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## Design of Fixed Bed Column for Lead Removal on Natural Zeolite Based on Batch Studies

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This paper presents the prediction of breakthrough curves for the fixed bed column based on batch studies. Batch equilibrium studies of lead removal on natural zeolite clinoptilolite have been performed. The obtained experimental data have been tested according to the Langmuir and the Freundlich isotherm, and their parameters have been calculated. These parameters and the Mass Transfer Model have been used to predict theoretical breakthrough curves. Theoretical breakthrough curves have been compared with the experimental ones and good agreement has been observed. This indicates that the Mass Transfer Model is applicable for prediction of breakthrough curves from batch studies. The overall mass transfer coefficient has been calculated from column experiments. This value allows for calculation of the height of the mass transfer zone as a very important parameter necessary for column design.

*Key words:*

Lead, natural zeolite, column modeling, Mass Transfer Model

### Introduction

Wastewaters generated in manufacturing and industrial processes contain various organic and inorganic substances and, when discharged into the environment without treatment, have harmful and toxic effects on humans, plants and animals. Among these substances, particularly dangerous are heavy metals, which are not biodegradable, and show a tendency of accumulating in living organisms causing many diseases. High concentrations of heavy metals from wastewater can be removed by precipitation, chemical oxidation and reduction. However, these conventional methods often cannot achieve the quality of effluent according to the maximum allowable values, so it is necessary to apply tertiary treatment methods such as ion exchange, adsorption and membrane filtration (ultrafiltration, reverse osmosis, nanofiltration and electro dialysis).<sup>1–3</sup> The application of natural zeolites as ion-exchangers and adsorbent materials is a relatively inexpensive and very effective

method of wastewater treatment. Many scientific studies examine natural zeolites due to their widespread deposits, simple exploitation and extensive environmental applications. Zeolites are hydrated aluminosilicate minerals that are characterized by an outstanding ability to exchange their own alkali and alkaline earth ions with heavy metal ions from aqueous solutions.<sup>4–6</sup> The removal of heavy metal ions on zeolite can be performed by a batch method and fixed bed column mode.<sup>7–12</sup> The effectiveness of heavy metal ions removal by zeolites depends on the type and method of activation of the zeolite, the species and concentration of metal ions, and the performance of the process. The batch method is easily applied in laboratory research and in practice for treatment of small wastewater volumes. The column performance is convenient for industrial scale applications where large volumes of wastewater are continuously being generated.<sup>7–8</sup> The specificity of column performance is that it allows for multiple repetitions of service and regeneration cycles, which means multiple use of the same weight of zeolite. In comparison to the original volume of wastewater, regeneration cycles produce a

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considerably smaller volume of effluent in which the concentration of metal ions is much higher and can be reused. Therefore, the fixed bed column performance is widely used in wastewater treatment process.<sup>10–12</sup>

Successful design and operation of an industrial fixed bed column requires the ability to predict its concentration-time profile or breakthrough curve.<sup>13–14</sup> For that reason, different kinetic models such as Bohart-Adams, Thomas, Wolborska, Yoon-Nelson, etc, which are based on column experimental data are mostly used to express the dynamic process in the column.<sup>13–17</sup> Contrary to these models, the Mass Transfer Model uses the experimental data from batch studies and provides the necessary data for the column design. This procedure can be performed in a shorter time compared to the procedure carried out in a column.<sup>2, 19–21</sup> Therefore, in this study, the Mass Transfer Model is used for prediction of breakthrough curves for lead removal on zeolite, based on data obtained from batch equilibrium studies. The overall mass transfer coefficient and the height of the mass transfer zone have been evaluated for different zeolite particle sizes and initial lead concentrations.

### Theoretical background – application of the mass transfer model to obtain the breakthrough curves

The results obtained from the batch experiment allow prediction of the breakthrough curve. This procedure consists of the following steps:<sup>2, 19–21</sup>

*Step 1.* Testing the experimental data from batch experiment to the Langmuir and the Freundlich isotherm.

The general form of the Langmuir and the Freundlich isotherm can be written as follows:

$$q_e = (b \cdot q_T \cdot \gamma_e) / (1 + b \cdot \gamma_e) \quad (1)$$

$$q_e = K_F \cdot \gamma_e^{1/n} \quad (2)$$

where:

$q_e$  – equilibrium amount of solute on the adsorbent,  $\text{mg g}^{-1}$

$q_T$  – total amount of solute required to create monomolecular layer on the surface of the particles of adsorbent,  $\text{mg g}^{-1}$

$\gamma_e$  – equilibrium concentration of solute in solution,  $\text{mg l}^{-1}$

$b$  – factor which depends on the type of adsorbent,  $\text{l mg}^{-1}$

$K_F$  and  $n$  – Freundlich constants characteristic of the system.

