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Column performance in lead removal from aqueous solutions by fixed bed of natural zeolite–clinoptilolite

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Abstract

The aim of this investigation is removal of lead ions from aqueous solutions using the column method with more successive service and regeneration cycles. The experiments were performed at constant temperature and dimensions of column and fixed bed of zeolite, with variation of zeolite particle sizes and flows through the bed, concentrations of lead solutions and the regenerate. Eight service and regeneration cycles were performed without changes of the breakthrough and exhaustion capacity. The highest effectiveness of the column performance has been attained for the zeolite particle size of 0.6–0.8 mm, at the initial concentration of 212.5 mg Pb/L and the flow rate of 2 mL/min. At these experimental conditions, the optimal values of the empty bed contact time and high of the mass transfer zone have been achieved.
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Keywords: Lead; Ion exchange; Column method; Natural zeolite; Clinoptilolite

1. Introduction

Heavy metals are dangerous for living organisms because of their stability, toxicity and tendency to accumulating in the environment. The industrial wastewaters are considered to be the main source of heavy metal impurities. Their purification prior to discharge into a recipient is, therefore, necessary. Various chemical and physico–chemical methods for heavy metal removal are known, such as chemical precipitation, adsorption, solvent extraction, ultrafiltration, ion exchange [1–4]. Ion exchange takes a special place, primarily as inexpensive natural materials, such as zeolites, can be used. Zeolites are widely spread in nature and the costs of their exploiting are low. Exchangeable cations in the zeolite structure, K, Ca, Na, and Mg, are not toxic, which makes the natural zeolites especially suitable for tertiary processes of wastewater treatment [3,5–9]. Additionally, many studies indicate it is possible to use zeolites saturated by heavy metals as additives to cement and similar materials, without adverse effects to the environment and mechanical properties of concrete [10,11].

Many researchers have studied the kinetics and the equilibrium of the metal ion exchange process on natural zeolites, using the batch method and the column method [12–17]. However, there are few studies dealing with the exchange in a column with several service and regeneration cycles [18–21]. It makes possible multiplied using of the same zeolite sample. This procedure yields a regenerate of a much smaller volume relative to the volume of the original wastewater, with much higher concentration of the metal ion. The metal ion from such concentrated solutions can be reused [8,22].

Taking into account numerous sources of lead contamination, e.g. production of petroleum products, accumulators, batteries, paints [23,24], etc., this study has examined lead removal by ion exchange on natural zeolites. The examinations were carried out on a column with multiple alternating work and regeneration cycles. The process parameters have been defined and their effects on zeolite capacity during the cycle have been examined.

2. Experimental

2.1. Zeolite sample

The natural zeolite sample originated from the Vranjska Banja (Serbia & Montenegro) deposit. The sample was crushed up and sieved to two particle size fractions: 0.1–0.5, and 0.6–0.8 mm. Each sample was, then, rinsed in doubly distilled water in order to remove possible impurities that might induce

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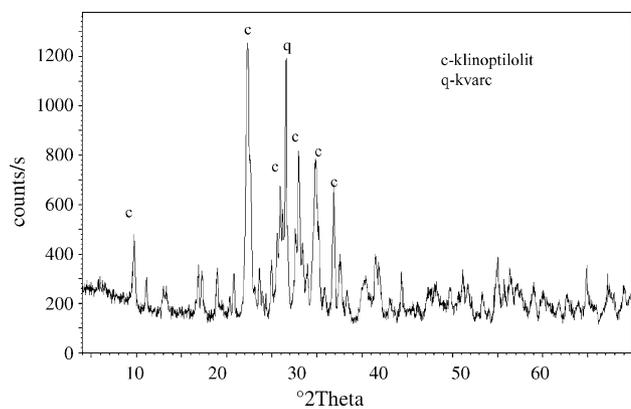*E-mail address:* nvukojev@ktf-split.hr (N.V. Medvidović).

Fig. 1. XRD analysis of zeolite sample. XRD pattern of natural zeolite has been compared with the diffraction pattern for clinoptilolite (reference pattern: 39–1383, 25–1349, 47–1870), taken from the International Center for Diffraction Data (1993) databases.

clogging during the exchange in the column. After drying at 60 °C, the samples were stored in the exsiccator.

