

## NATURAL ZEOLITE AS A PERMEABLE REACTIVE BARRIER - PREDICTION OF LEAD CONCENTRATION PROFILE THROUGH ZEOLITE BARRIER

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### ABSTRACT

This paper has investigated the application of natural zeolite as a permeable reactive barrier (PBR) for lead removal from contaminated water. The retardation coefficient was evaluated from batch and column studies. The Brigham method was used to evaluate the hydrodynamic dispersion coefficient from the column study and the lead concentration profile through the zeolite barrier was predicted for different distances within the barrier.

Keywords: zeolite, permeable reactive barrier, hydrodynamic dispersion coefficient, lead concentration profile

### INTRODUCTION

One of the most promising alternative technologies to conventional remediation methods such as the pump and treat is in situ treatment of groundwater using the permeable reactive barriers (PRBs). The basic idea of this technology is presented in Fig. 1. The PBR is placed in the subsurface area opposite to the path of a plume. Contaminated water passes through the barrier under natural gradient condition, and the remediated water comes out at the other side. Recently, zeolites have been recognized as effective materials for remediation of heavy-metals-polluted water, due to their sorption properties, environmental compatibility, and ease of application [1, 2]. In this paper some batch and column tests were performed to examine the application of natural zeolite as a PBR for lead removal. The hydrodynamic dispersion coefficient was estimated and the lead transport through zeolite barrier was predicted.

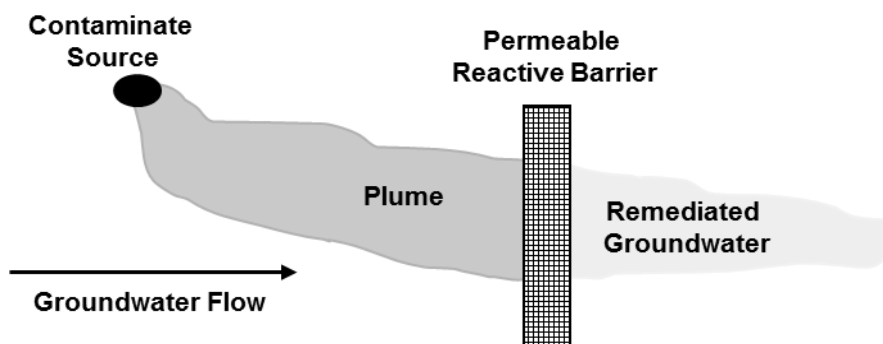


Fig. 1. Schematic presentation of permeable reactive barrier.

### MATERIALS AND METHODS

The zeolite sample was prepared from natural zeolite originating from the Vranjska Banja deposit with the particle zeolite size of 0.6-0.8 mm, treated with a 2 mol/l NaCl solution for five days at 37 °C. The zeolite porosity and zeolite density (g/cm<sup>3</sup>) were 0.693 and 0.699, respectively.

Batch examinations in the zeolite-lead aqueous solution system were carried out at 25 °C and at a constant mixing rate of 230-250 rpm. 0.5 g of pretreated zeolite samples were equilibrated with 50 ml of the lead solution with initial concentrations ranging 104.09 -

1842.39 mg/l (0.503-8.894 mmol/l), during 3 days. Afterwards, the suspension was filtered through the vacuum filtration apparatus and the lead concentration in the filtrate was determined.

The column experiments were performed using a glass column with the inner diameter of 12 mm and the height of 500 mm. The fixed zeolite bed depth in the column was 115 mm, which corresponds to the bed volume and the zeolite weight of 13 cm<sup>3</sup> and 9.0975 g, respectively.

Service cycles were performed by passing lead solutions with initial concentrations 212.5 - 520.5 mg/l range, through the fixed bed at the constant flow rate of 1 ml/min. After each service cycle, the regeneration was performed with the solution of NaNO<sub>3</sub>, with the concentration of 15 g/l. Our previous papers have presented the experimental results with the breakthrough and regeneration curves [1].

