THE EFFECT OF AXIAL DISPERSION ON LEAD REMOVAL ON THE FIXED BED OF NATURAL ZEOLITE

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ABSTRACT

In this study, the dispersed plug flow model has been applied in order to analyse the effect of axial dispersion on lead removal on the fixed bed of natural zeolite. The axial dispersion coefficient and time to saturate the bed per transversal area unit were determined. These parameters were related to process variables such as the flow rate and initial solute concentration, bed depth and particle size of zeolite.

Keywords: axial dispersion, lead, natural zeolite, dispersed plug flow model.

INTRODUCTION

Axial dispersion is one of the mechanisms responsible for broadening of concentration profiles in the fixed bed. Therefore the operational column conditions should be selected in such a way as to minimise its influence. An attempt was made here to apply the dispersed plug flow (DPF) model to analyse the effect of axial dispersion on the breakthrough curve dynamics of lead removal on the fixed bed of natural zeolite [1, 2]. The axial dispersion coefficient was determined for process variables such as the flow rate and initial solute concentration, bed depth and particle size of zeolite.

Theoretical background of the model Modelling of the breakthrough curve was achieved by assuming a dispersed plug flow model with an axial dispersion coefficient D_L . The model is described by the differential mass balance equation given below [1,2]:

$$v_{i}\frac{\partial c}{\partial z} - D_{L}\frac{\partial^{2} c}{\partial z^{2}} + \frac{\partial c}{\partial t} + \left(\frac{1-\varepsilon}{\varepsilon}\right)\frac{\partial q}{\partial t} = 0$$
(1)

where:

 v_i - interstitial velocity of the solution, m/h

c - solute concentration in the solution, mmol \mbox{Pb}/\mbox{l}

- q solute concentration on zeolite, mmol Pb/l
- z distance from the inlet of the column, m
- ϵ void fraction of the fixed bed, -
- t operating time, h.

The proposed model is based on the following assumptions: (1) constant temperature and flow rate inside the column, (2) no chemical reaction occurs in the column, (3) only mass transfer by convection is significant, (4) radial dispersion is negligible. For a long fixed bed and with a constant inlet concentration c_0 , initially the effluent is free of solute, and the solution of equation (1) can be expressed as:

$$\frac{c}{c_0} = \frac{1}{2} \left\{ 1 + \operatorname{erf}\left[\left(\frac{v_i \cdot H}{4 \cdot D_L} \right) \frac{V - V_{\min}}{\left(V \cdot V_{\min} \right)^{1/2}} \right] \right\}$$
(2)

where:

erf - error function

V- total volume referred to the transversal area unit of the void bed, $V = v \cdot \varepsilon \cdot t$, $m^3/m^2 V_{min}$ - minimum volume to saturate the bed per transversal area unit, $V = v \cdot \varepsilon \cdot t_{min}$, m^3/m^2

 t_{min} - minimum time to saturate the bed per transversal area unit, h

H - bed depth, m.

Equation (2) includes two adjustable parameters, D_L and $V_{min.}$ These parameters were determined by fitting the experimental data to a derived form of equation (2) using non-linear regression analysis in the MathCAD Professional program.

$$\frac{\mathrm{d}}{\mathrm{d}\mathrm{Y}} = \sum_{i=1}^{n} \left\{ \mathbf{f}_{i} - \left[\frac{1}{2} \cdot \left(1 + \mathrm{erf}\left((\frac{\mathrm{v} \cdot \mathrm{H}}{4 \cdot \mathrm{D}_{\mathrm{L}}}) \cdot \frac{\mathrm{V}_{i} - \mathrm{V}_{\mathrm{min}}}{(\mathrm{V}_{i} \cdot \mathrm{V}_{\mathrm{min}})^{1/2}} \right) \right) \right] \right\}$$
(3)

where:

 $Y = adjustable parameters D_L and V_{min}$

 $f_i = c/c_o$

n = number of experimental points.

EXPERIMENTAL

The natural zeolite sample containing ≈ 80 % of clinoptilolite originated from the Vranjska Banja (Serbia) deposit. The sample was crushed and sieved to two particle size fractions of 0.6-0.8 mm 0.1-0.5 mm, and dried at 60°C. The column experiments were performed using two glass columns with the inner diameter of 12 mm and height of 500 mm filled with zeolite samples up to 115 mm. The void fractions of the beds filed with particle size fractions of 0.6-0.8 mm and 0.1-0.5 mm were 0.693 and 0.659, respectively. Service cycles were performed by passing the 1.026 mmol/l of lead solution through the fixed zeolite bed using the down flow mode with the 0.06 l/h flow rate. The effect of flow rates (Q= 0.06-0.18 l/h), initial lead concentrations (c_0 =1.026-2.513 mmol Pb/l) and bed depths of zeolite (H=40 - 115 mm) have been investigated for the particle size fraction of 0.6-0.8 mm. At selected time intervals the lead concentration in the effluent was determined complexometrically in the acid medium, using a highly selective indicator methylthymolblue [3]. After each service cycle, regeneration was performed with the solution of NaNO₃ [4].

