PREDICTION OF ZEOLITE BARRIER CAPABILITY IN TREATMENT OF GROUNDWATER POLLUTED BY Pb, Cd AND Zn

Ivona Nuić, Matea Šušnjara, Marina Trgo, Nediljka Vukojević Medvidović, Marin Ugrina

Faculty of Chemistry and Technology, Department of Environmental Engineering, University of Split, Ruđera Boškovića 35, 21 000 Split, Croatia

E-mail: ivona@ktf-split.hr

ABSTRACT

This paper considers the possible use of natural zeolite as filler in permeable reactive barrier (PRB). From the column experimental results, the distribution and retardation coefficients were calculated in order to evaluate the Pb, Cd and Zn distribution and immobilization within the zeolite barrier. Calculation of hydrodynamic dispersion coefficients enabled prediction of contaminants spreading in the groundwater.

Key words: natural zeolite, heavy metals, polluted groundwater, permeable reactive barrier.

INTRODUCTION

The environment pollution by heavy metals progress intensively, especially due to rapid industrialization and agricultural activities. Heavy metals are daily emitted into the air, soil and surface waters, and can endanger groundwater, which is the main source of water for human consumption. Therefore, it is necessary to develop methods of protecting water in aquifers from different types of pollution. Permeable reactive barriers (PRBs) are one of the very promising methods of groundwater protection [1]. The PRB is an underground structure located across the groundwater flow, downstream of pollution source, whose main purpose is to reduce or completely remove pollutants. Many reactive materials are used as fillers in PRB, depending on the target pollutant. Zeolites have been recognized as effective materials for the treatment of heavy metal contaminated waters [2]. In order to protect groundwater from hazardous heavy metals, prior developing a remediation plan, it is necessary to determine their mobility in the groundwater environment. The column experiments [3] are intended to simulate underground dynamic conditions and to quantify the sorption of heavy metals relative to groundwater flow. This study investigates natural zeolite clinoptilolite as possible filler material in PRB for *in situ* remediation of simulated groundwater contaminated by Pb, Cd and Zn.

EXPERIMENTAL

The column experiments were performed at 23 ± 2 °C in glass column (height, 50 cm; inside diameter, 1.2 cm) on the H = 8 cm high fixed bed of natural zeolite clinoptilolite (Zlatokop deposit in Serbia). An equimolar binary Pb+Zn and Cd+Zn solutions of total initial concentration ≈ 1 mmol/L, were passed through the column in down-flow mode at flow rates Q = 1, 2, 3 and 4 mL/min. All effluents collected at the bottom of the column were analysed for Pb, Cd and Zn concentrations by the complexometric method or the ion chromatography on the Metrohm 761 Compact IC using the Nucleosil 5SA column.

RESULTS AND DISCUSSION

The obtained column results are presented as breakthrough curves in Figure 1. All curves for both binary solutions have a characteristic S-shape, indicating the establishment of stationary conditions. With increasing in flow rate the Pb, Cd and Zn ions from the binary solutions appeared earlier at the column outlet (breakthrough point).
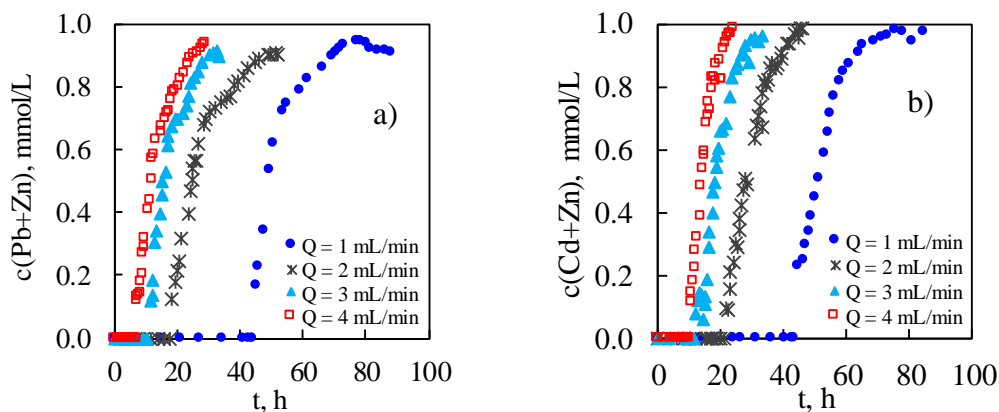
Figure 1. Breakthrough curves as total effluent concentration *vs.* retention time for a) Pb+Zn [3], and b) Cd+Zn solutions at different flow rates.