## RESULTS AND DISCUSSION

The experimental results from batch studies were used to calculate the equilibrium amount of lead retained on zeolite,  $q_e$ , (mmol/g), the retained lead percentage  $\alpha$  (%), the distribution coefficient  $K_d$  (l/g) and the retardation coefficient  $R_d$  (-), using the following equations [2]:

$$q_e = (c_o - c_e) \cdot \frac{V}{m} \quad (1) \quad \alpha = \left( \frac{c_o - c_e}{c_o} \right) \cdot 100 \quad (2)$$

$$K_d = \left( \frac{c_o - c_e}{c_e} \right) \cdot \frac{V}{m} \quad (3) \quad R_d = \left( 1 + \frac{\rho}{\varepsilon} \cdot K_d \cdot 1000 \right) \quad (4)$$

where  $c_o$  and  $c_e$  are the initial and equilibrium lead concentrations (mmol/l),  $V$  is the solution volume (l),  $m$  is the zeolite mass (g),  $\rho$  is the zeolite density (g/cm<sup>3</sup>),  $\varepsilon$  is the zeolite porosity (-). The results are presented in Fig. 2.

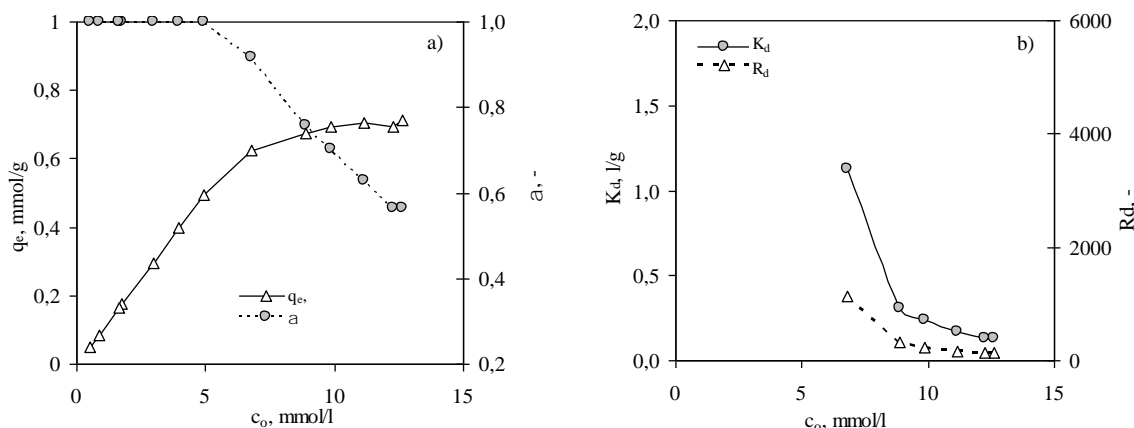


Fig. 2. (a) Equilibrium amount and percentage of the retained lead on zeolite vs. initial lead concentration; (b) Distribution and retardation coefficients vs. initial lead concentration.

The equilibrium amount of lead removed by zeolite increases with the initial lead concentrations due to the increase in the concentration driving force. The percentage of the retained lead, distribution and retardation coefficients show a decreasing trend with the increase of the initial concentration, indicating that zeolite will lose its efficiency in retaining the lead contaminate in highly contaminated sites.

Experimental results from the column study are shown by the breakthrough curve in Fig. 3a. The results show that with increasing initial concentrations, the zeolite bed becomes exhausted earlier. Based on the column experimental results, the hydrodynamic dispersion coefficient  $D_L$  was estimated by means of the Brigham method. According to Brigham, if the plot of the effluent relative concentration ( $c/c_o$ ) as a function of  $(U-1)/U^{1/2}$  is presented as a

straight line (Fig. 3b.), in which U is the number of effluent pore volume, then the hydrodynamic dispersion coefficient,  $D_L$  ( $m^2/min$ ) can be calculated as follows [2, 3]:

$$D_L = \frac{v \cdot L \cdot (c_{0.84} - c_{0.16})}{8 \cdot \varepsilon} \quad (5)$$

where  $v$  is the discharge linear velocity ( $m/min$ ),  $L$  is the length of the zeolite bed ( $m$ );  $c_{0.84}$  and  $c_{0.16}$  correspond to the relative concentration  $c/c_o$  of 0.84 and 0.16, respectively. The results for  $D_L$  are shown in Table 1.

