

This article was downloaded by: [Trgo, M.]

On: 6 October 2009

Access details: *Access Details: [subscription number 915664581]*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Separation Science and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title-content=t713708471>

The Effect of Zeolite Fixed Bed Depth on Lead Removal from Aqueous Solutions

J. Peri ^a; M. Trgo ^a; N. Vukojevi Medvidovi ^a; I. Nui ^a

^a Faculty of Chemistry and Chemical Technology, University of Split, Croatia

Online Publication Date: 01 January 2009

To cite this Article Peri, J., Trgo, M., Medvidovi, N. Vukojevi and Nui, I.(2009)'The Effect of Zeolite Fixed Bed Depth on Lead Removal from Aqueous Solutions',*Separation Science and Technology*,44:13,3113 — 3127

To link to this Article: DOI: 10.1080/01496390903182230

URL: <http://dx.doi.org/10.1080/01496390903182230>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The Effect of Zeolite Fixed Bed Depth on Lead Removal from Aqueous Solutions

J. Perić, M. Trgo, N. Vukojević Medvidović, and I. Nuić

Faculty of Chemistry and Chemical Technology,
University of Split, Croatia

Abstract: The effect of zeolite bed depth on lead removal from aqueous solutions by the column method has been examined. The results indicate that the increase of bed depth delays the breakthrough point and exhaustion point, and increases the contact time of the zeolite – lead solution, and the height of the mass transfer zone, h_z . The increase of the bed depth lowers the effect of axial dispersion on the mass transfer process. In order to predict the time necessary for exceeding the defined effluent concentration for a constant bed depth, the bed depth service time (BDST) approach has been used. Experimentally obtained breakthrough curves for the flow rate of 1 ml/min were used to derive the BDST approach equations. These equations were successfully used for modelling of the system for flow rates of 2 and 3 ml/min. The BDST equations have yielded modelled linear equations used for calculation of h_z . The increase of the flow rate increases h_z , which indicates that the zeolite–solution contact time is not sufficient. This may be attributed to the affect of axial dispersion on mass transfer on the solid-liquid interface.

Keywords: BDST approach, fixed bed, lead, natural zeolite

INTRODUCTION

Lead belongs to the group of heavy metals with highly toxic effects on living organisms. The most frequent signs of lead poisoning are related

Received 8 September 2008; accepted 27 April 2009.

Address correspondence to M. Trgo, Faculty of Chemistry and Chemical Technology, University of Split, Croatia, Teslina, Split 21000, Croatia Tel.: 385 21 329 454; Fax: 385 21 329-461. E-mail: mtrgo@ktf-split.hr

to the digestive system and to the central nervous system. Lead is used in batteries, cables, glass, fuses, in welding, for X-ray protection, and in many devices in the chemical industry, pumps, pipes, etc. It is used in the manufacture or coating of vessels for storage and transportation of corrosive chemicals and gases. Lead foils and tubes are used for packaging. It can still be used in paints and fuels. The consequence of its wide application is the increasing quantity of wastewaters polluted by lead (1,2). High concentrations of lead are usually removed by chemical precipitation. Removal of lead up to low concentrations can be performed by tertiary treatment, e.g. ion exchange and adsorption, electro-dialysis, membrane methods (3,4). Among them, ion exchange and/or adsorption become an economically and ecologically feasible method of lead removal from wastewaters. Therefore, scientific research has been directed towards finding various low-cost materials, such as lignite, fly ash, blast furnace slag, biogas residual slurry, olive mill products, and natural zeolites as potential adsorption or ion exchange materials (5–10). Table 1 provides the removal capacities of these materials compared with very expensive commercially activated coal. Among the given adsorbents the natural zeolite becomes the most effective material for the removal of lead ions from aqueous solutions.

The results of our previous studies suggest many advantages of the continuous column method in treatment of wastewaters (10). A specific feature of the column method is the possibility of regeneration of zeolite for several service cycles. This enables multiple reuse of the same zeolite, and treatment of a greater quantity of wastewaters.

