

Testing of Breakthrough Curves for Removal of Lead Ions from Aqueous Solutions by Natural Zeolite-Clinoptilolite According to the Clark Kinetic Equation

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Abstract: The kinetics of removal of lead ions from aqueous solutions using the column method with a fixed bed of natural zeolite clinoptilolite has been examined. Experimental results are presented as breakthrough curves, and tested according to the kinetic equation developed by Clark by means of the linear and non-linear regression analysis. Both mathematical methods attain the same values for parameters A and r of the Clark equation. These parameters are used for the calculation of the sorption rate coefficient k and the removal capacity q . The removal capacity obtained from the experimental results and the capacity calculated using the Clark kinetic equation have shown excellent agreement. The Clark kinetic equation has been found suitable for description of removal of lead on zeolite for different experimental conditions. Based on the calculated parameters, the theoretical breakthrough curves have been plotted and compared with the experimental ones. Applicability of the kinetic equation used has been additionally confirmed by the good fit of experimental and modelled breakthrough curves. Based on the parameters calculated, the behavior of modelled breakthrough curves was predicted for different depths of fixed bed of zeolite.

Keywords: Lead, natural zeolite, clinoptilolite, breakthrough curve, Clark equation

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INTRODUCTION

Water is one of most important natural resources, and its pollution is commonly associated with the discharge of effluents from sewers or sewage treatment plants, drains, and industrial plants to the water body of rivers, seas, and marines. Heavy metals are a group of most dangerous pollutants in natural waters and have become a global problem in their treatment. There are too many sources of heavy metal pollution, including coal, mining, metal finishing, electroplating and paper industries. In response to the growing problems, competent organizations have instituted environmental regulations to protect the quality of surface and ground water. The main role in the prevention of pollution by heavy metals is played by wastewater treatment before discharge into the environment (1–3). Among all conventional methods for removal of heavy metal ions from wastewater, the tertiary treatment using adsorption and ion exchange on natural zeolite has become a very efficient one. Zeolites are hydrated aluminosilicate minerals characterized by an outstanding capability of exchange of alkaline and earth-alkaline cations from their structure by cations from aqueous solutions. Natural zeolites are widely spread, easy, and cost-effective for exploitation, therefore the research into their application is of great scientific and practical interest (4–6). The uptake of heavy metal ions on natural zeolite takes place mostly by the mechanism of ion exchange, where adsorption also participates in dependence on the concentration and the pH of the solution (7). The adsorption on zeolitic particles is a complex process because of their porous structure, inner and outer charged surface, mineralogical heterogeneity, and existence of crystal edges, broken bonds, and other imperfections of the surface (8). The examination of removal of heavy metals on natural zeolites is often performed using the column method, where the contaminated solution passes through a fixed bed of natural zeolite at defined particle size, flow and concentration of the solution. The results of examinations are presented by breakthrough curves for exact experimental conditions. It is very complicated to predict theoretical breakthrough curves for varying experimental conditions because the behavior and the shape of the curves depend on many factors, including the flow rate and concentration of the solution, characteristics of adsorption/ion exchange equilibrium, and the diffusion mechanism through the fixed bed and through zeolitic particles. The mass transfer of exchangeable ions through the fixed bed and on the solid-liquid interface can be described mathematically by a system of differential equations, defined by their initial and final conditions. Attempts have been made, based on experimental results, to develop equations that describe the removal of metal ions by the fixed bed of natural zeolite. In literature, several models have been proposed to describe the breakthrough curves in the column method (9, 10). Among them, Clark proposed an evaluation of the breakthrough curve expressed through a generalized logistic function, which includes the n parameter of the Freundlich isotherm (11–13). It is

therefore necessary to perform the testing of the equilibrium points from experiments in the column by the Freundlich isotherm to obtain exponent n .

According to literature, the kinetic equation proposed by Clark is usually tested on experimental data by means of non-linear regression analysis, such as for biosorption of phenol on active mud, biosorption of organic pollutants by biomass, removal of Cr(VI) by Chitin, and cementation of cadmium ions by zinc powder, etc. (14–17). However, the testing of the Clark equation by means of the linear regression analysis is found for paint removal on beech sawdust treated by calcium chloride, for removal of natural organic matter on activated carbon, and for removal of methylene blue by cedar sawdust (18–20). This was interesting because the testing by linear regression analysis is faster, easier, and less complicated. As far as we know, this study is the first attempt to use the Clark equation to describe the behavior of breakthrough curves in the zeolite—aqueous heavy metal ions solution system.