*Step 2.* Construction of the operating line. The operating line can be constructed by considering mass balance over the column. Namely, the amount of solute on the adsorbent can be expressed as:

$$q_e = \gamma / \gamma_0 \cdot (q_e - q_r) + q_r \quad (3)$$

where:

$q$  – amount of solute on adsorbent,  $\text{mg g}^{-1}$

$\gamma$  – concentration of solute in solution,  $\text{mg l}^{-1}$

$\gamma_0$  – initial solute concentration in solution,  $\text{mg l}^{-1}$

$q_e$  – value of  $q$  in equilibrium with initial solute concentration  $\gamma_0$ ,  $\text{mg g}^{-1}$

$q_r$  – residual amount of solute on the adsorbent after regeneration,  $\text{mg g}^{-1}$

Assuming the fresh adsorbent is being used,  $q_r = 0$  and Equation (3) becomes:

$$q = \gamma / \gamma_0 \cdot q_e \quad (4)$$

In the column experiment, equilibrium is reached at  $\gamma_0 = \gamma_e$ . Thus, when  $\gamma = \gamma_e$ ,  $q$  is equal to  $q_e$ , and coordinate  $[\gamma_e, q_e]$  represents the first point of the operating line, while a second point is the origin, as shown on Fig. 1. The value of  $q_e$  is calculated by inserting the value of initial solute concentration into the Langmuir or the Freundlich isotherm, which was obtained by analyzing the results from a batch experiment in a previous step.

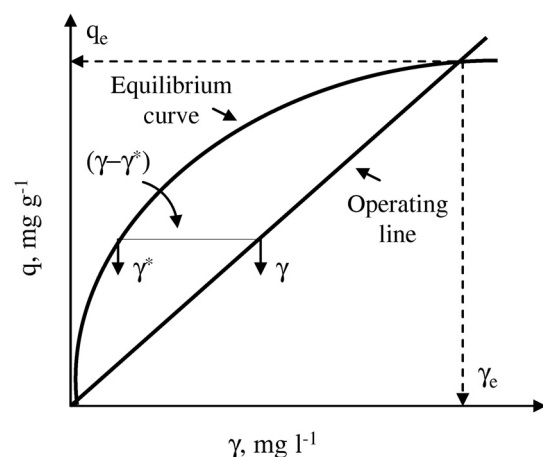


Fig. 1 – Construction of operating line and equilibrium curve

*Step 3.* Equilibrium curve is obtained by calculating the value  $\gamma^*$  from the Langmuir and the Freundlich isotherm equations, in the range from 0 to  $q_e$ . Thus, for each ordinate  $q$ , two values of the abscise are obtained: one for the equilibrium curve ( $\gamma^*$ ), a second for the operating line ( $\gamma$ ).

*Step 4.* Mass transfer rate of solute from solution through the column at different bed depths,  $dh$ , is given by the following equation:

$$G_w d\gamma = K_a \cdot (\gamma - \gamma^*) dh \quad (5)$$

where:

$G_w$  – mass flux of solution,  $\text{kg min}^{-1} \text{m}^{-2}$

$K_a$  – overall mass transfer coefficient which includes resistance to diffusion through the film and diffusion through the pores,  $\text{kg min}^{-1} \text{m}^{-3}$

$\gamma^*$  – equilibrium concentration of solute in solution corresponding to the adsorbed concentration  $q$ ,  $\text{mg l}^{-1}$ .

Expression  $(\gamma - \gamma^*)$  is the driving force of sorption, and it is equal to the distance between the operating line and the equilibrium curve for any value of  $q$ . By integrating the above expression in the range from  $\gamma_B$  to  $\gamma_E$ , where  $\gamma_B$  is the concentration of solute at breakthrough point, and  $\gamma_E$  is the concentration of solute at exhaustion point, we obtain an expression for the height of the mass transfer zone:

$$h_z = (G_w / K_a) \int_{\gamma_B}^{\gamma_E} d\gamma / (\gamma - \gamma^*) \quad (6)$$

where  $h_z$  is the height of the mass transfer zone in m.