The process parameters effect on the process equilibrium and kinetics, i.e., the shape and position of the breakthrough curve. Their examination enables the evaluation of optimum operating conditions. The ratios of the bed depth to the column diameter (H/d) and to the zeolite particle diameter (H/d_p) are very important parameters in column design. The contact time between the solution and zeolite, and the axial dispersion in the bed depend of zeolite bed depth. In order to minimize the channelling in the bed and appearance of axial dispersion, it is important to evaluate optimum H/d and H/d_p ratios (11). In practice is also necessary to predict service time in which the effluent concentration would not exceed the defined value. For this purpose, according to scientific results in literature, the experimental data are tested using the bed depth/service time (BDST) kinetic model, which correlates the service time and the bed depth (12–14). As far as we know, this is the first attempt to test the experimental results of lead removal on zeolite using the BDST model.

Table 1. Comparison of different adsorbents for lead

| Low-cost material | Source | Removal capacity | | Reference |
|---|---|-----------------------|------------------------|-----------|
| | | Batch method, mg Pb/g | Column method, mg Pb/g | |
| lignite | Turkey (Ilgin and Beysehir deposits) | 56.7–68.5 | – | (5) |
| fly ash | generated during burning of coal | 5.10 | 21 | (6) |
| blast furnace sludge | by-product of the steel-making industry | 55 | – | (7) |
| biogas residual slurry | by-product of a biogas plant | 28 | – | (8) |
| olive mill product | solid residue of olive mill product | 21 | – | (9) |
| natural zeolite | Serbia (the Vranjska Banja deposit) | 70 | 104–133 | (10) |
| coconut shell based granulated activated carbon enriched with sulphur | — | 29.44 | 2.89 | (3) |
| activated carbon | commercial AC | 62.3 | – | (5) |

MATERIALS AND METHODS

Sample and Solution Preparation

The natural zeolite sample used in this study originates from the Vranjska Banja (Serbia) deposit. The sample was milled and sieved to the particle size fraction of 0.6–0.8 mm. Natural zeolite was pre-treated into the Na-form according to the procedure described in our previous paper (15).

The chemical composition of the Na-form of the zeolite sample was determined by the chemical analysis of aluminosilicates (16). Expressed in mass percentages the composition was: SiO₂–65.15; Al₂O₃–11.56; Fe₂O₃–1.35; MgO–1.76; CaO–0.91; K₂O–0.72; Na₂O–4.40; loss of ignition–11.66.

X-ray diffraction was used for qualitative mineralogical analysis, using a “Philips-CubiX XRD” type diffractometer (CuK α radiation, $2\theta = 0\text{--}60$, $0.03\ 2\theta/s$). The main mineral component of zeolite was clinoptilolite, whose content in the sample was $\approx 80\%$. Lead and regeneration

solutions were prepared by dissolving the $\text{Pb}(\text{NO}_3)_2$ and NaNO_3 in ultra pure water.

Column Studies

Experiments were carried out in glass columns with an inner diameter of 12 mm and the height of 500 mm. Lead removal on zeolite was performed isothermally ($T = 23^\circ\text{C}$) with three zeolite bed depths: 120, 80, and 40 mm, with the same initial concentration $c_o(\text{Pb}) = 1.026 \text{ mmol/l}$ and the lead solution flow rate of $Q = 1 \text{ ml/min}$. Experiments were then performed with zeolite bed depths of 40 and 120 mm and with flow rates of 2 and 3 ml/min, using the solution of the same initial concentration. During the service cycle service lead ions solution has been flowing from the top of the column through the zeolite bed (the down flow mode). At selected time intervals lead concentration was determined in the effluent by complexometrical titration in an acid medium, using the highly selective indicator, methylthymolblue (17). The process was interrupted when the concentration of lead in the effluent became equal to the influent concentration. The flow rate constancy was maintained by a vacuum pump.

Column Regeneration

After the service cycle, regeneration was carried out with the sodium nitrate solution $c_o(\text{NaNO}_3) = 176.5 \text{ mmol/l}$ and the flow rate of $Q = 1 \text{ ml/min}$, also using the down flow mode.