In this study, the experimental points of breakthrough curves for removal of lead on natural zeolite taken from our previous study (21), were tested by the kinetic equation developed by Clark. The experimental data have been tested by means of the linear least squares method and non-linear trial-and-error method. The effect of the method used to solve the values of model parameters has been discussed. The parameters evaluated from the Clark equation have been used for determination of the sorption rate coefficient and removal capacity. The kinetic equation can be used for calculation and plotting of theoretical breakthrough curves corresponding to other experimental conditions, what is confirmed with new experiments at lower bed depths.

MATERIALS AND METHODS

Zeolite Sample

The natural zeolite sample originated from the Vranjska Banja deposit (Serbia). The qualitative mineralogical analysis performed on the Philips-CubiX XRD type diffractometer (CuK α radiation, $2\theta = 0-60$, $0.03\ 2\theta/s$) has shown the main mineralogical component ($\approx 80\%$) to be clinoptilolite (21, 22). The chemical composition of the zeolite sample was determined by chemical analysis of the aluminosilicate (23). The sample was crushed and sieved to the particle size 0.6–0.8 mm, and then rinsed with doubly distilled water to remove possible impurities. After drying at 60°C, the sample was placed in the desiccator.

Column Studies

The experiments were performed in a glass column with the inner diameter of 12 mm and a height of 500 mm. The column was filled with the zeolite sample

up to the height of 11.5 cm, which corresponds to bed volume of 13 cm³. The sample was carefully placed in the column to prevent retention of air among the particles, which made the bed more compact. The experiments were performed at isothermal conditions ($25 \pm 2^\circ\text{C}$), with varying initial concentrations ($c_0 = 212.5 - 520.5$ mg Pb/l) and flow rates of the solution through the column ($Q = 0.06, 0.12, 0.18$ l/h). Different initial concentrations were prepared by dissolving precisely weighted quantity of $\text{Pb}(\text{NO}_3)_2$ in doubly distilled water without arranging the initial pH value. The exact lead concentrations were determined complexometrically, using the highly selective indicator, methylthymolblue (24). Binding of lead ions on the zeolite bed in the column took place when the lead solution passed from the top of the column through the zeolite bed (the so-called down-flow mode), with a vacuum pump maintaining the constancy of the flow. Lead concentrations in the effluent were determined at selected time intervals. The process was interrupted when Pb^{2+} concentration in the effluent became equal to the initial concentration in the influent.

The experimentally obtained breakthrough curves for lead removal on zeolite have been taken from our previous study (21). An additional experiment were performed with lower bed depths of 8 cm and 4 cm, at initial concentration of 212.5 mg Pb/l, and flow rate of 0.06 l/h, following the same experimental procedure described above.

Mathematical Description

Determination of Equilibrium Parameters in the Fixed Bed Column

The quantity of heavy metal ions bound on natural zeolite at the equilibrium q_e corresponds to the maximum capacity of the zeolite in exhaustion point q_E , and it is defined as the total amount of lead ions bound per gram of zeolite at the exhaustion time (14):

$$q_e = q_E = n_E/m \text{ [mmol/g]}, \quad (1)$$

where n_E – quantity of lead ions bound during the process in the column, mmol and m – the mass of zeolite, g.

The concentration of lead that remains unbound at equilibrium (c_e) corresponds to the area under the breakthrough curve, and can be defined as:

$$c_e = (n_T - n_E)/V_E \text{ [mmol/l]}, \quad (2)$$

where n_T – total amount of lead ions sent to the column, mmol; n_E – total amount of lead ions bound in a fixed bed of zeolite, mmol; and V_E – effluent volume at the point of exhaustion, l.