Any value of  $h$  less than  $h_z$ , corresponds to  $\gamma$  concentration, so the  $h$  value can be calculated from equation (6) in range from  $\gamma_B$  to  $\gamma$ :

$$h_z = (G_w / K_a) \int_{\gamma_B}^{\gamma} d\gamma / (\gamma - \gamma^*) \quad (7)$$

Dividing equations (7) and (6) results in:

$$h / h_z = \int_{\gamma_B}^{\gamma} d\gamma / (\gamma - \gamma^*) / \int_{\gamma_B}^{\gamma_E} d\gamma / (\gamma - \gamma^*) \quad (8)$$

$$= (V - V_B) / (V_E - V_B)$$

where:

$V_B$  – volume of solution up to breakthrough point, l

$V_E$  – volume of solution up to exhaustion point, l

$V$  – volume of solution between  $V_B$  and  $V_E$ , l.

*Step 5.* graphical plotting of  $\gamma/\gamma_0$  vs.  $(V - V_B) / (V_E - V_B)$  represents the breakthrough curve.

## Experimental

### Zeolite samples

*Natural zeolite sample* – The natural zeolite sample containing  $\approx 80\%$  of clinoptilolite originated from the Vranjska Banja (Serbia) deposit. The sample was crushed and sieved to particle size

0.6–0.8 mm and 0.1–0.5 mm, then rinsed in doubly distilled water and dried at 60 °C.

*Pretreated natural zeolite sample* – Natural zeolite sample was pretreated with a 2 mol  $\text{l}^{-1}$  NaCl solution, with stirring in incubator shaker at a speed of 230–250 rpm for five days at 37 °C. After equilibration the solution was filtered and the precipitate rinsed up to a negative reaction to chloride. After drying at 60 °C, the sample was stored in a desiccator.

### Solutions

Solutions of different initial lead concentrations were prepared by dissolving an appropriate amount of  $\text{Pb}(\text{NO}_3)_2$  in ultrapure water, without adjusting the initial pH values. The exact lead concentration was determined by complexometrical titration in acid medium, using highly selective indicators metiltimol blue.<sup>22</sup> The solution for the regeneration was prepared by dissolving  $\text{NaNO}_3$  in ultrapure water.

### Batch experiment

Examinations in the system of zeolite-lead aqueous solution were performed by batch methods. 0.5 g pre-treated zeolite sample of each zeolite particles sizes was mixed with 50 ml of lead solution of different initial concentration in a glass vessel, during 3 days at 25 °C and at constant mixing rate of 230–250 rpm. Initial concentrations of lead solution were in range from 118.5 – 1700.5  $\text{mg l}^{-1}$ . Afterwards, the suspension was filtered through a vacuum filtration apparatus and the lead concentration in the filtrate was determined by complexometrical titration in acid medium, using highly selective indicator metiltimol blue.<sup>22</sup>

### Column experiment

The experiments were performed using two glass columns with inner diameter of 12 mm and height of 500 mm. A column was filled with zeolite of particle size 0.6 – 0.8, and another with zeolite of particle size 0.1–0.5 mm. The height of fixed zeolite bed in both columns was 115 mm, which corresponds to bed volume of 13  $\text{cm}^3$ . Porosity of the fixed bed filled with zeolite of particle size 0.6–0.8 and 0.1–0.5 mm, were 0.693 and 0.659, respectively.

Service cycles were performed by passing the lead solutions with different initial lead concentrations ranging between 212.5–520.5  $\text{mg l}^{-1}$ , through the fixed zeolite bed using down flow mode at a constant flow rate of 1  $\text{ml min}^{-1}$ . At selected time intervals the lead concentration in the effluent was determined. The process was stopped when the Pb

concentration in the effluent became equal to the initial. After each service cycle, the regeneration was performed with a solution of  $\text{NaNO}_3$ , with concentration of  $15 \text{ g l}^{-1}$ . Our previous paper had presented the experimental results with breakthrough and regeneration curves.<sup>10</sup>

## Results and discussion

### Batch experiment

Batch experiments were performed to investigate lead removal on pretreated natural zeolite. Based on the results of equilibrium concentrations, the equilibrium amounts of lead removed per gram of zeolite ( $q_e$ ) and metal removal degree ( $\alpha$ ) were calculated according to the following equations:

$$q_e = (\gamma_o / \gamma_e) \cdot V / m \quad (9)$$

$$\alpha = (\gamma_o / \gamma_e) / \gamma_o \quad (10)$$

where:

- $\alpha$  – metal removal degree, –
- $V$  – solution volume, l
- $m$  – zeolite weight, g.

Fig. 2 shows the graphical dependence of the equilibrium amounts of lead removed per gram of zeolite ( $q_e$ ) and metal removal degree ( $\alpha$ ).