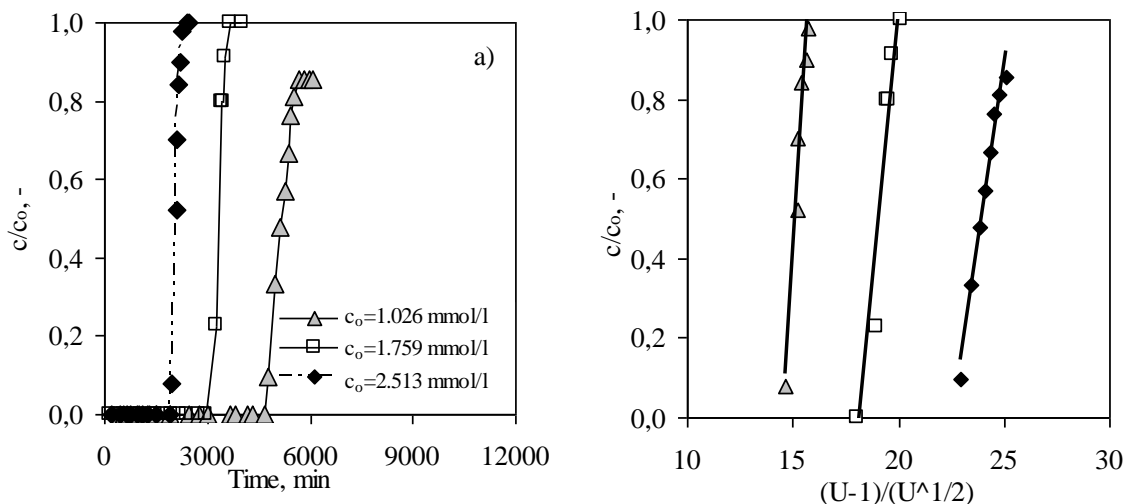


Fig. 3. (a) Breakthrough curves for lead removal on zeolite. (b) Application of the Brigham method.

The values of retardation coefficient  $R_d$  were also calculated from the equilibrium experimental data from the column study using equation (4), and the results for  $D_L$  are shown in Table 1. Also, the values of retardation hydrodynamic dispersion ( $D_{LR}=D_L/R_d$ ) are given in Table 1.

Table 1. Retardation and hydrodynamic dispersion coefficients estimation.

$c_o$ mmol/l	$q_e$ mmol/g	$c_e$ mmol/l	$V$ l	$K_d$ l/g	$R_d$ -	$D_L \cdot 10^4$ $m^2/min$	$D_{LR} \cdot 10^8$ $m^2/min$
1.026	0.585	0.108	5.680	5.249	5295.59	0.243	0.459
1.759	0.644	0.151	3.671	4.297	4335.26	1.000	2.307
2.513	0.574	0.109	2.427	5.884	5935.71	1.464	2.466

Extremely high values of  $K_d$  and  $R_d$  given in Table 1 indicate the ability of the zeolite barrier to retain the contaminate. The values of  $D_L$  and  $D_{LR}$  increased with increasing initial lead concentration. Based on the calculated values of  $D_{LR}$  given in Table 1, 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 contaminate can be predicted according to the following equation [2]:

$$c(x, t) = \frac{c_o}{\sqrt{4 \cdot \pi \cdot D_{LR} \cdot t}} \exp\left(-\frac{(x - v_r \cdot t)^2}{4 \cdot D_{LR} \cdot t}\right) \quad (6)$$