The zeolite sample chemical composition was determined by the chemical analysis of aluminosilicates [25], and was, in mass%: SiO_2, 66.36; Al_2O_3, 13.81; Fe_2O_3, 1.69; MgO, 1.03; CaO, 3.65; K_2O, 0.99; Na_2O, 1.03; loss of ignition, 13.40.

The X-ray diffraction method was used for qualitative mineralogical analysis, on a "Philips-CubiX XRD" diffractometer (Cu Kα radiation, $2\theta = 0$–60, 0.03 2θ/s). XRD pattern of natural zeolite has been compared with the diffraction pattern for clinoptilolite (reference pattern: 39–1383, 25–1349, 47–1870), taken from the International Center for Diffraction Data (1993) databases (Fig. 1). Semiquantitative mineralogical analysis has been shown that the major zeolite mineralogical component was clinoptilolite whose part in the sample was ≈80%, and quartz as impurity [26,27].

2.2. Ion exchange

The experiments were carried out in two glass columns with the inner diameter of 12 mm and the height of 500 mm. One column was filled with the 0.6–0.8 mm particle size zeolite sample, the other with the 0.1–0.5 mm particle size zeolite sample. The zeolite bed height was 115 mm in both columns, corresponding to the bed volume of 13 cm³. The sample was put into the column carefully so that no air remained between the particles, which helped attain compact layers.

The examination of Pb^{2+} removal on the zeolite was carried out on solutions with different initial concentrations ($\gamma_0 = 212.5$–520.5 mg Pb/L) prepared by dissolving the exactly weighted quantity of $Pb(NO_3)_2$ salt in doubly distilled water without setting the initial pH value. Exact lead concentrations were determined complexometrically in the acid medium, using a highly selective indicator, methylthymolblue [28].

The experiments were carried out at isothermal conditions ($T = 25 \pm 2$ °C), with variations in initial concentrations and solution flows through the column ($Q = 1$–3 mL/min). The solution was brought to the top of the column, passed through the zeolite fixed bed, and the flow constancy was maintained using a vacuum pump. At selected time intervals, the lead concentration was determined in the out-flowing solution (effluent). The process was stopped, when the Pb concentration in the effluent became equal to the initial concentration in the influent.

After each service cycle of the exchange, a regeneration cycle took place with the solution of sodium nitrate with the concentration of $\gamma(NaNO_3) = 15$ and 30 g/L, by passing the solution from the top of the column through the fixed bed of zeolite (Table 1). The regeneration process was stopped when the Pb ion concentration in the effluent became <0.1 mmol/L.

During ion exchange process, the changes of pH value were measured in the influent and the effluent.

3. Results and discussion

3.1. Qualitative interpretation of breakthrough curves

The results of examinations in the column are represented by breakthrough curves. A breakthrough curve represents the solute outlet concentration versus time (or effluent volume, or BV). The outlet concentration can be expressed as absolute c, or normalized to the inlet concentration c/c_0. Bed volume, BV,