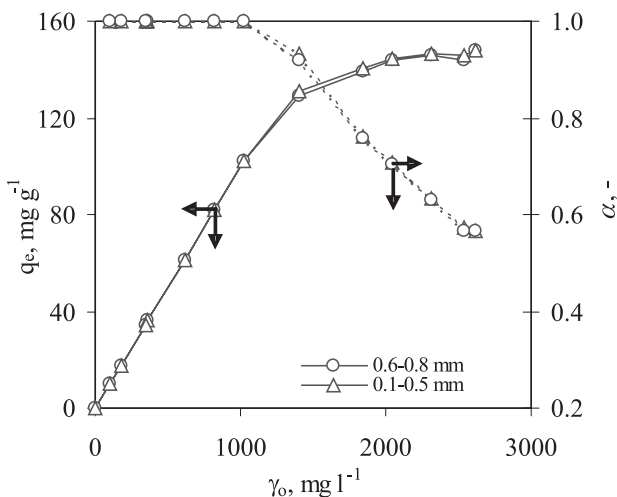


Fig. 2 – Dependence of the equilibrium amounts of lead removed per gram of zeolite ( $q_e$ ) and metal removal degree ( $\alpha$ ) vs initial concentration

The results in Fig. 2 show that the equilibrium amount of lead bound on zeolite  $q_e$  increases with the increase of the initial concentration up to  $\gamma_o = 1800 \text{ mg l}^{-1}$ , followed by an insignificant further increase. This permits for determination of the usable capacity which equals  $147 \text{ mg Pb g}^{-1}$  zeolite for

both particle sizes. This indicates that the removal capacity does not depend on particle surface in the examined range of particle sizes.

In practice, it is very important to achieve a higher degree of removal. From Fig. 2 it is evident that the degree of lead removal decreases with increasing initial concentration. The total lead removal ( $\alpha = 1$ ) for both zeolite samples is achieved for initial solution concentrations up to  $1000 \text{ mg Pb l}^{-1}$ .

### Calculation of breakthrough curve from batch experiment

Experimental data from the batch experiments presented in Fig. 2 were tested according to the Langmuir (Equation 1) and the Freundlich isotherm (Equation 2). From the linear graphical dependence of forms of isotherms, the parameters of the Langmuir and the Freundlich isotherm are calculated and presented in Table 1.

Table 1 – Parameters of Langmuir and Freundlich isotherms

Zeolite particle size mm	Langmuir		Freundlich			
	b $\text{l mg}^{-1}$	$q_T \text{ mg g}^{-1}$	$R^2$	$K_F$	n	$R^2$
0.6–0.8	0.061	147.06	0.935	99.86	18.215	0.942
0.1–0.5	0.084	147.06	0.933	105.99	21.186	0.969

An operating line and equilibrium curve were constructed according the previously described steps 2 and 3. Fig. 3 presents the operating lines and equilibrium curves based of the Freundlich isotherm for different initial lead concentrations and zeolite particle sizes.

Fig. 4 presents the graphical dependence of  $1/(\gamma - \gamma^*)$  vs. concentration. By graphical integration of the area under each curve, the value of integrals  $\int_{\gamma_B}^{\gamma_E} d\gamma / (\gamma - \gamma^*)$  was obtained, and the term  $(V - V_B) / (V_E - V_B)$  calculated. Plots of  $\alpha$  vs.  $(V - V_B) / (V_E - V_B)$  represent the theoretical breakthrough curves. The breakthrough curves were compared with the experimental ones in Fig. 5 and 6.

The goodness of fitting between calculated and experimental data was evaluated by the values of the root mean square error (RMSE), calculated according to the following equation:<sup>23</sup>

$$\text{RMSE} = \sqrt{\frac{1}{n} \left[ \sum_{i=1}^n [(\gamma / \gamma_o)_{\text{cal}} - (\gamma / \gamma_o)_{\text{exp}}]^2 \right]} \quad (11)$$

Calculated values of root mean square error (RMSE) presented in Fig. 5 indicate that the calculated breakthrough curves from the Freundlich iso-