where  $x$  is the distance within the barrier ( $m$ ),  $t$  is time ( $min$ ),  $D_{LR}$  is the retardation hydrodynamic dispersion ( $D_{LR}=D_L/R_d$ ),  $v_r$  is the groundwater velocity ( $v_r = 0.00003 m/min$ ). Fig. 4 illustrates the results of lead transport through the zeolite barrier at 0.3, 0.4, 0.5 and 0.6 m for the initial concentrations examined. The concentration profile shows an almost symmetrical peak for all three concentrations. The peak is broadening with increasing initial

concentrations of the lead solution and with the distance within barrier. As distance through the barrier increases, the time to reach the peaks is prolonged and shifted to the higher time values.

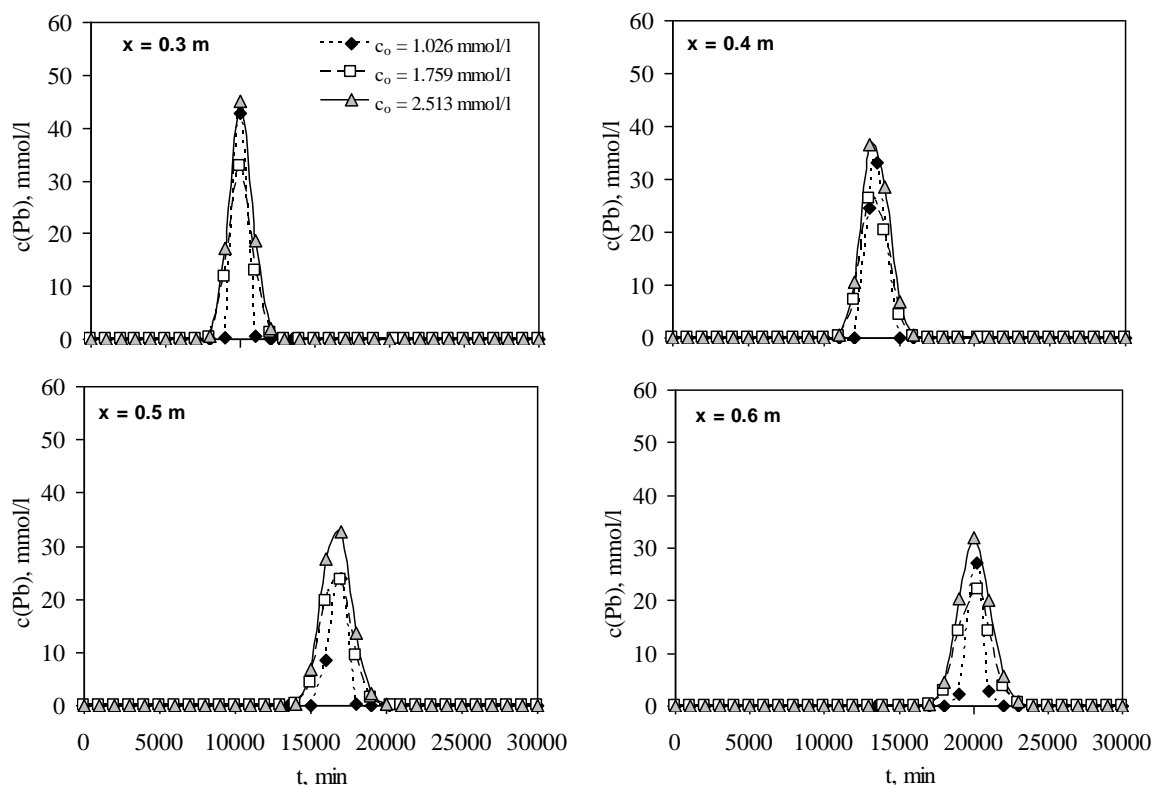


Fig. 4. Effect of lead initial concentration on the lead concentration profile through the zeolite barrier at 0.3 m, 0.4 m, 0.5 m and 0.6 m.

## CONCLUSION

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

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