Table 1
Experimental conditions for service cycles and regeneration cycles

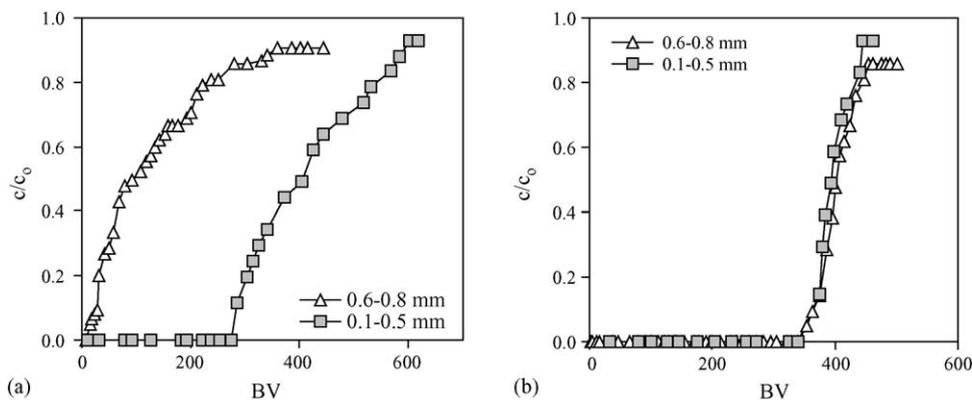| Cycle no.	Service cycle				Regeneration cycle	
	c_0(Pb) (mmol/L)	γ_0 (Pb) (mg/L)	Q (mL/min)	Q (BV/h)	$\gamma(NaNO_3)$ (g/L)	Q (mL/min)
Particle size 0.6–0.8 mm						
1st	1.026	212.5	1.0	4.6	15	
2nd	1.026	212.5	1.0	4.6	15	
3rd	1.026	212.5	1.0	4.6	15	
4th	1.759	364.3	1.0	4.6	15	
5th	2.513	520.5	1.0	4.6	15	1.0
6th	1.026	212.5	2.0	9.2	15	
7th	1.026	212.5	3.0	9.2	15	
8th	1.026	212.5	3.0	13.9	30	
Particle size 0.1–0.5 mm						
1st						
2nd	1.026	212.5	1.0	4.6	15	1.0

Fig. 2. Breakthrough curves of lead removal under conditions $\gamma_0 = 212.5$ mg/L and $Q = 1$ mL/min for both particle size of zeolite sample during: (a) 1st cycle and (b) 2nd cycle.

represents the volume of effluent equal to the volume of packed bed. The breakthrough is the point on the S-shaped curve at which the solute concentration reaches its maximum allowed value (usually 5% of its influent value), and the point of column exhaustion is the point where the effluent concentration reaches 95% of its influent value [29].

3.1.1. The effect of particle size

Fig. 2 shows the breakthrough curves for examined particle sizes, for a solution with the concentration of 1.026 mmol Pb/L and the flow of 1.0 mL/min.

It can be noticed that breakthrough curves in the first cycle for both particle size fractions do not have an expressed S-shape. In the second cycle, after regeneration, the curves assume the typical S-shape and show agreement for both particle size fractions, and breakthrough points are shifted to the right towards higher BV values. This may be explained by establishment of stable exchange condition, better contact of solid and liquid phases, as well as preparation of near homoionic form. The calcium, potassium and magnesium exchangeable ions origin from original sample have been replaced by sodium ions during regeneration. The comparison of the third and second cycle curves for the particle size fraction of 0.6–0.8 mm (Fig. 3), has been shown and confirm that breakthrough behavior remain unchanged with successive regeneration.
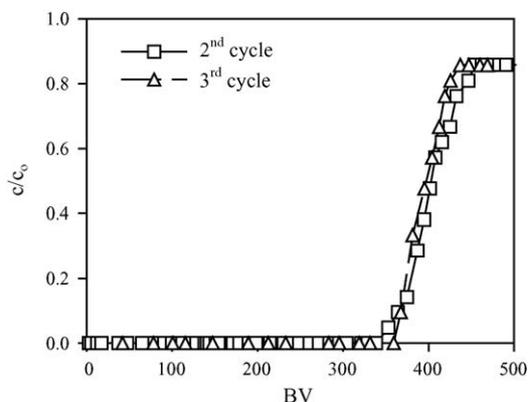

Fig. 3. Breakthrough curves of lead removal during 2nd and 3rd cycles for zeolite particle size 0.6–0.8 mm.
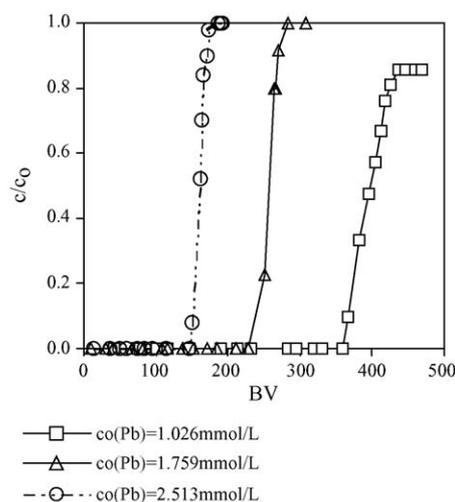

Fig. 4. Breakthrough curves of lead removal for various initial concentrations of lead solution.