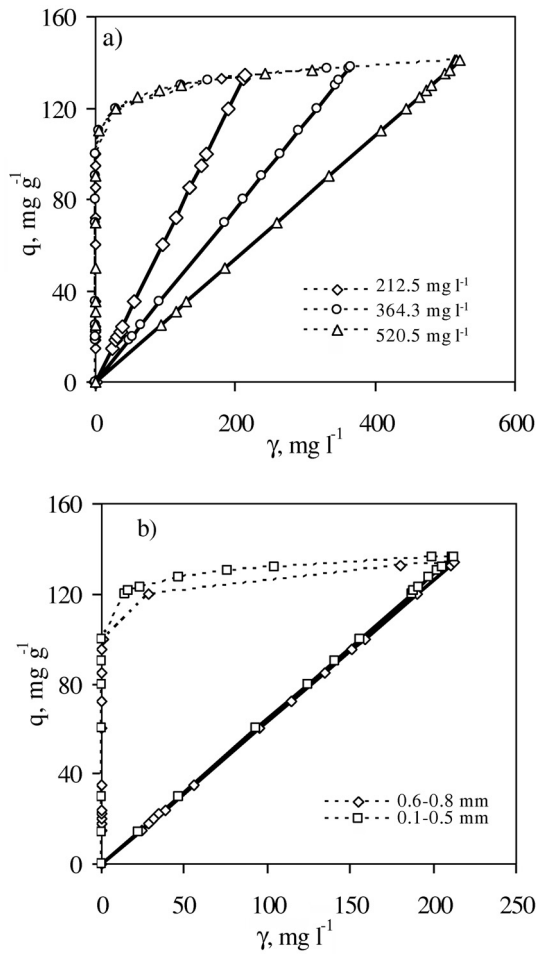


Fig. 3 – Equilibrium curves (dashed line) and operating line (full line) for determination of breakthrough curve of lead removal by fixed bed of zeolite for: a) different initial concentrations and particle size 0.6–0.8 mm, b) two different particle sizes of zeolite and initial lead concentration of 212.5 mg l<sup>-1</sup>

them are in good agreement with the experimentally obtained curves of lead removal from the aqueous solution on a fixed bed of zeolite. Similar results have been obtained for the Langmuir isotherm (Fig. 6). This indicates that the parameters of the Langmuir and the Freundlich isotherm obtained from batch experiments and the design approach based on the Mass Transfer Model are suitable for prediction of column experiments.

**Calculation of the height of the mass transfer zone**

The height of the mass transfer zone is a very important parameter necessary for column design. From the expression (6), and with known values of  $g_w$  and  $K_a$ , the height of mass transfer zone  $h_z$  can be calculated. However, there are major difficulties in evaluation of the overall mass transfer coefficient,  $K_a$ . With assumption that film diffusion controls mass transfer in the column, a graphical de-

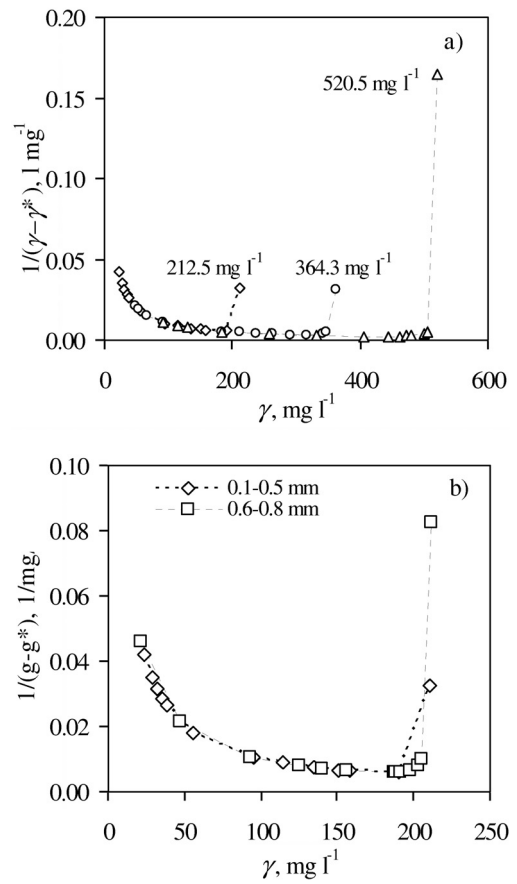


Fig. 4 – Dependence of  $1/(\gamma-\gamma^*)$  vs. concentration for: a) different initial concentrations and particle size of 0.6–0.8 mm, b) two different particle sizes of zeolite and initial lead concentration of 212.5 mg l<sup>-1</sup>

pendency of  $\gamma/\gamma_o$  vs.  $1 + \ln(\gamma/\gamma_o)$  is suggested in which the following equation is valid:<sup>24</sup>

$$1 + \ln(\gamma/\gamma_o) = N \cdot (\tau - 1) \tag{12}$$

where:

- $\tau$  – dimensionless time, –
- $N$  – number of mass transfer units, – .

The values of  $t$  can be calculated as:

$$\tau = t_B / t_E \tag{13}$$

where:

- $t_B$  – time at breakthrough point, min
- $t_E$  – time at exhaustion point, min.

Ratio of  $t_B/t_E$  is proportional to the total capacity of the fixed bed. From the graphic dependence of  $\gamma/\gamma_o$  vs.  $1 + \ln(\gamma/\gamma_o)$ , the value  $1 + \ln(\gamma/\gamma_o)$  is evaluated at the point when  $\gamma/\gamma_o \sim 0.05$ , as shown in Fig. 7.