The total quantity of lead ions bound in a fixed bed of zeolite for a given feed concentration and flow rate through the column is determined by

integration of the area above the breakthrough curve, and can be calculated according to the equation:

$$n_E = Q \cdot \int_0^{t_E} (c_o - c) dt \text{ (mmol)}, \quad (3)$$

where c_o – initial concentration of the lead, mmol/l; c – concentration of the lead in the effluent, mmol/l; Q – flow rate, l/h; t – time, h; and t_E – time necessary to reach the point of exhaustion of the zeolitic bed, h.

The total amount of lead ions sent to the column (or loading into the column) is calculated by:

$$n_T = c_o \cdot Q \cdot t_E \text{ (mmol)}. \quad (4)$$

The effluent volume (V_E) can be calculated from the equation:

$$V_E = Q \cdot t_E \text{ (l)}. \quad (5)$$

The total lead removal percent is the ratio of the total quantity of lead removed until exhaustion (n_E) to the total amount of lead sent to the column (n_T), and is given by the equation:

$$\text{Total removal (\%)} = (n_E/n_T) \cdot 100. \quad (6)$$

Various simple mathematical models have been developed to describe or even to predict the dynamic behavior of the removal of lead ions from the solution using experimental data of the column method. In the following text, the kinetic equation developed by Clark has been discussed in detail.

Application of the Clark Kinetic Equation to the Breakthrough Curve

The kinetic equation developed by Clark assumes that the sorption behaviour of pollutants follows the Freundlich adsorption isotherm, and the sorption rate is determined by the outer mass transfer step (17). Using the mass transfer coefficient concept within a differential depth of the bed, dh yields (12):

$$v \frac{dc}{dh} = K(c - c_e) \quad (7)$$

where h – bed depth, m; K – mass transfer coefficient, h^{-1} ; and v – linear velocity, m/h.

Clark has resolved this system and obtained the following solution (12–14), (17–20):

$$\left(\frac{c}{c_o}\right)^{n-1} = \frac{1}{1 + Ae^{-rt}}, \quad (8)$$

where A and r are parameters of the kinetic equation. The previous equation is a generalized logistic function that mathematically describes the S-shape of the breakthrough curve, and it has been modified by Clark by incorporation

of n that corresponds to the exponent of the Freundlich isotherm, which is calculated from the Freundlich and Langmuir-Freundlich equations (15):

$$q_e = \frac{abc_e^{1/n}}{1 + bc_e^{1/n}} \quad (9)$$

$$q_e = K_F c_e^{1/n} \quad (10)$$

Due the similarity of ion exchange and adsorption, the adsorption isotherms can be used for description of both processes, which are commonly named sorption. The Langmuir-Freundlich model is essentially the Freundlich isotherm that approaches homogeneous sorption of the solute including the interaction with the solid surface, and the maximum removal at high concentration of the solution (15). In equation (9), constants a and b are related to monolayer capacity and energy of sorption.

For a particular process on a fixed bed and a chosen treatment objective, the values of A and r can be determined from equation (8) by linear and non-linear regression analysis. These parameters are used additionally for calculation of the sorption rate coefficient (k) and the capacities of removal (q and q_m) that can be estimated from the A and r values (19):

$$\ln A = h \cdot k \cdot q / \nu \quad (11)$$

$$q_m = q \cdot V_{BS} / m \quad (12)$$

$$r = k \cdot c_o, \quad (13)$$

where the linear velocity ν is calculated as the ratio of flow rate and cross section area.

RESULTS AND DISCUSSION

Lead removal in fixed bed of natural zeolite clinoptilolite was examined for conditions of different initial concentrations and flow rates of the lead ions solution (19). Table 1 shows the equilibrium results expressed in terms of quantity of lead removed at equilibrium per gram of zeolite in q_e , concentration of lead remaining in the solution c_e , and total removal percentage, calculated according to equations (1, 2), and (6).