The percentage of metals uptake by the zeolite, α (%), was calculated using following equation:

$$\alpha = (\frac{c_o - c_e}{c_o}) \cdot 100 \qquad (1)$$

where c_o and c_e are initial and equilibrium metal concentrations (mmol/L) in solution. The obtained values for each metal in both binary solutions are presented in Figure 2.
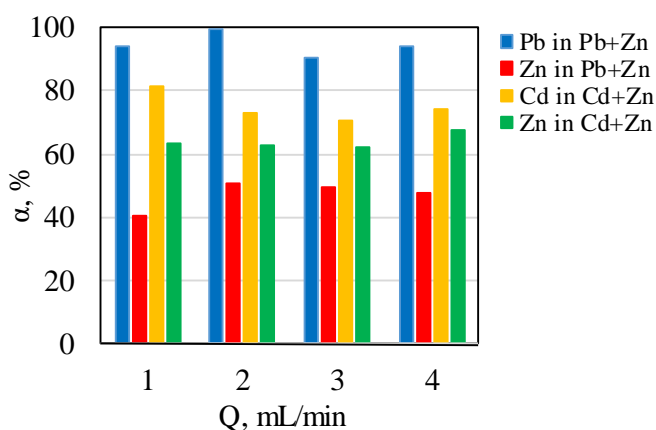

Figure 2. The uptake of each metal for both binary solutions in relation to different flow rates.

The Pb is best removed (90.1–99.4%) by the natural zeolite, compared to Cd (70.8–81.3%) and Zn (40.6–50.6% for Pb+Zn, and 62.3–67.4% for Cd+Zn). The Zn was less bound for both binary solutions, especially for the Pb+Zn. This is a consequence of competition between ions, and their hydrated ionic radius, which is lowest for the Pb, and highest for the Zn [4], making it more difficult to access zeolite binding sites.

To estimate the potential for the sorption of dissolved contaminants on the zeolite, the distribution coefficient, K_d (L/g) was calculated:

$$K_d = (\frac{c_o - c_e}{c_e}) \cdot \frac{V_e}{m} \qquad (2)$$

where V_e is the remediate volume of solution in equilibrium (L) and m is the zeolite mass (g) in the column. The ability of the zeolite in retaining contaminants is quantified by the retardation coefficient R_d (-):