RESULTS AND DISCUSSION

The Effect of Zeolite Bed Depth

At the constant flow rate and particle size, the bed depth of zeolite in the column must be properly evaluated. This ensures good wetting of zeolite particles and optimum contact time between the solid and liquid phase, which is important for interface mass transfer and achieving of equilibrium conditions. To minimize possible wall and axial dispersion affect in the fixed bed column, the bed depth-to-particle diameter ratio (H/d_p) must be greater than 20 (11). In this paper, the zeolite bed depth varied in the range from 40 to 120 mm and the diameter of zeolite particles

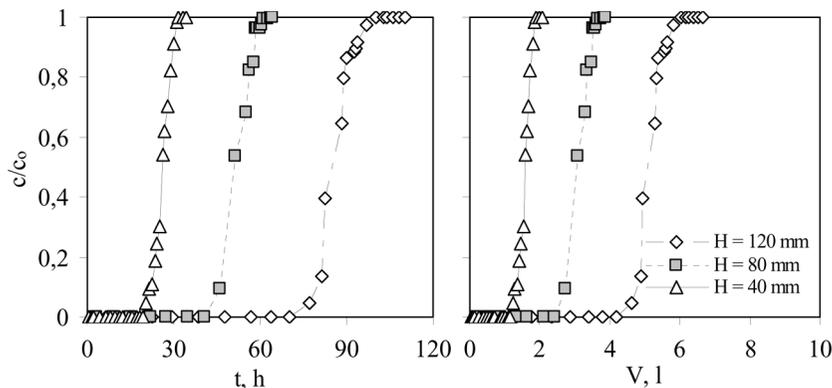


Figure 1. Breakthrough curves for three zeolite bed depths at the lead solution flow rate of 1 ml/min, expressed as c/c_0 vs. t and c/c_0 vs. V .

was 0.6–0.8 mm, so that the ratio (H/d_p) was greater than 20 in all experiments.

Figure 1 shows the breakthrough curves for different bed depths for the constant initial concentration of 1.026 mmol Pb/l and the flow rate of 1 ml/min.

The effect of bed depth is evident both on time and on the volume in the breakthrough and exhaustion point. With the decrease of bed depth, the breakthrough and exhaustion points shift towards lower values of volume and time. The experimentally obtained breakthrough curves were used to calculate the characteristic parameters, applying the equations published in our previous paper (10). Table 2 shows these parameters.

Table 2. Breakthrough curve data of different zeolite bed depths for lead removal

| H mm | Breakthrough point | | | q_B mg Pb/g | q_E mg Pb/g | η – | F – | h_z mm | EBCT min |
|------|--------------------|-------|-------|------------------|------------------|-------------|--------|-------------|-------------|
| | BV, – | V, l | t, h | | | | | | |
| 120 | 334 | 4.530 | 75.51 | 106.35 | 114.39 | 0.930 | 0.295 | 28.5 | 13.56 |
| 80 | 304 | 2.750 | 54.82 | 98.52 | 111.62 | 0.883 | 0.340 | 27.5 | 9.04 |
| 40 | 271 | 1.225 | 20.42 | 89.68 | 110.97 | 0.781 | 0.500 | 17.5 | 4.52 |

Note. BV–bed volume; q_B – capacity at the breakthrough point, q_E – capacity at the exhaustion point, η – efficiency (q_B/q_E), F–parameter measuring the symmetry of the breakthrough point, h_z – height of the mass transfer zone, EBCT – empty bed contact time.

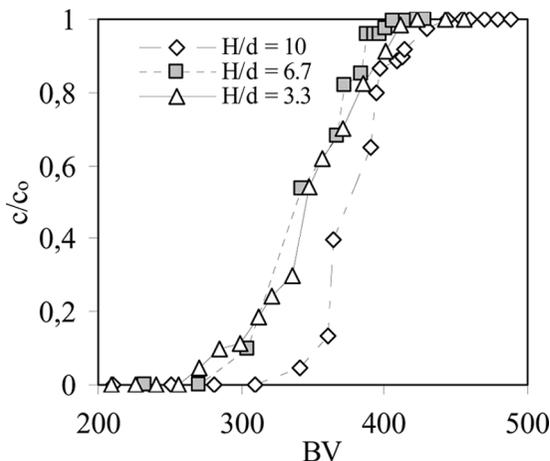


Figure 2. Breakthrough curves for different H/d ratios.

Figure 2 shows breakthrough curves for different values of the H/d ratio. The effluent volumes were calculated to the BV values:

$$BV = \frac{V}{V_s} \quad (1)$$

where:

- BV – bed volume,-
- V – effluent volume, l
- V_s – zeolite bed volume, l.