3.1.2. The effect of initial concentration

The effect of the initial lead concentration on the breakthrough curve shape has been examined on the zeolite with particle size of 0.6–0.8 mm, with the flow of 1.0 mL/min (Fig. 4).

The comparison of these breakthrough curves shows that when the initial Pb concentration increases from 212.5 to 520.5 mg/L, the breakthrough point is reached earlier, i.e. at lower BV values (from 360 to 147 BV). Therefore, with the increase of initial Pb concentration the zeolite becomes exhausted earlier.

3.1.3. The effect of flow

Fig. 5 shows the breakthrough curves obtained for zeolite with particle size of 0.6–0.8 mm and initial concentration of 1.026 mmol Pb/L at different solution flows. When the flow through the column increases from 1 to 3 mL/min, the breakthrough point is reached earlier, i.e. at lower BV values (from 360 to 303 BV).

The time needed to reach the breakthrough point and the exhaustion point is longer by approximately four times for the flow of 1.0 mL/min than for the flow of 3.0 mL/min (78.0 h in
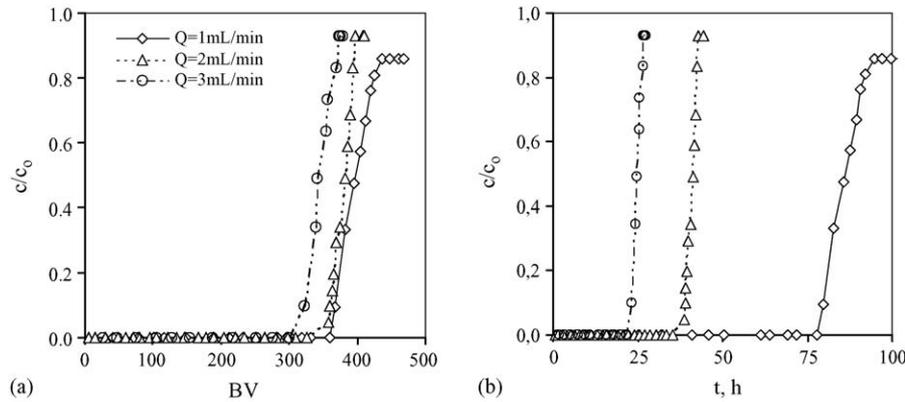
Fig. 5. Comparison of breakthrough curves for different flows through the bed expressed as: (a) c/c_0 vs. BV and (b) c/c_0 vs. t.

compared to 21.9 h) (Fig. 5b). Therefore, the same lead solution volume can be processed in a four-time shorter period.

3.1.4. Regeneration

In order to examine the effect of regeneration on the ion exchange, after each service cycle a regeneration cycle took place with the sodium nitrate solution with the concentration of 15 g/L, and the flow of 1 mL/min. The results are shown in lead elution curves as Pb concentration in the effluent relative to the regeneration solution volume flowed through the bed, expressed by BV. Regeneration achieves elution of bound lead ions and restoration of zeolite for the next service step. As the same elution curves were obtained for all regeneration cycles, Fig. 6a shows the curves for only first-three cycles.

All curves first show a rapid increase in the Pb concentration in the exit solution, followed by a rapid decrease, until the Pb concentration in the effluent reaches <0.1 mmol/L. Only 70–75 BV of the regenerate solution is needed for complete regeneration of the zeolite bed, which is 4–5 times less compared to the lead solution volume each service cycle. Due to reduce volume, the Pb concentration is very high and attains the value of 8000–10 000 mg Pb/L.

The effect of higher regeneration agent concentration was examined using solution of 30 g/L of sodium nitrate. Fig. 6b shows the regeneration curves for different sodium nitrate con-

centrations after 7th and 8th service cycles. The curves obtained are very similar, which indicates that the same regeneration effect can be obtained if half of the regeneration agent quantity is used [30].