At higher initial concentrations and higher flow rates, the volume of treated solution at the exhaustion point as well as exhaustion time decreases so the zeolite becomes exhausted earlier. The percentage of total removed lead ions on zeolite is high (from 89.50% to 95.66%) for all initial concentrations and flows of the solution through the column. The equilibrium points of the breakthrough curves, shown in Table 2, were tested by means of the Langmuir-Freundlich (L/F) and Freundlich (F) empirical adsorption isotherms shown by equations (9) and (10). Test was performed by non-linear regression analysis using MS MathCAD Professional. The same

Table 1. Calculated equilibrium parameters for removal of lead ions in a fixed bed of natural zeolite, for different experimental conditions

Experimental condition		t_E (h)	V_E (l)	n_E (mmol)	n_T (mmol)	Total removal (%)	q_E (mmol/g)	c_e (mmol/l)
c_0 (mg Pb/l)	c_0 (mmol Pb/l)							
212.5	1.026	98.32	5.899	5.428	6.051	89.70	0.597	0.106
212.5	1.026	96.92	5.815	5.339	5.965	89.50	0.585	0.108
364.3	1.759	60.70	3.642	5.856	6.405	91.43	0.644	0.151
520.5	2.513	36.04	2.162	5.196	5.432	95.66	0.574	0.109
Q (l/h)	Q (BV/h)							
0.06	4.62	96.92	5.815	5.339	5.965	89.50	0.585	0.108
0.12	9.23	43.00	5.161	5.052	5.295	95.40	0.555	0.047
0.18	13.85	26.86	4.834	4.597	4.960	92.69	0.505	0.075

Table 2. Parameters of the Clark equation calculated using the linear and non-linear regression analysis

Experimental condition		Linear regression analysis					Non-linear regression analysis					
		A (-)	r (h ⁻¹)	k (l/mmol h)	q _m (mmol/g)	R ²	A (-)	r (h ⁻¹)	k (l/mmol h)	q _m (mmol/g)	RMSE	R ²
c ₀ (mg Pb/l)	Q (l/h)											
212.5	0.06	1.36 · 10 ¹²	0.305	0.297	0.620	0.986	1.90 · 10 ¹²	0.309	0.301	0.618	6.70 · 10 ⁻²	0.975
364.3	0.06	2.08 · 10 ³⁰	1.217	0.692	0.666	0.986	2.08 · 10 ³⁰	1.218	0.692	0.665	1.30 · 10 ⁻²	0.999
520.5	0.06	1.39 · 10 ²⁸	1.805	0.718	0.595	0.979	1.39 · 10 ²⁸	1.805	0.718	0.595	3.50 · 10 ⁻²	0.994
Q (l/h)	c ₀ (mg Pb/l)											
0.06	212.5	1.36 · 10 ¹²	0.305	0.297	0.620	0.986	1.90 · 10 ¹²	0.309	0.301	0.618	6.70 · 10 ⁻²	0.975
0.12	212.5	1.81 · 10 ³¹	1.720	1.676	0.567	0.972	1.81 · 10 ³¹	1.722	1.678	0.565	5.50 · 10 ⁻²	0.990
0.18	212.5	3.99 · 10 ¹⁴	1.319	1.286	0.517	0.977	3.99 · 10 ¹⁴	1.260	1.228	0.540	7.20 · 10 ⁻²	0.987

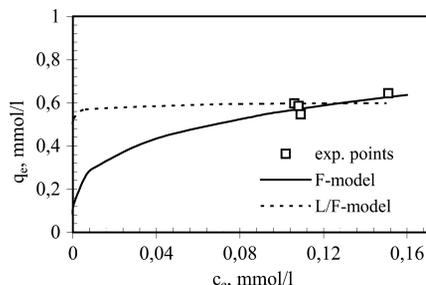


Figure 1. Testing of equilibrium experimental points with the Langmuir-Freundlich (L/F) and Freundlich (F) sorption isotherms.

value of the exponent $n = 3.65$ has been calculated from both isotherms, and their fit to the experimental points is very good which confirms high values of R^2 (Fig. 1). The equation of each isotherm is as follows:

$$q_e = 1.2c_e^{1/3.65} \quad R^2 = 0.991 \quad (14)$$

$$q_e = \frac{45 \cdot 0.62 \cdot c_e^{1/3.65}}{1 + 0.62 \cdot c_e^{1/3.65}} \quad R^2 = 0.990. \quad (15)$$

Testing of the equation (8) with the results from the column experiment ($c/c_o = f(t)$), has been performed by linear and non-linear regression analysis using MS MathCAD Professional. The parameters A and r were calculated using non-linear method, from the derived form of equation (8):

$$\frac{d}{dY} \left[\sum_{i=1}^z \left[f_i - \left(\frac{1}{1 + A \cdot e^{-r \cdot t_i}} \right)^\beta \right]^2 \right] = 0, \quad (16)$$

where $f_i = c/c_o$; $Y =$ adjustable parameter A or r ; $\beta = 1/n - 1 = 0.38$; and $z =$ number of experimental points.