Figure 2 and data in Table 2 indicate that the breakthrough point appears later and the curve is steeper for the breakthrough curve with the highest ratio of H/d = 10. A higher bed depth is reflected in the increase of contact time (10), height of mass transfer zone h_z , and column efficiency η . The increase of the H/d ratio, with the same size of zeolite particles in the bed, reduces the effect of axial dispersion on the overall mass transfer process in the column (18).

The advantage of the use of natural zeolite in lead removal is the possibility of regeneration of the same zeolite. Figure 3 shows the regeneration curves for three different bed depths. The regeneration curves are evidently very similar. They first display an abrupt increase in the concentration of lead in the effluent, followed by a rapid decrease and then slow decrease. The maximum of lead concentration in the effluent increases

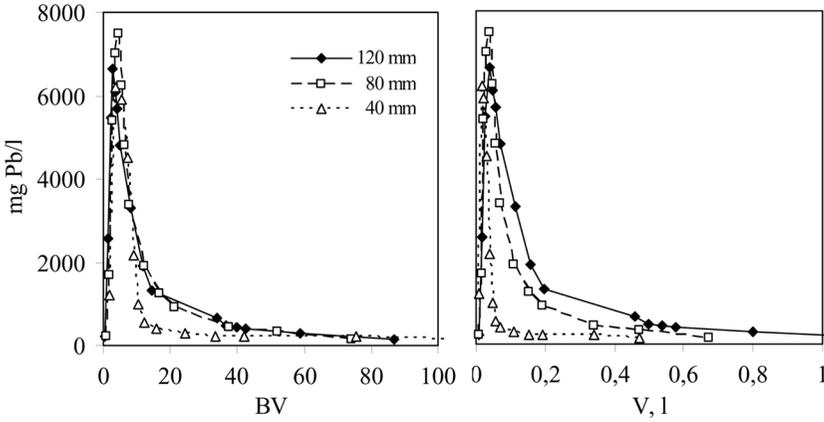


Figure 3. Regeneration curves at three different zeolite bed depths, expressed as mg Pb /l vs. BV and mg Pb /l vs. V.

with the increase of bed depth, due to a higher quantity of lead bound to zeolite. To complete the regeneration of the zeolite bed, the increased bed depth required increased volumes of regeneration solution from 42 BV to 60 BV, and 75 BV, i.e., from 0.1891 to 0.542 l and 1.016 l. These volumes represent only 15, 19, and 22% of the lead solution volume up to the breakthrough point during the service cycle.

Design Based on Bed Depth/Service Time (BDST) Approach

Experimentally obtained breakthrough curves were tested by the BDST model. The BDST model was originally derived by Bohart & Adams for adsorption on activated coal. It is based on the assumption that the adsorption rate is determined by the surface reaction between the adsorbate and unused adsorbent capacity, and is given by the following Eqs. (12–14):

$$\ln\left(\frac{c_o}{c_t} - 1\right) = \ln\left(e^{(k_a q_v^H)} - 1\right) - k_a \cdot c_o \cdot t. \tag{2}$$

As the term $e^{(k_a q_v^H)}$ is much higher than 1, Eq. (2) can be simplified to the form:

$$\ln\left(\frac{c_o}{c_t} - 1\right) = \ln e^{(k_a q_v^H)} - k_a \cdot c_o \cdot t. \tag{3}$$

where:

- t – time, h
- c_o – influent solute concentration, mmol/l
- c_t – defined solute concentration in the effluent at time t , mmol/l
- q – quantity of solute adsorbed at time t , mmol/l or mmol/g
- H – bed depth of the adsorbent, m
- k_a – rate constant, l/mmol h.
- v – influent velocity, m/h.

Equation (3) is applied to the zeolite–lead solution system, and when solved for time t , yields (12–14):

$$t = \frac{q}{c_o \cdot v} \cdot H - \frac{1}{k_a \cdot c_o} \ln\left(\frac{c_o}{c_t} - 1\right) \quad (4)$$

where:

- c_o – influent concentration of lead, mmol/l
- c_t – defined concentration of lead in the effluent at time t , mmol/l
- q – quantity of lead bound on zeolite at time t , mmol/l or mmol/g
- H – bed depth of the zeolite, m.