3.2. Quantitative interpretation of breakthrough curves

For quantitative interpretation of breakthrough behavior in the column, a method proposed by Michaels was applied [4,11,31]. According to this interpretation, the exchange process occurs in a restricted region of the bed called the mass transfer zone—MTZ that represents the layer between the equilibrium bed zone and the unused bed zone. During the process, as the feed solution containing the solute passes through the fixed bed of packed material, the ion exchange zone moves in the direction of the flow and reaches the exit.

The total (equilibrium) capacity of the bed per unit amounts of the exchanger C_E is defined as the total amount of solute stored in the exchanger (or exchanged during the process of ion exchange in fixed bed of packed materials). It is determined by integration of the area above the S-curve up to the exhaustion point.

$$C_E = \frac{\int_0^{V_E} (c_0 - c)\, dV}{\rho H A} = \frac{\int_0^{V_E} (c_0 - c)\, dV}{m} \quad \text{(mmol/g)}, \qquad (1)$$
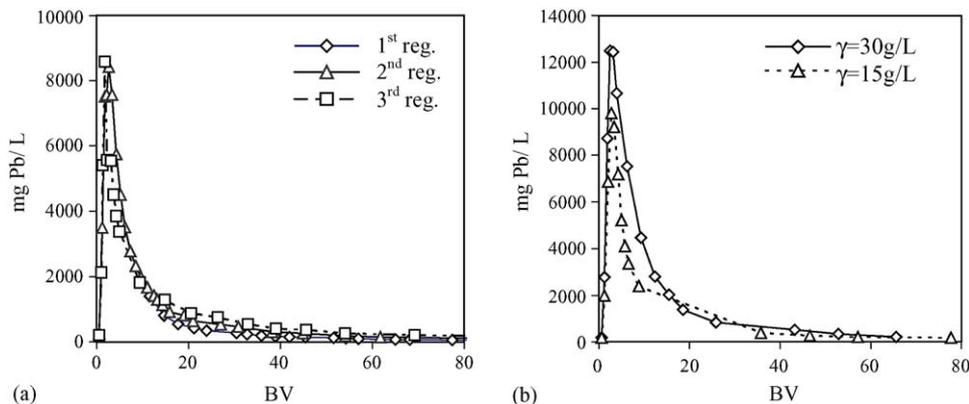

Fig. 6. The elution of lead during regeneration: (a) after 1st, 2nd and 3rd service cycles and (b) for two different concentration of regenerate after 7th and 8th service cycles.

where c_0 is the influent concentration in mmol/L; c the effluent concentration in mmol/L; V_E the effluent volume at which the point of exhaustion of the bed occurs (absolute or normalized to the bed volume) in mL; ρ the packing density of the bed in g/cm^3; H the length of the bed in cm; A the cross-section area of the bed in cm^2; m is the mass of the exchanger in g.

Similarly, the breakthrough capacity C_B of the bed per units amount of the exchanger may be calculated by the following expression:

$$C_B = \frac{\int_0^{V_B}(c_0 - c)\,dV}{\rho H A} = \frac{c_0 V_B}{m} \text{ (mmol/g)}, \tag{2}$$

where V_B is the effluent volume collected up to the breakthrough point in mL.

The degree of saturation or column efficiency η can be calculated as:

$$\eta = \frac{C_B}{C_E}. \tag{3}$$

If t_Z is the time required for MTZ to move through its own length down the bed, t_E the time required for MTZ to become established and move completely out of the bed, and t_F is the time needed for MTZ formation, then, the length h_Z of MTZ is given by the expression:

$$h_Z = v_Z t_Z = H\left(\frac{t_Z}{t_E - t_F}\right) \text{ (cm)}, \tag{4a}$$

where v_Z is the rate of shift of MTZ along the length of the bed.