$$R_d = 1 + \frac{\rho}{\varepsilon} \cdot K_d \cdot 1000 \qquad (3)$$

where ρ is the zeolite bulk density of 0.699 g/cm³ and ε is the zeolite fixed bed porosity of 0.693. Calculated coefficients are presented in Figure 3.
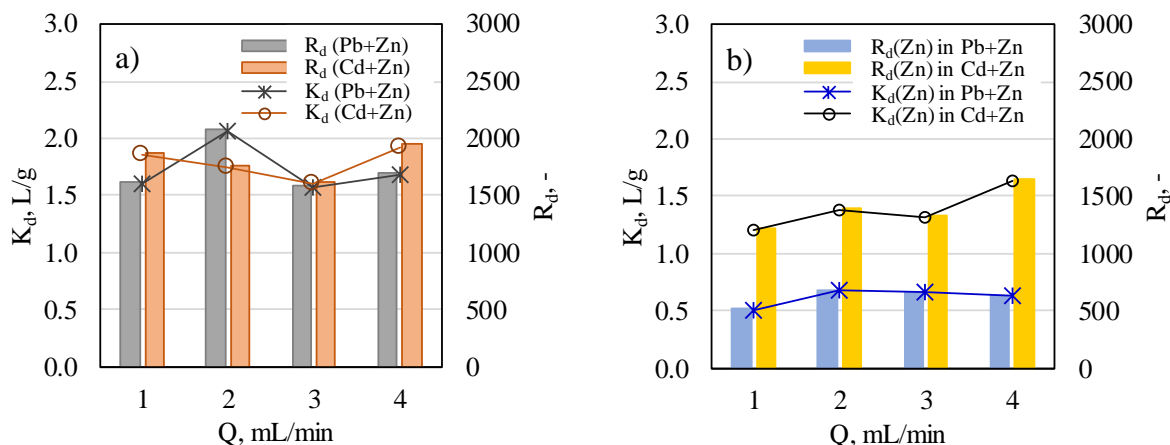

Figure 3. Distribution and retardation coefficients for a) total Pb+Zn and Cd+Zn concentration and b) Zn concentration in both binary solutions.

A higher value of K_d indicates a good distribution leading to better uptake of contaminants by the zeolite, while higher R_d points on good immobilization of the contaminants. Values of K_d and R_d in Figure 3a are very similar for both binary solutions and for all flow rates. Contrary, the differences of the K_d and R_d values of Zn (Figure 3b) in different binary solutions are quite notable. The Zn is better distributed and retained on the zeolite in case of Cd+Zn, compared to Pb+Zn system, as well as with increased flow rate. The reason for such behaviour of Zn is less pronounced competition between Cd and Zn caused by closer values of hydrated ionic radii, comparing to Pb and Zn, as well as shorter contact times. This is in line with the α values presented in Figure 2.

The degree of expansion of the contaminant in the liquid phase flowing downstream through the porous medium depends on the hydrodynamic dispersion coefficient, D_L (m²/min) which is calculated according to the Brigham method [5] by the following equation:

$$D_L = \frac{v \cdot H}{8} \left[\left(\frac{U-1}{\sqrt{U}} \right)_{0.84} - \left(\frac{U-1}{\sqrt{U}} \right)_{0.16} \right]^2 \tag{4}$$

where v is the mean velocity (m/min) of water through pores, $v = Q/(A \cdot \varepsilon)$, A is the cross-sectional area of the column of 1.1304 cm², U is the number of effluent pore volumes equals to $U = V_t/V_p = V_t/(A \cdot H \cdot \varepsilon)$, where V_t (mL) is the volume at time t. The subscripts 0.84 and 0.16 correspond to the $(U-1)/U^{1/2}$ values in $c/c_o = 0.84$ (exhaustion) and $c/c_o = 0.16$ (breakthrough), on the breakthrough curves, which are normally used as the midpoint concentration for defining the movement and velocity of the contaminant plume.

The retardation hydrodynamic dispersion coefficient D_{LR} (m²/min) is calculated as:

$$D_{LR} = \frac{D_L}{R_d} \tag{5}$$

Lower values of D_L and D_{LR} are preferable in order to mitigate the hydrodynamic dispersion, since it causes extra spreading of contaminants in the underground. The calculated parameters are presented in Figure 4. It can be seen that D_L and D_{LR} for Pb+Zn and Cd+Zn solutions in Figure 4a increase with increasing in flow rate, especially in case of Cd+Zn. The same happened for Zn in both binary solutions in Figure 4b, and is more pronounced for Cd+Zn.