When Eq. (4) is solved for depth H , and for $t = 0$, it yields:

$$H_o = \frac{v}{k_a \cdot q} \ln\left(\frac{c_o}{c_t} - 1\right) \quad (5)$$

where:

- H_o – critical bed depth, i.e., the theoretical bed depth of zeolite in the column sufficient to prevent the lead concentration exceeding c_t at time $t = 0$ (19).

Equation (4) makes it possible to determine the time t at which, for a given bed depth H , the defined concentration c_t is reached in the effluent. The values q and k_a have to be determined experimentally for the flow rate interval as wide as possible, i.e., linear flow rates of the solution through the bed, v . To that purpose it is necessary to perform at least nine individual experiments in the column (to provide the breakthrough curves for each of three bed depths and each of three solution flow rates), which is expensive and time consuming. Hutchins (12) has proposed a modification of the Bohart-Adams equation, which requires only three

individual experiments. This is called the bed depth/service time (BDST) approach.

The linear Eq. (4) can be simplified to (12–14):

$$t = a \cdot H - b \tag{6}$$

where *a* is the slope and *b* is the intercept, respectively:

$$a = \frac{q}{c_o \cdot v} \tag{7}$$

$$b = -\frac{1}{k_a \cdot c_o} \ln\left(\frac{c_o}{c_t} - 1\right). \tag{8}$$

Experimental breakthrough curves obtained for three bed depths (Fig. 1) were processed according to the BDST model. Breakthrough curves were used to read the time needed for the percentage of lead removal on the zeolite to be 95, 80, 50, and 5% (service time) for each zeolite bed depth of 40, 80, 120 mm. This is shown in Table 3, and graphically in Fig. 4.

Plots of service time vs. bed depth exhibit linearity, and corresponding equations are determined. The values obtained for the correlation coefficient *R*² are higher than 0.996, indicating the validity of the BDST model for the present system.

At 50% of breakthrough curves (*c*_o/*c*_t) = 2, the logarithmic term in Eq. (4) is reduced to zero, and the expression can be written as (20,21):

$$t = \frac{q}{c_o \cdot v} \cdot H. \tag{9}$$

Figure 4 shows that the BDST lines obtained for different lead removal percentages are parallel and pass very near to the origin.

The mass transfer zone is defined as a part of the bed in which the lead concentration ranges from 5–95% of the concentration in the influent. The height of this zone, *h*_z, is determined by the horizontal distance between these two BDST lines in Fig. 4 (14,22). Equations of these lines were used to calculate their distance relative to the *x* axis, which amounts to 13.84 mm. The slope of the BDST plots represents the time required for the moving down of the mass transfer zone for its own height (23). The intercept corresponds to the theoretical bed depth *H*_o.

Equation (7) was used to calculate the removal capacity of zeolite for lead binding, *q*, from the slope of BDST lines. The rate constant *k*_a calculated from the intercept of the BDST line by means of Eq. (8) represents the rate of transfer of lead ions from the solution to zeolite (24)

Table 3. The BDST model constants calculated for the flow rate of 1 ml/min

| Removal percentage, % | Service time, h | | | | BDST equation | R^2 | k_a , l/mmol h | q, mmol/l | q, mg/g | H_o , mm |
|-----------------------|-----------------|-----------|------------|--|--------------------|-------|------------------|-----------|---------|------------|
| | H = 40 mm | H = 80 mm | H = 120 mm | | | | | | | |
| 95 | 20.42 | 45.83 | 77.08 | | $t = 0.71H - 8.89$ | 0.996 | 0.322 | 386.06 | 119.60 | 12.51 |
| 50 | 25.00 | 51.67 | 85.67 | | $t = 0.75H - 6.11$ | 0.996 | 0.006 | 407.84 | 126.72 | 8.66 |
| 20 | 29.00 | 56.17 | 89.50 | | $t = 0.76H - 2.28$ | 0.999 | - | 413.27 | 128.41 | 2.73 |
| 5 | 33.34 | 63.67 | 97.08 | | $t = 0.78H + 0.94$ | 0.999 | - | 424.00 | 131.79 | - |

Note: for removal percentages lower than 20%, the calculated values for k_a and H_o assume unrealistic (negative) values.