The testing of the Clark model by the non-linear regression analysis was done with two forms of derived equation (13): one by variable A , the other by variable r . Using the number of experimental results from $i = 1$ to z , for each initial concentration and flow of the solution, the solution of these equation were parameters A and r . The correlation coefficient (R^2) was calculated as an indicator of correspondence of the experimental results with the kinetic equation. The root mean square error (RMSE) was also calculated according to the following equation (25):

$$RMSE = \sqrt{\frac{1}{z} \sum_{i=1}^z \left[(c/c_o)_{cal} - (c/c_o)_{exp} \right]^2}. \quad (17)$$

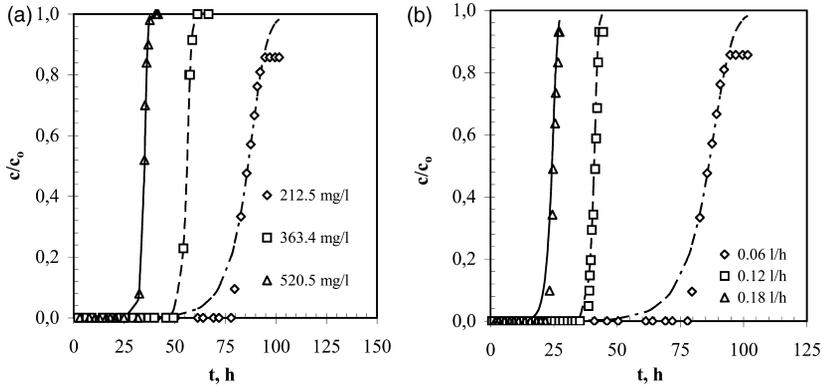


Figure 2. Comparison of experimental values (symbols) with those predicted by the Clark model (lines) calculated using the non-linear regression analysis for a) different initial concentrations of lead in the solution at the solution flow rate of 0.06 l/h, b) different flows through the column at the lead concentration in solution of 212.5 mg/l.

The parameters A and r calculated by means of the non-linear regression analysis, as well as the sorption rate coefficient (k) and removal capacity (q_m) calculated by relations (10) to (12), are presented in Table 2. To estimate the validity of the evaluated parameters it is necessary to completely model the breakthrough curves. The parameters A and r are inserted into equation (8) for randomly chosen values of t, and modelled curves are obtained, presented and compared with experimental breakthrough curves in Fig. 2. These experimental curves are obtained from our previous paper (21).

To solve the Clark equation by means of the linear regression analysis (15), equation (8) is transformed into:

$$\left(\frac{c_0}{c}\right)^{n-1} - 1 = Ae^{-rt}. \tag{18}$$

If equation (18) is made linear:

$$\ln\left[\left(\frac{c_0}{c}\right)^{n-1} - 1\right] = \ln A - rt. \tag{19}$$

From this equation, the values describing the characteristic operational parameters of the column, A and r, are determined from the slope and the intercept of plots of $\ln((c/c_0)^{n-1} - 1)$ versus t that are shown in Fig.3. The values of A and r parameters calculated by the linear regression analysis as well as the corresponding sorption rate coefficient (k) and removal capacity (q_m) have also been calculated by relations (11) to (13), and presented in Table 2.