The times t_Z, t_E and t_F are given by the following expressions:

$$t_Z = \frac{V_E - V_B}{vA} \text{ (min)}, \tag{4b}$$

$$t_E = \frac{V_E}{vA} \text{ (min)}, \tag{4c}$$

$$t_F = (1 - F)t_Z \text{ (min)}, \tag{4d}$$

where v is the feed solution velocity (or linear flow rate through the column) in m^3 m^{-2} h^{-1} and F is the parameter measuring the symmetry of the breakthrough curve.

F is defined by:

$$F = \frac{S_Z}{S_{max}} = \frac{\int_{V_B}^{V_E}(c_0 - c)\,dV}{c_0(V_E - V_B)}$$

$$= \int_0^1 \left(1 - \frac{c}{c_0}\right) d\left(\frac{V - V_B}{V_E - V_B}\right), \tag{5}$$

where S_Z is the amount of solute removed by the exchanger from breakthrough to exhaustion in mmol and S_{max} is the amount of solute removed by the exchanger when the exchanger is completely exhausted in mmol.

The F value varies between 0 and 1. If the MTZ is essentially saturated at breakthrough, the value F will be very close to zero ($F \cong 0$), and the time required for zone formation t_F, will be approximately the same as the time required for the zone to move down a distance equal to its own height t_Z.

If the adsorption zone is practically free of solute at the breakthrough point, and $F \cong 1$, the time required for zone formation is very short. In a rather common case of a symmetrical curve, F is approximately 0.5, and expression (4d) becomes:

$$t_F = 0.5t_Z \text{ (min)}. \tag{6}$$

Rearranging Eqs. (4a)–(4d) provides expressions for the height of the MTZ, as an important design parameter:

$$h_Z = \frac{H(V_E - V_B)}{V_E - (1 - F)(V_E - V_B)} \text{ (min)}. \tag{7}$$

The empty bed contact time, EBCT, or residence time is usually defined as the relation between the length of the bed exchanger in the column and the feed solution velocity [31]:

$$\text{EBCT} = \frac{H}{v} \text{ (min)}. \tag{8}$$

Table 2 shows the results calculated from experimental data according to the above expressions.

The breakthrough point capacity and the exhaustion point capacity in the second cycle, in comparison to the first cycle, are higher for both particle size fractions after regeneration. Although the breakthrough curves in the second cycle for both particle size fractions are identical (Fig. 2b), the calculated

Table 2
Parameters calculated from breakthrough curves

Cycle no.	Breakthrough point (BV)	Breakthrough time (h)	C_B (mmol/g)	C_E (mmol/g)	η	F	h_Z (cm)	EBCT (min)
Particle size 0.6–0.8 mm								
1st	25	5.42	0.036	0.182	0.196	0.331	27.71	13.00
2nd	336	72.80	0.517	0.597	0.867	0.539	2.84	13.00
3rd	360	78.00	0.527	0.585	0.901	0.506	2.24	13.00
4th	228	49.37	0.573	0.644	0.890	0.519	2.44	13.00
5th	147	31.77	0.529	0.574	0.917	0.332	2.88	13.00
6th	358	38.78	0.523	0.555	0.943	0.590	1.16	6.50
7th	303	21.90	0.444	0.527	0.844	0.634	3.03	4.33
8th	300	21.67	0.440	0.505	0.870	0.622	2.40	4.33
Particle size 0.1–0.5 mm								
1st	275	57.74	0.364	0.553	0.658	0.436	7.47	13.00
2nd	339	71.19	0.448	0.528	0.850	0.559	2.52	13.00

C_B, capacity at the breakthrough point; C_E, capacity at the exhaustion point; η, efficiency (C_B/C_E); F, parameter measuring the symmetry of the breakthrough point; h_Z, mass transfer zone; EBCT, empty bed contact time.

capacity was lower for the smaller particle size fraction. The results obtained are contrary to the results obtained by the batch method where it has been established that the exchange capacity increases with the decrease of the particle size [32]. It is obvious that the capacity can be affected not only by the size and specific surface of zeolite particles, but also by the compactness of the fixed bed. Lower granulation attains higher compactness, which in turn increases the hydraulic resistance, forms channels and pores in the layer etc.