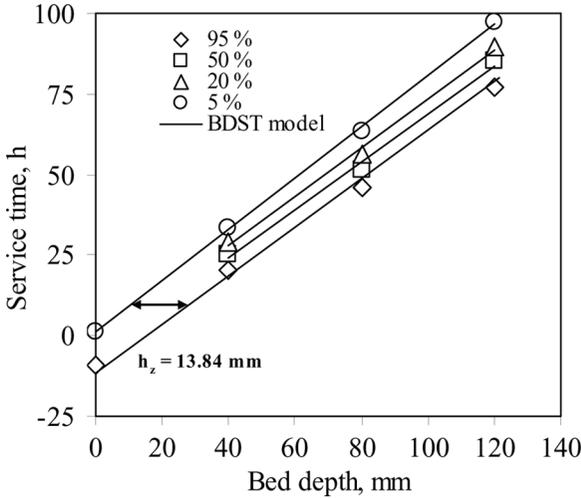


Figure 4. BDST plots for different lead removal percentages ($Q = 1 \text{ ml/min}$).

(Table 3). It can be observed that the values of capacities for all lead removal percentages on zeolite are of the same order of magnitude, and that they show good correspondence with the experimental capacities in the exhaustion point (q_E) for three bed depths (see Table 2). This indicates that the calculated model parameters can be used to scale up the process for other operating conditions without additional experiments.

Design the Fixed Bed Column for Different Flow Rates

The BDST model can be used to design the column. According to equation (7), the slopes of lines in Fig. 4 are inversely proportional to the linear rate, i.e., the flow rate (since $v = Q/A$, where A – cross section area of the column). Therefore, if a corresponds to the slope at flow rate Q , the value of the slope a_1 at another flow rate Q_1 will be (3,11):

$$a_1 = a \cdot \left(\frac{Q}{Q_1}\right). \tag{10}$$

When the flow rate changes, the intercept b remains unchanged. From the slope a and intercepts b of the BDST plots, the slopes of lines in Fig. 4 were calculated for flow rates of 2 and 3 ml/min. When the values of the slopes a_1 and intercepts $b_1 = b$ for these flow rates are inserted into the equation (6) for the specific bed depth H , the t_{mod} times

Table 4. Comparison of service times at different breakthrough percentages, experimentally observed and calculated from the BDST model at flow rates of 2 and 3 ml/min

| Removal percentage, % | H, mm | Q = 2 ml/min | | Q = 3 ml/min | |
|-----------------------|-------|----------------------|----------------------|----------------------|----------------------|
| | | t_{mod} , h | t_{exp} , h | t_{mod} , h | t_{exp} , h |
| 95 | 120 | 33.71 | 38.78 | 19.51 | 21.90 |
| | 40 | 5.31 | 10.13 | 0.58 | 6.58 |
| 50 | 120 | 38.89 | 41.13 | 23.89 | 26.00 |
| | 40 | 8.89 | 14.20 | 3.89 | 9.30 |
| 20 | 120 | 43.32 | 42.40 | 28.12 | 27.00 |
| | 40 | 12.92 | 15.50 | 7.85 | 10.69 |
| 5 | 120 | 47.74 | 43.00 | 32.14 | 28.30 |
| | 40 | 16.54 | 17.37 | 11.34 | 12.11 |

are calculated. In order to compare experimental and modelled values, experiments were carried out at these conditions, and the values t_{exp} were calculated. Table 4 shows the model and experimental values for time (t_{mod} and t_{exp}) for different lead removal percentages of 95, 50, 20, and 5, for zeolite bed depths of 40 and 120 mm, and at flow rate of 2 and 3 ml/min.

Figure 5 shows the comparison of BDST plots predicted by the model (lines) and those confirmed by the experiment (symbols) at flow rates of 2 and 3 ml/min.

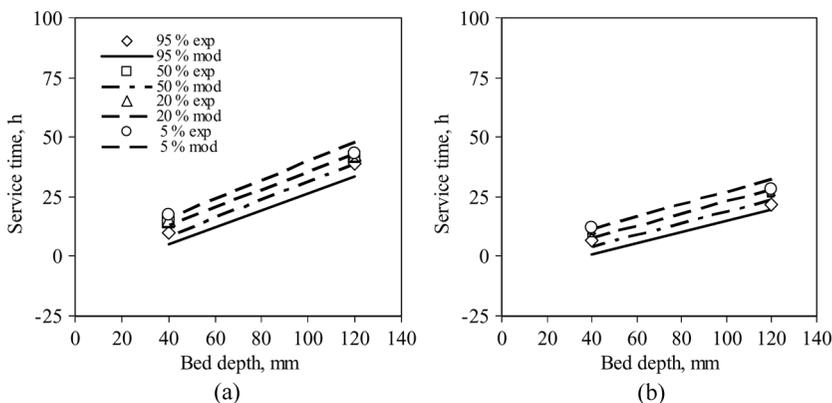


Figure 5. BDST plots for different lead removal percentages at flow rates of: (a) 2 ml/min; (b) 3 ml/min.

