)
- aluminosilicates such as clay and zeolites, ...

Zeolites have been recognized as an effective material for remediation of heavy-metals-polluted water due to their sorption properties, environmental compatibility, widespread deposits and simple exploitation.
Hydrological processes important for contaminant transport

- quantity of water available for transport – mass flow
- degree of dispersion - variability in pore size distribution

Contaminant characteristic important contaminant transport

- contaminant solubility in water
- adsorption / desorption onto soil and from soil ($K_d$, $R_d$)
- diffusive properties
- degradation and volatilization
- source of contaminants
Spread of contaminants

Development of a plume from a continuous source

Groundwater flow

Travel of a contaminants slug from a point source

t0  t1  t2  t3
**Distribution coefficient, $K_d$**

- **Tightly adsorbed** $K_{d_1}$
- **Lightly adsorbed** $K_{d_2}$

**Adsorption Isotherm** – equilibrium relationship between $C_s$ and $C_i$

**Distribution Coefficient $K_d$** - the slope of the line

**Retardation Coefficient $R_d$** – degree of retaining contaminants by soil

\[
K_d = \frac{C_s}{C_i} = \frac{c_o - c_e}{c_e} \cdot \frac{V}{m}
\]

\[
R_d = (1 + \frac{\rho}{\varepsilon} \cdot K_d \cdot 1000)
\]
Contaminant migration in porous medium is subject to:
- ADVECTION
- DISPERSION
- DIFFUSION

Groundwater flow
Contaminant dissolution into flowing groundwater

Contaminant
DIFFUSION

Contaminant
ADVECTION and
DISPERSION
EXPERIMENTAL STUDY

The zeolite sample
- originating from the Vranjska Banja deposit
- particle zeolite size of 0.6-0.8 mm
- treated with a 2 mol/l NaCl solution for five days at 37 °C
Zeolite porosity and zeolite density (g/cm³) were 0.693 and 0.699, respectively.
Batch examination

Single metal solutions: \( c_0(\text{Pb}) = 0.503 - 8.894 \text{ mmol/l (104.09 - 1842.39 mg/l)} \), were prepared by dissolving \( \text{Pb(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O} \) in ultrapure water.

The saturation of NaZ:

- mixing 0.5 g of MNZ with 0.05 L of metal solution, S/L = 10 g/l in the batch mode
- 72 hours at room temperature
- the pH values and concentrations of lead were measured continuously by complexometric titration
2. Column examination

- glass column: \( d_u = 12 \text{ mm} \) i \( H = 500 \text{ mm} \)
- zeolite bed length in column \( L = 115 \text{ mm} \)

**SERVICE CYCLE**
- Lead solution: \( c_o = 1.026-2.513 \text{ mmol/l} \) and \( Q = 1 \text{ ml/min} \)
- down flow mode.

**REGENERATION CYCLE**
- solution of \( \text{NaNO}_3 \)
- \( c_o = 15 \text{ g/l} \) i \( Q = 1 \text{ ml/min} \),
- down flow mode

- pH values were measured continuously, while concentrations of lead in efluent were equal to the concentration in influent
RESULTS AND DISCUSSION
Equilibrium amount and percentage of the retained lead on zeolite vs. initial lead concentration

\[ q_e = (c_o - c_e) \cdot \frac{V}{m} \]

\[ \alpha = \left( \frac{c_o - c_e}{c_o} \right) \cdot 100 \]

Results from the batch study
Distribution coefficients ($K_d$) and retardation coefficients ($R_d$) vs. initial lead concentration

\[ K_d = \left( \frac{c_o - c_e}{c_e} \right) \cdot \frac{V}{m} \]

\[ R_d = (1 + \frac{\rho}{\varepsilon} \cdot K_d \cdot 1000) \]
Results from the column study

**SERVICE CYCLE**

![Graph showing service cycle](image)

\[
q_E = \frac{\int_0^{V_E} (c_0 - c) \, dV}{\rho \cdot H \cdot A} = \frac{n_E}{m}
\]

\[
c_e = \frac{n_T - n_E}{V}
\]

\[
V = q_E \cdot t_E
\]

\[
K_d = \left( \frac{c_o - c_e}{c_e} \right) \cdot \frac{V}{m}
\]

\[
R_d = (1 + \frac{\rho}{\varepsilon} \cdot K_d \cdot 1000)
\]