The greater hydrated ionic radii of Cd and Zn compared to Pb preventing them binding to less accessible sites within the zeolite barrier, enhancing their spreading. Moreover, affinity of natural zeolite toward Pb is much higher than for Cd and Zn.
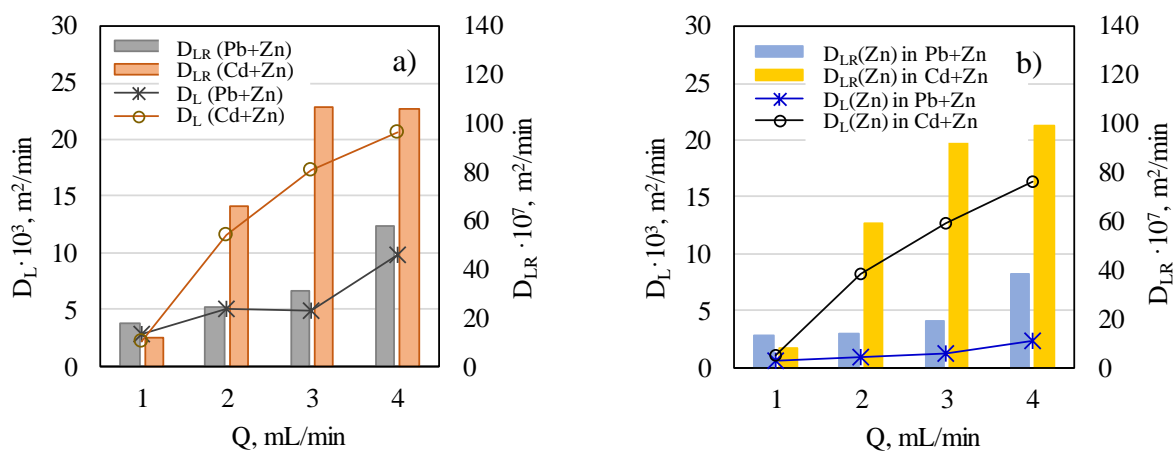

Figure 4. The hydrodynamic dispersion and retardation hydrodynamic dispersion coefficients for a) total Pb+Zn and Cd+Zn concentration and b) Zn concentration in both binary solutions.

Comparing all calculated parameters, the best distribution and retention, with minimum spreading of contaminants is achieved for the lowest flow rate of 1 mL/min in both binary solutions. This flow rate corresponds to mean velocity through the zeolite pores of v = 0.01277 m/min, which is higher than average groundwater flow rate of ≈ 0.00003 m/min [5]. This indicates that at lower flow rates than those examined, the retention of contaminants by natural zeolite barrier is even better. Otherwise, the distance within the barrier should be increased to ensure optimal contact time and longevity of the barrier.

CONCLUSION

Natural zeolite clinoptilolite showed good binding properties of Pb, Cd and Zn from binary solutions. The Pb uptake was higher than 90% for all examined flow rates, while for Cd it was in the range 70.8–81.3%. Uptake of Zn was better from binary Cd+Zn (62.3–67.4%) than from Pb+Zn solution (40.6–50.6%) due to less expressed competition between Cd and Zn compared to Pb and Zn. The retardation coefficients point on good retention of contaminants within the zeolite barrier, while hydrodynamic dispersion coefficients increase with flow rate, indicating the broadening of the contaminants plume. The best behaviour of contaminants inside the zeolite barrier was achieved at the lowest flow rate, which is closest to the real groundwater velocity comparing to other examined flow rates. These findings suggest possible application of natural zeolite as filler in PRB in treatment of groundwater contaminated with heavy metals, especially for low flow rates common in the underground environment.

REFERENCES

[1] F. Obiri-Nyarko, S.J. Grajales-Mesa, and G. Malina, *Chemosphere*, 2014, **111**, 243-259.
[2] P. Misaelides, *Micropor. Mesopor. Mat.,* 2011, **144** (1-3) 15-18.
[3] I. Nuić, M. Trgo, and N. Vukojević Medvidović, *Chem. Eng. J.*, 2016, **295**, 347-357.
[4] L. Canet, and P. Seta, *Pure Appl. Chem.*, 2001, **73** (12), 2039-2046.
[5] N. Vukojević Medvidović, I. Nuić, M. Ugrina, and M. Trgo, *Water Air Soil Pollut.*, 2018, **229**:367.