Small deviations of experimental points from the modelled BDST plots are probably due to the consequences of the effect of the flow rate on the overall process rate. The increase in the flow rate leads to the reduced contact time between zeolite particles and lead ions in the solution, as well as to the increased effect of axial dispersion. In order to confirm this, the height of the mass transfer zone h_z was calculated for increased flow rates. Specifically, according to the BDST model, the mass transfer zone is defined as the part of the zeolite bed in which the concentration of lead ranges from 5–95% of that in the influent. The height of this zone h_z is determined by the horizontal distance between these two BDST lines. These lines for the flow rates of 2 and 3 ml/min (Fig. 5) were used to calculate their distance relative to the x axis, amounting to 27.69 mm at the flow rate of 2 ml/min, i.e., 41.53 mm at the flow rate of 3 ml/min, which corresponds to the heights of the mass transfer zone, h_z .

When the values for h_z for all three flow rates are compared, it can be seen that h_z increases with the increase of the flow rate, which may be attributed to the reduction of the contact time and the effect of axial dispersion.

CONCLUSION

The following conclusions may be made based on the research done in this study:

The zeolite bed depth in a column of specific diameter must be selected in such a way that it ensures good wetting and sufficient contact time of the zeolite – lead solution at a constant flow rate and particle size.

When the bed depth increases, the breakthrough point and the exhaustion point shift to higher values of volume and time, and the slope of the breakthrough curves becomes steeper. When the bed depth increases and the flow rate remains constant, the contact time between the lead solution and zeolite increases, also increasing the height of the mass transfer zone h_z and column efficiency η .

Volumes of regeneration solution needed for complete regeneration of the zeolite bed increase with the increase of bed depth. However, these volumes represent only 15, 19, and 22% of the lead solution volume treated up to the breakthrough point during the service cycles.

The BDST model was used to evaluate the time at which the concentration of lead in the effluent will not exceed the defined value. To that purpose, experimentally obtained breakthrough curves were tested by the BDST model, for different lead removal percentages, 95, 50, 20, and 5%. The relation of time t to bed depth H provides linearity with the values of the correlation coefficients exceeding 0.996. Slopes a and

intercepts b of these lines were used to calculate the characteristic parameters of the model, q and k_a . The values obtained for capacity q are of the same order of magnitude, and show good correspondence with experimental capacities in the exhaustion point.

Based on equations of BDST plots at three bed depths and the flow rate of 1 ml/min, the behavior of the system was predicted for flow rates of 2 and 3 ml/min. Small discrepancies of experimental points and the BDST model lines are probably due to the effect of the flow rate on the overall process rate. This has been confirmed by calculation of the high mass transfer zone h_z value for all three flow rates. Specifically, h_z increases with the increase in the flow rate, which is attributed to the reduced contact time between the zeolite and metal ion in the solution, and to the effect of axial dispersion in the zeolite bed.

ACKNOWLEDGEMENT

We extend our thanks to the Ministry of Science, Education, and Sports of the Republic of Croatia, which has been financing a project a part of which is presented in this paper.