RESULTS AND DISCUSSION

The testing of the model by non-linear regression analysis was done with two forms of the derived form of equation (3): one by variable D_L , the other by variable V_{min} . Using the number of experimental results from i = 1 to n, for each initial lead concentration and flow of the solution, particle size and fixed bed depth of zeolite, the solutions of these equations were parameters D_L or V_{min} . A statistical assessment of the agreement between experimental and calculated breakthrough curves was made by computing absolute errors (E) and root mean square errors (RMSE) using the followings equations:

$$E = \frac{\sum \left| (c/c_0)_{\exp} - (c/c_0)_{\text{model}} \right|}{n} \cdot 100$$
(4)

$$RMSE = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n} \left[k/c_{o} - \frac{1}{2} - \frac{1}{2} \right]}.$$
(5)

The parameters D_L and V_{min} calculated by means of non-linear regression are presented in Table 1. To estimate the validity of the evaluated parameters it is necessary to complete modelled breakthrough curves. The parameters D_L and V_{min} are inserted into equation (2) for randomly chosen values of V, and modelled curves are obtained, presented and compared with experimental breakthrough curves in Figures 1 and 2.

			$D_{Lmodel} \cdot 10^5$	V _{min}	t _{min}	Е,	DMSE	+ *
Experimental conditions			m²/h	m^3/m^2	h	(%)	KNISE	t [•] _{min}
co	Q	Н						
mmol/l	l/h	mm						
1.026	0.06	115	27.0	45.92	86.47	2.10	0.039	79.58
1.759	0.06	115	5.6	29.59	55.72	0.29	0.007	54.28
2.513	0.06	115	5.0	18.51	34.85	0.81	0.020	32.43
Q	co	Н						
l/h	mmol/l	mm						
0.06	1.026	115	27.0	45.92	86.47	2.10	0.039	79.58
0.12	1.026	115	34.0	44.94	41.57	2.67	0.059	38.76
0.18	1.026	115	44.0	39.65	24.88	1.27	0.022	23.31
particle	co	Q						
size mm	mmol/l	l/h						
0.1-0.5	1.026	0.06	26.0	44.20	83.25	2.10	0.039	78.67
0.6-0.8	1.026	0.06	27.0	45.92	86.47	1.92	0.033	79.58
Н	co	Q						
mm	mmol/l	1/h						
115	1.026	0.06	27.0	45.92	86.47	2.10	0.039	79.58
80	1.026	0.06	26.0	27.50	51.68	1.75	0.030	45.83
40	1.026	0.06	19.0	13.90	26.12	1.47	0.027	20.42
t_{min}^* - experimentally obtained value of t_{min}								

Table 1. Parameters of the DPF model.



Figure 1. Comparison of experimental (points) and breakthrough curves calculated by the model (line) for different: a) initial lead concentrations, b) flow rates of the lead solution.

From the obtained value of V_{min} , the minimum time necessary to saturate the bed per transversal area unit t_{min} has been calculated (Table 1). These values are in very good agreement with the experimental ones, t^*_{min} . These imply that the DPF model can be used to

analyse the effect of axial dispersion on the breakthrough curve dynamics of lead removal on the fixed bed of natural zeolite.



Figure 2. Comparison of experimental (points) and breakthrough curves calculated by the model (line) for different: a) bed depths, b) particle sizes of zeolite.

CONCLUSION

The DPF model can be used to analyse the effect of axial dispersion on the breakthrough curve dynamics of lead removal on the fixed bed of natural zeolite. The results show that the axial dispersion coefficient (D_L) doesn't change in the examined ranges of zeolite particle size. The increase of bed depth and flow rate increases the axial dispersion coefficient, but decreases the time necessary to saturate the bed per transversal area unit (t_{min}). Although Table 1 shows a significant decrease of value D_L with the increase in concentration, this effect is attributed to better mass transfer due to a higher concentration gradient on the liquid-solid interface. Among all examined system variables, the axial dispersion resistance depends on the flow rate.

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