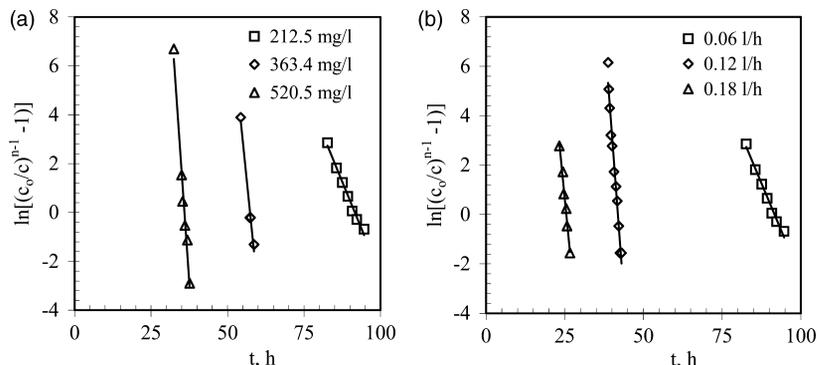


Figure 3. Clark model solved by the linear regression analysis: a) for different initial concentrations at the solution flow rate of 0.06 l/h, b) for different flows through the column at the lead concentration in solution of 212.5 mg/l.

Fitting of the experimental and modelled breakthrough curves in Fig. 2 and straight lines on the Fig. 3, indicates an excellent applicability of the Clark kinetic equation that is confirmed by high values of the square correlation coefficient (R^2) (Table 2), and with satisfactory fitting of experimental (q_E) and calculated capacities (q_m), for both methods of solving of equation (8), by linear and by non-linear regression. The similarity of parameters A and r given for linear and non-linear method yields almost identical modelled curves; therefore, Fig. 2 presents only curves calculated by applying the non-linear regression to equation (8). Figure 2 and Table 2 clearly indicate that at lower initial concentrations and flow rates of the inlet solution there appears a slight disagreement of the experimental points with modelled curves. That assumes the existence of a restricted area of experimental conditions (bed depth, flow rate, initial concentration, zeolite particle size) in which the Clark equation can describe the behavior of this system. Furthermore, it was interesting to find out how the change of one experimental condition such as bed depth (h) affected the change of position and shape of the modelled breakthrough curve plotted by evaluated Clark equation. For this purpose we have plotted the modelled curves for the decrease of bed depth from 11.5 cm to 8 cm and 4 cm.

Parameters A and r calculated in Table 2 are plotted in dependence of different flow rates i.e., empty bed contact time (EBCT) (Fig. 4). In order to provide modelled curves for different bed depths the values have been calculated for EBCT for bed depths of 8 cm and 4 cm using equation (20). These values of EBCT are in the range of experimentally obtained values on the x-axis in Fig. 4. From the plot A and r versus EBCT, the values of A and r were evaluated for each bed depth. These data are given in Table 3.

$$\text{EBCT} = h/v = h \cdot S/Q. \quad (20)$$

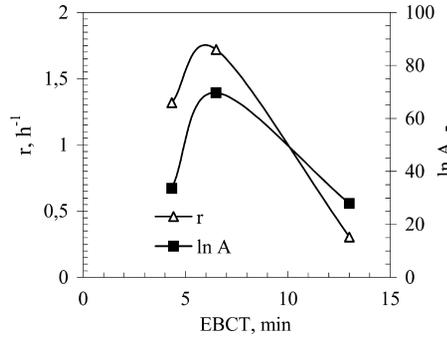


Figure 4. Dependence of parameters A and r of examined EBCT.

The parameters A and r evaluated for h = 8 cm and h = 4 cm have been inserted into equation (21) for randomly chosen values of t, the modelled curves have been obtained and presented in Fig. 5.

$$\frac{c}{c_0} = \frac{1}{(1 + Ae^{-r \cdot t_B})^{1/(n-1)}} \tag{21}$$

The validity of these modelled curves has been confirmed by a new experiment made at bed depth of 8 cm and 4 cm, flow rate of 0.06 l/h, and initial concentration of 212.5 mg Pb/l. The experimental (symbols) and modelled curves (lines) in Fig. 5 show a very good fit which is confirmed by the fitting of their breakthrough and exhaustion times, t_B and t_E. From these

Table 3. Parameters of modelled and experimental breakthrough curves for bed depths of h = 8 cm and h = 4 cm