The values of capacities C_B and C_E do not show significant oscillations with the increase in the initial concentration and flow through the column, even though the breakthrough points are attained at lower BV values, i.e. in a shorter exchange period. This indicates that optimal operation parameters have been chosen (e.g. the ratio of particle size to column diameter, the ratio of particle size to bed high, and the range of initial concentration and flow troughs the column).

The mean value of equilibrium capacity C_E calculated from the breakthrough curve is equal 0.57 mmol/g zeolite, and it is about 70% of the theoretical capacity ($C_T = 0.82$ mmol/g zeolite) calculated from chemical analysis of homoionic sodium form of the sample [33,34].

The height of the mass transfer zone (h_Z) in the first cycle is higher than in the following cycles. Moreover, the h_Z height for the first cycle is much higher than the height of the zeolite bed, which may be due to the presence of channels in the layer, incomplete wetting and the contact between the solid and liquid phases. Already in the second cycle and onwards, the h_Z heights are much shorted and rather uniform throughout the cycle.

The flow through the column determines the empty bed contact time—EBCT [35]. The comparison of changes in flows in solutions of the same initial concentrations (for 3rd, 6th and 7th cycles) shows that the contact time decreases with the increase in the flow (Table 2).

For flows of 1.0 and 2 mL/min, the calculated EBCT values were 13.00 and 6.50 min, respectively with almost the same values for the C_B and C_E capacity. For the flow of 3 mL/min, the calculated EBCT was 4.33 min, and the values for the capacity were somewhat lower, which indicates that the contact time was not long enough. This is, also, confirmed by the h_Z value which doubled with the increase of the flow (from 1.16 to 3.03 cm).

The data calculated indicate that the best efficiency ($\eta = 0.9425$) for the examined concentrations and flows of the lead solution was achieved for the initial lead concentration of 1.026 mmol/L and flow of 2 mL/min.

In the process of alternating exchange and regeneration, the same zeolite mass was used eight times, so that when capacities at exhaustion points are summarized, it can be seen that a total of 850 mg Pb was removed by a gram of natural zeolite sample.

3.3. Changes in the pH value during the exchange and regeneration process

The pH value of the prepared lead solutions (influent) was approximately 5. During the service cycle pH values changed, following the opposite shape of the breakthrough curves (Fig. 7).
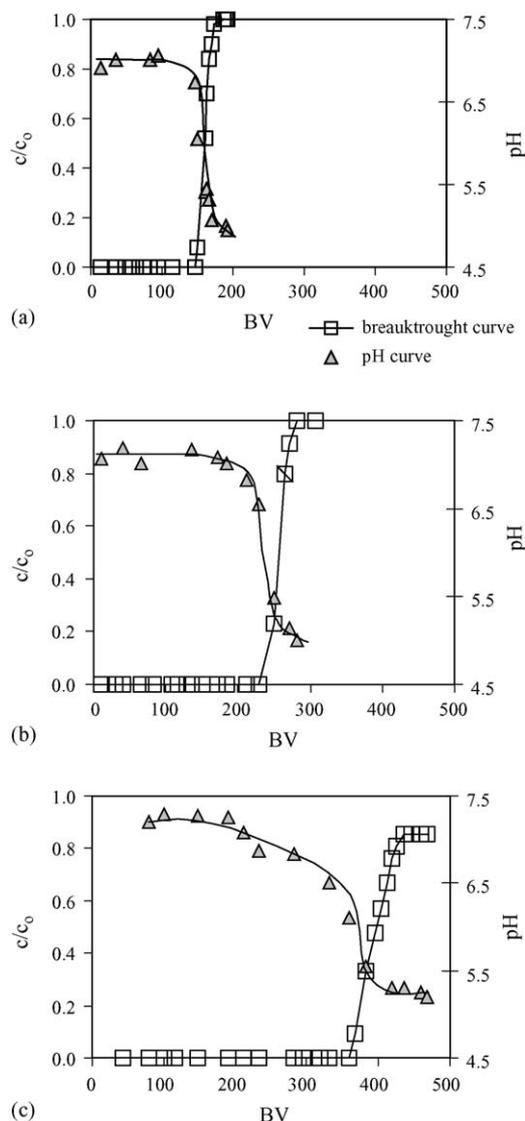

Fig. 7. Monitoring of pH value in effluent during service cycles of different initial concentrations: (a) $\gamma_0 = 512.5$ mg/L, (b) $\gamma_0 = 364.3$ mg/L and (c) $\gamma_0 = 212.5$ mg/L.