**Distribution and Retardation Coefficients estimation.**

<table>
<thead>
<tr>
<th>( c_o ) mmol/l</th>
<th>( q_e ) mmol/g</th>
<th>( c_e ) mmol/l</th>
<th>( V ) l</th>
<th>( K_d ) l/g</th>
<th>( R_d )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.026</td>
<td>0.585</td>
<td>0.108</td>
<td>5.680</td>
<td>5.249</td>
<td>5295.59</td>
</tr>
<tr>
<td>1.759</td>
<td>0.644</td>
<td>0.151</td>
<td>3.671</td>
<td>4.297</td>
<td>4335.26</td>
</tr>
<tr>
<td>2.513</td>
<td>0.574</td>
<td>0.109</td>
<td>2.427</td>
<td>5.884</td>
<td>5935.71</td>
</tr>
</tbody>
</table>
Estimation of hydrodynamic dispersion coefficients

\[ U = \frac{V}{V_p} = \frac{V}{A \cdot L \cdot \varepsilon} \]

where:
- \( V \) - volume of effluent discharge over time, cm³
- \( V_p \) - pore volume, cm³
- \( A \) - cross sectional area of the column, cm²
- \( L \) - length of the zeolite bed, cm
- \( \varepsilon \) - porosity.

\[ D_L = \frac{v \cdot L \cdot (c_{0.84} - c_{0.16})}{8 \cdot \varepsilon} \]

where:
- \( v \) is the discharge linear velocity (m/min),
- \( c_{0.84} \) and \( c_{0.16} \) correspond to the relative concentration \( c/c_0 \) of 0.84 and 0.16, respectively.
Hydrodynamic dispersion coefficients estimation

<table>
<thead>
<tr>
<th>$c_0$ (mmol/l)</th>
<th>$q_e$ (mmol/g)</th>
<th>$c_e$ (mmol/l)</th>
<th>$V$ (l)</th>
<th>$K_d$ (l/g)</th>
<th>$R_d$</th>
<th>$D_L \cdot 10^4$ (m²/min)</th>
<th>$D_{LR} \cdot 10^2$ (m²/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.026</td>
<td>0.585</td>
<td>0.108</td>
<td>5.680</td>
<td>5.249</td>
<td>5295.59</td>
<td>0.243</td>
<td>0.459</td>
</tr>
<tr>
<td>1.759</td>
<td>0.644</td>
<td>0.151</td>
<td>3.671</td>
<td>4.297</td>
<td>4335.26</td>
<td>1.000</td>
<td>2.307</td>
</tr>
<tr>
<td>2.513</td>
<td>0.574</td>
<td>0.109</td>
<td>2.427</td>
<td>5.884</td>
<td>5935.71</td>
<td>1.464</td>
<td>2.466</td>
</tr>
</tbody>
</table>

The transport of lead from the point source through the barrier can be analyzed by a simple analytical pulse model, in which the input pulse contamination has been injected at $x=0$, and the spreading of contaminant can be predicted according to the following equation:

$$c(x, t) = \frac{c_0}{\sqrt{4 \cdot \pi \cdot D_{LR} \cdot t}} \exp\left(- \frac{(x - v_r \cdot t)^2}{4 \cdot D_{LR} \cdot t}\right)$$

$x$ is the distance within the barrier (m)

$D_{LR}$ is the retardation hydrodynamic dispersion ($D_{LR}=D_L/R_d$)

Note: $v_r$ is the groundwater velocity ($v_r = 0.00003$ m/min).
POSSIBLE SOLUTION OF SPREADING OF CONTAMINANT DUE TO ADVECTION, DIFFUSION AND DISPERSION
Effect of lead initial concentration on the lead concentration profile through the zeolite barrier at 0.3 m, 0.4 m, 0.5 m and 0.6 m.
CONCLUSION

Natural zeolite can be effectively used as a permeable reactive barrier for lead removal from contaminated water.

The values of the distribution and retardation coefficient evaluated from the batch and column studies indicate the ability of the zeolite barrier to retain the contaminant.

The hydrodynamic dispersion coefficient was evaluated from the column study by applying the Brigham method. The lead concentration pattern through the zeolite barrier is predicted for distances of 0.3, 0.4, 0.5 and 0.6 m within the barrier.

The results indicate that certain dimension of the barrier is required to ensure an adequate contact time between the contaminants and the zeolite, which depends on groundwater velocity and the initial concentrations of contaminates.
Thank you for your attention
QUESTIONS?