Parameters	Experimental conditions	
	h = 4 cm Q = 0.06 l/h c ₀ = 212.5 mg/l EBCT = 4.52 min	h = 8 cm Q = 0.06 l/h c ₀ = 212.5 mg/l EBCT = 9.04 min
ln A, -	35	56
r, h ⁻¹	1.35	1.10
t _B , h (model)	20.17	40.26
t _B , h (exp)	20.42	40.66
t _E , h (model)	35.74	56.90
t _E , h (exp)	31.83	58.50
q _m , mmol/g	0.549	0.556
q _E , mmol/g	0.554	0.539

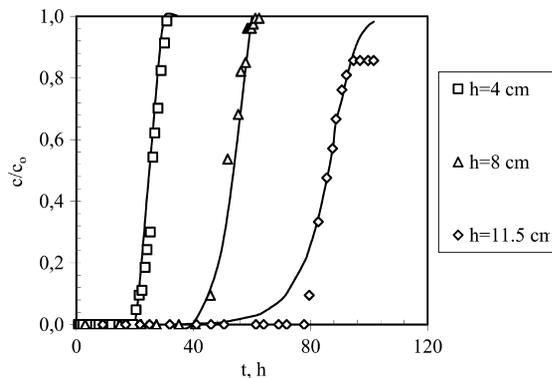


Figure 5. Comparison of experimental (symbols) and modelled curves (lines) at different bed depths $h = 11.5$ cm, $h = 8$ cm and $h = 4$ cm, ($Q = 0.06$ l/h, $c_0 = 212.5$ mg/l).

examinations, it is clear that the applicability of the Clark equation to this system is possible in the examined range of flows i.e., empty bed contact time, and initial concentrations for which their dependence on parameters A and r have been defined, as shown in Fig. 4. Moreover, this makes it possible to predict the breakthrough curves without experimental performance.

CONCLUSIONS

The removal of lead ions from aqueous solution was successfully performed by a fixed bed of natural zeolite clinoptilolite. The breakthrough curves have a typical “S” shape, and the calculated percentage of total removal of lead is satisfactory for all examined initial concentrations of lead ions and flows of the solution, and equals 89.50%–95.66%. The testing of experimental breakthrough curves by the Clark kinetic equation has shown excellent fitting of experimental points with modelled curves. The linear and the non-linear method of solving of the equation yields almost identical values of parameters A and r , which means similar values of the sorption rate coefficient and removal capacity. The excellent fit of the experimental obtained capacity q_E and calculated capacity q_m , additionally confirms the suitability of the Clark equation for mathematical description of experimental points. The predicting of the breakthrough curve using the Clark equation at decreased bed depths was successfully performed. The validity of predicted breakthrough curves is confirmed by the fitting of modelled curves with new experimental points at the bed depth of 8 cm and 4 cm. Therefore the examined kinetic equation can be used for predicting of the shape of the breakthrough curves for a restricted examined interval of experimental conditions. It is important

for scaling up of the process, where the ratio of the dimensions has to remain constant if the value of the empty bed contact time remains in the range of experimentation in laboratory scale.

NOMENCLATURE

a	constant in the Langmuir-Freundlich equation
A	parameter of the Clark equation, –
b	constant in the Langmuir-Freundlich equation
c	concentration of lead in the effluent, mmol/l
c_o	concentration of lead in the influent, mmol/l
c_e	concentration of lead that remains in the effluent at equilibrium, mmol/l
EBCT	empty bed contact time, min
h	bed depth, m
K	mass transfer coefficient, h^{-1}
K_F	constant in the Freundlich equation, –
k	sorption rate coefficient, l/mmol h
m	the mass of the zeolite, g
n	exponent of the Freundlich isotherm, –
n_E	quantity of lead removed until exhaustion point, mmol
n_T	total quantity of lead sent to the column, mmol
Q	flow rate, l/h
q_e, q_E	maximum experimental removal capacity, mmol/g
q	calculated removal capacity, mmol/l
q_m	calculated removal capacity, mmol/g
r	parameter of the Clark equation, h^{-1}
S	cross sectional area of the bed, m^2
t	service time, h
t_B	breakthrough time, h
t_E	exhaustion time, h
V_E	total effluent volume in the point of exhaustion, l
V_{BS}	bed volume, l
v	linear velocity, m/h
z	number of experimental points, –

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