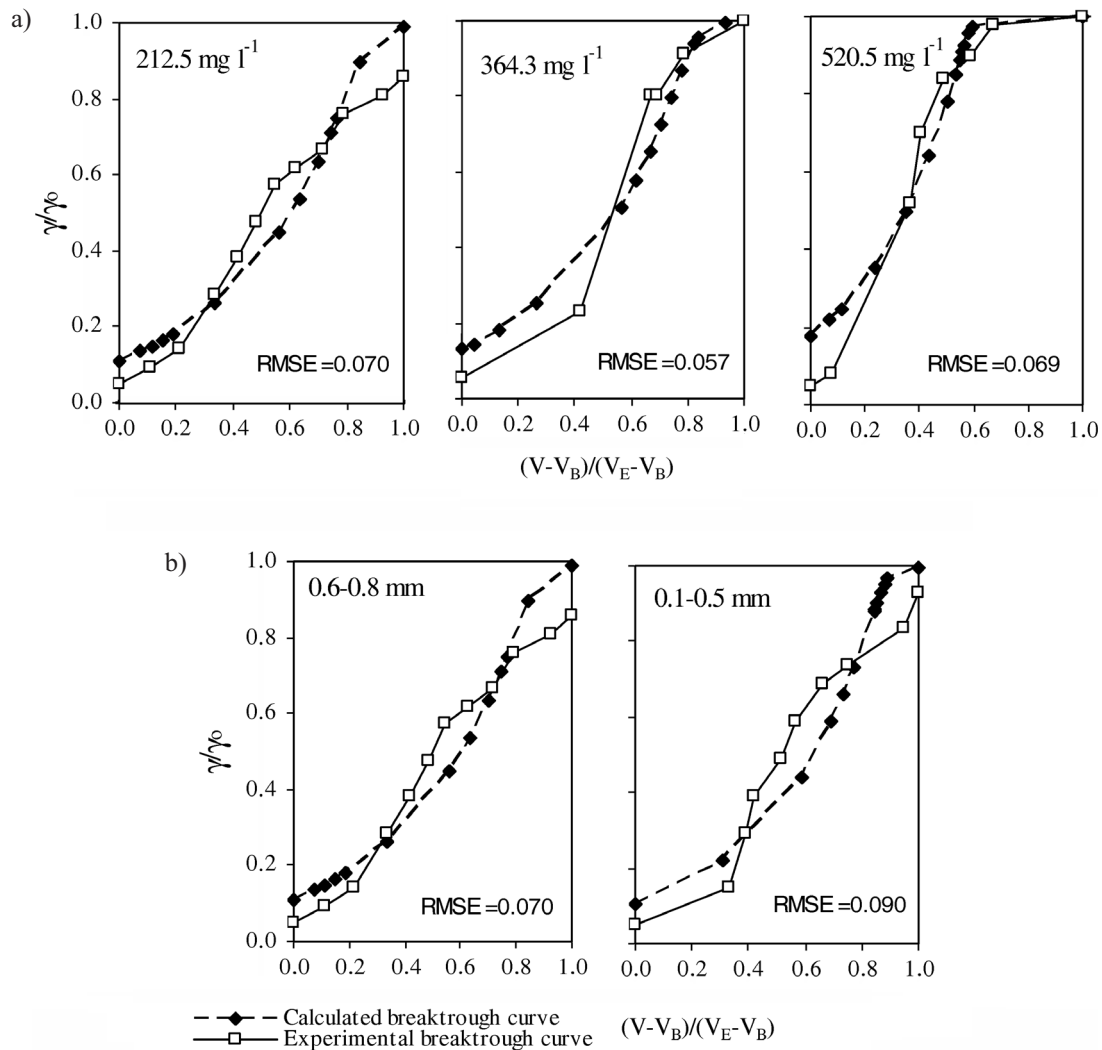


Fig. 5 – Comparison of breakthrough curve obtained from the Freundlich isotherm equations with the experimentally obtained breakthrough curves for: a) different initial lead concentrations, b) the two particle sizes of zeolite

Since  $1 + \ln(\gamma/\gamma_0) = N \cdot (\tau - 1)$  and for known values of  $\tau$ , the values of  $N$  are calculated and presented in Table 2.

The overall mass transfer coefficient,  $K_a$ , is given by the following equation:

$$K_a = (N \cdot G_w) / H \quad (14)$$

where  $H$  is the height of the fixed bed in the column in m.