REFERENCES

1. Dimitrova, S.V. (2002) Use of natural slag columns for lead removal. *Water Res.*, 36: 4001.
2. Filchak, K. (1997) Lead in and around the home: Identifying and Managing its sources. In: *Home-A-System: An environmental Risk-Assessment Guide for the Home*, Andrews, E.; Bosmans, R.; Castelnoro, R.; Du Poldt, C.; Eagan, D.J. eds.; Natural Resource, Agricultural and Engineering Service.
3. Goel, J.; Kadirvelu, K.; Rajagopal, C.; Greg, V.K. (2005) Removal of lead (II) by adsorption using treated granular activated carbon: Batch and column studies. *J. Hazard. Mater.*, B125: 211.
4. Benefield, L.D.; Judkins, J.F.; Weand, B.L. (1982) *Process Chemistry for Water and Wastewater Treatment*; Prentice-Hall, Inc.: New Jersey.
5. Pehlivan, E.; Arslan, G. (2007) Removal of metal ions using lignite in aqueous solution – Low cost biosorbent. *Fuel Process. Technol.*, 88: 99.
6. Alinnor, I.J. (2007) Adsorption of heavy metal ions from aqueous solution by fly ash. *Fuel*, 86: 853.
7. Lopez-Delgado, A.; Perez, C.; Lopez, F.A. (1998) Sorption of heavy metals on blast furnace sludge. *Water Res.*, 32: 989.
8. Namasivayam, C.; Yamuna, R.T. (2005) Waste biogas residual sludge as an adsorbent for the removal of Pb(II) from aqueous solution and radiator manufacturing industry wastewater. *Bioresource Technol.*, 52: 125.

9. Gharaibeh, S.H.; Abu-el-sha'r, W.Y.; Al-Kofahi, M.M. (1998) Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products. *Water Res.*, 32: 498.
10. Vukojević Medvidović, N.; Perić, J.; Trgo, M. (2006) Column performance in lead removal from aqueous solution by fixed bed of natural zeolites-clinoptilolite. *Sep. Purif. Technol.*, 49: 237.
11. Zhou, D.; Zhang, L.; Zhou, J.; Guo, S. (2004) Development of a fixed-bed column with cellulose/Chitin beads to remove heavy-metals ions. *J Appl. Polym. Sci.*, 94: 684.
12. Hutchins, R. A. (1973) New method simplifies design of activated-carbon systems. *Chem. Eng.*, 20: 133.
13. Al-Ghouti, M.A.; Khraisheh, M.A.M.; Ahmad, M.N.; Allen, S.J. (2007) Microcolumn studies of dye adsorption onto manganese oxide modified diatomite. *J. Hazard. Mater.*, 146: 316.
14. Kumar, U.; Bandyopadhyay, M. (2006) Fixed bed column study for Cd(II) removal from wastewater using treated rice husk. *J. Hazard. Mater.*, B129: 253.
15. Trgo, M.; Perić, J. (2003) Interaction of the zeolitic tuff with Zn-containing simulated pollutant solution. *J. Colloid. Interf. Sci.*, 260: 166.
16. Voinovitch, I.; Debrad-Guedon, J.; Louvrier, J. (1966) *The Analysis of Silicates, Israel Program for Scientific Translations*; Jerusalem, Israel.
17. Merck, E. (1982) *Complexometric Assay Methods with Triplex*; Darmstadt.
18. Lv, L.; Wang, K.; Zhao, X.S. (2007) Effect of operating conditions on the removal of Pb^{2+} by microporous titanosilicate ETS-10 in a fixed-bed column. *J. Colloid. Interf. Sci.*, 305: 218.
19. Walker, G.M.; Weatherley, L.R. (2001) COD removal from textile industry effluent: Pilot plant studies. *Chem. Eng. Sci.*, 84: 125.
20. Zulfadhly, Z.; Mashitah, M.D.; Bhatia, S. (2001) Heavy metals removal in fixed-bed column by macro fungus *Pycnoporus sanguineus*. *Environ. Pollut.*, 112: 463.
21. Ayoob, S.; Gupta, A.K. (2007) Sorptive response profile of an adsorbent in the defluoridation of drinking water. *Chem. Eng. J.*, 133: 273.
22. Maji, S. K.; Pal, A.; Pal, T.; Adak, A. (2007) Modelling and fixed bed column adsorption of As(III) on laterite soil. *Sep. Purif. Technol.*, 56: 284.
23. Ghorai, S.; Pant, K.K. (2005) Equilibrium, kinetics and breakthrough studies for adsorption of fluoride on activated alumina. *Sep. Purif. Technol.*, 42: 265.
24. Han, R.; Ding, D.; Xu, Y.; Zou, W.; Wang, Y.; Li, Y.; Zou, L. (2008) Use of rice husk for the adsorption of congo red from aqueous solution in column mode. *Bioresource Technol.*, 99: 2938.