Until the breakthrough point, the pH values in the effluent were changing only slightly and amounted to approximately 7. At the breakthrough point, a rapid change in the pH value occurred, coinciding with the rapid increase in the lead concentration according to the breakthrough curve. At the exhaustion point, the pH value of the effluent became equal to the pH value of the influent. This is due to the increased lead concentration in the effluent and its hydrolysis according to the reaction [4,36]:

$$Pb^{2+} + H_2O \Leftrightarrow Pb(OH)^+ + H^+. \tag{9}$$
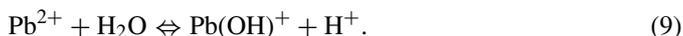
Therefore, if the pH value in the effluent is continuously monitored, one can predict the breakthrough and exhaustion points [37].

The change of pH value shown in curve of regeneration cycle has opposite shape than shape of regeneration curve. Namely, a rapid decrease of pH curve is following with increase of concentration of lead in regeneration curve.
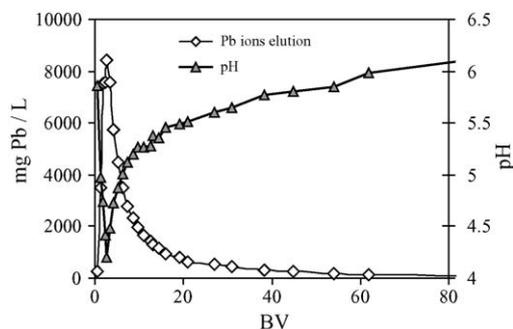
Fig. 8. Monitoring of pH during the regeneration cycle.

Specifically, already when the first milliliters of the regeneration solution pass through the zeolite layer, the Pb concentration abruptly increases, causing the pH value to drop suddenly from the initial pH ~ 5.60 to pH ~ 4.20. As the regeneration process progresses, the lead concentration in the regenerate decreases, and the pH value increases to approximately 6 (Fig. 8). Such curves were obtained for all regeneration cycles, which indicate that the completion of regeneration can be established by continuous monitoring of the pH value.

4. Conclusions

Lead can be removed from aqueous solutions very successfully by means of the column exchange process on natural zeolite–clinoptilolite, with successive service and regeneration cycles. Already after the first cycle of regeneration with the sodium nitrate solution, the sample is transformed to near homoionic sodium form, which results in the increase of capacity that remains unchanged with successive regenerations. This makes it possible to reuse the same zeolite sample several times.

The BV at the breakthrough point decreases with the increase of lead concentration in the initial solution, at the same flow. When the flow increases for the solutions of the same lead concentration, the BV at breakthrough points remains nearly the same, but the time it takes to reach the breakthrough point becomes shorter as the flow increases.

The change in the initial concentration and flow through the column has no significant effect on capacity C_B and C_E, which indicates that the optimal operational parameters have been chosen. These include the ratio of particle size to column diameter, the ratio of particle size to bed high, and the range of initial concentrations and flow through the column.

Eight service and regeneration cycles have been performed with only 70–75 BV of the sodium nitrate solution needed for regeneration. This is a volume 4–5 times smaller than the lead solution volume per service cycle. The lead concentration in the regenerate is higher so that the solution of lead can be reused. During eight service and regeneration cycles on the same zeolite mass, the total of 850 mg of lead was removed per gram of zeolite.

The column experiment has shown that the best efficiency is obtained at the initial lead concentration of 1.026 mmol/L and the flow of 2 mL/min.

Measuring the change of the pH value in the effluent can very successfully monitor the progress of the lead service cycle and of the zeolite regeneration cycle. This can indicate both the breakthrough point and the completion of the regeneration process, which is very important for practical application.

Acknowledgement

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