Mass flux of solution in the column was calculated from the following relation:

$$G_w = (Q \cdot \rho) / (A \cdot \varepsilon) \quad (15)$$

where:

$Q$  – flow of solution through the column,  $\text{m}^3 \text{min}^{-1}$

$A$  – cross-sectional area of the column,  $\text{m}^2$

$\rho$  – density of water at 25 °C,  $\rho = 997.13 \text{ kg m}^{-3}$

$\varepsilon$  – fixed bed porosity, –.

The calculated values of  $K_a$  for different initial lead concentration and zeolite particle sizes are given in Table 2. From known value of  $K_a$ , the height of mass transfer zone  $h_z$ , can be calculated according to Equation (6). Table 2 also compares the results of experimentally obtained  $h_z$  with the value of  $h_z$  calculated according to the Mass Transfer Model.

It can be observed that the calculated values of  $K_a$  are independent of concentration, and have similar value for both sizes of zeolite particles. Experimentally obtained values of  $h_z$  show very good

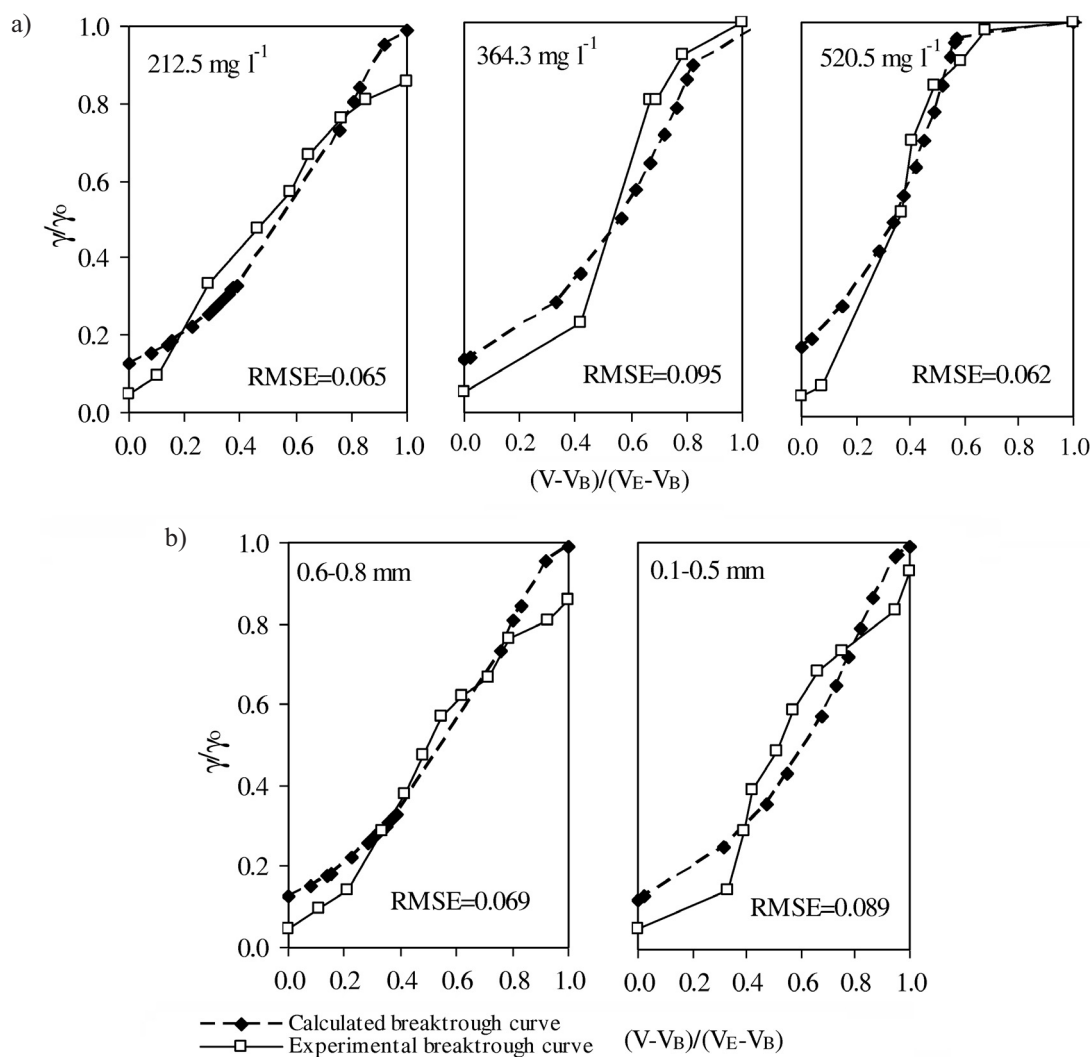


Fig. 6 – Comparison of breakthrough curve obtained from the Langmuir isotherm equations with the experimentally obtained breakthrough curves for: a) different initial lead concentrations, b) the two particle sizes of zeolite

Table 2 – Calculations of the overall mass transfer coefficient  $K_a$  and height of the mass transfer zone  $h_z$

	$\tau$	N	$G_w$	$K_a$	Langmuir		Freundlich		$h_z$ exp.
					$\int_{\gamma_B}^{\gamma_E} \frac{d\gamma}{\gamma(\gamma - \gamma^*)}$	$h_z$ calc.	$\int_{\gamma_B}^{\gamma_E} \frac{d\gamma}{\gamma(\gamma - \gamma^*)}$	$h_z$ calc.	
$\gamma_0, \text{ mg l}^{-1}$									
212.5	0.858	10.54	12.73	1166	2.775	3.03	2.528	2.76	2.84
364.3	0.807	10.46	12.73	1158	2.768	3.04	2.355	2.59	2.24
520.5	0.785	9.41	12.73	1042	3.284	4.01	2.997	3.66	2.44
d, mm									
0.6–0.8	0.858	10.54	12.73	1166	2.775	3.03	2.528	2.76	2.84
0.1–0.5	0.760	8.43	11.41	1012	2.581	2.91	2.716	3.06	2.52

Note:  $\gamma_0$  – initial lead concentration,  $\text{mg l}^{-1}$ ; d – particle zeolite size, mm;  $\tau$  – dimensionless time, –; N – number of mass transfer units, –;  $G_w$  – mass flux of solution in  $\text{kg min}^{-1} \text{m}^{-2}$ ;  $K_a$  – overall mass transfer coefficient,  $\text{kg min}^{-1} \text{m}^{-3}$ ;  $h_z$  – height of mass transfer zone, cm.

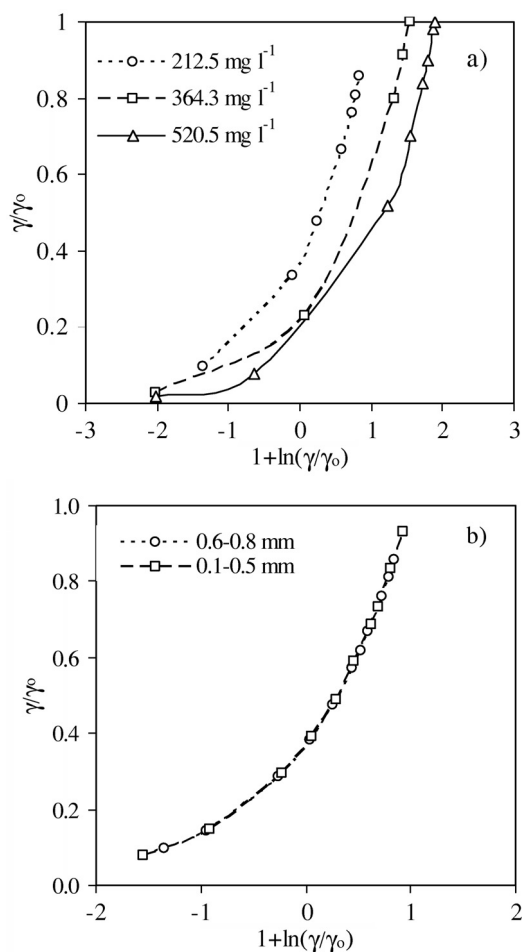


Fig. 7 – Plots of  $\gamma/\gamma_0$  vs.  $1+\ln(\gamma/\gamma_0)$  for: a) different initial concentrations and zeolite particle size of 0.6–0.8 mm, b) two different particle sizes and initial lead concentration of  $212.5 \text{ mg l}^{-1}$

agreement with the values of  $h_z$  calculated according to the Mass Transfer Model (see Table 2), indicating validity of calculated  $K_a$  values.

The Mass Transfer Model allows reaching the necessary data for column design based on batch experiments. This is very important because a batch experiment can be performed quicker and cheaper in relation to tests carried out in a column, which other models usually require.

## Conclusions

The design approach, based on a batch experiment is presented. The Mass Transfer Model has been applied to the experimental data of a batch experiment, in order to predict the breakthrough curve for lead removal onto a fixed bed of zeolite. Good agreement between experimental and calculated breakthrough curves indicates that the Mass Transfer Model is applicable for prediction of the breakthrough curve from batch experiments.

The overall mass transfer coefficient has been evaluated for different zeolite particle sizes and initial lead concentrations. This value permits calculation of the height of the mass transfer zone as a very important parameter required for column design.

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