

# Effects of operating conditions on the removal of heavy metals by zeolite in fixed bed reactors

V.J. Inglezakis, Helen Grigoropoulou\*

*Department of Chemical Engineering, Section II: Process Analysis and Plant Design, Laboratory of Chemical Process Engineering, Zografou Campus, GR-15780 Athens, Greece*

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## Abstract

This work investigates the effects of flow rate (5–15 Bed Volumes/h), particle size (0.8–1.7 mm), concentration (0.005–0.02 N) and  $\text{Na}^+$ -enrichment of natural clinoptilolite on the removal efficiency of  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  in aqueous solutions. Ion exchange is performed in an upflow fixed bed reactor. The removal efficiency is increased with decreasing flow rate, particle size and concentration and is improved by a factor of 2–10, depending on the specific metal. The modification of the natural sample is favorable, leading to an increase of removal efficiency by 32–100%. For the experimental conditions examined, removal efficiency order is the following:  $\text{Pb}^{2+} > \text{Cr}^{3+} > \text{Fe}^{3+} \geq \text{Cu}^{2+}$ . Finally, the operation is influenced by the studied parameters, following the order: concentration > volumetric flow rate > particle size > modification of the material.

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## 1. Introduction

Industrial wastewaters frequently contain high levels of heavy metals and treatment is needed before disposal, in order to avoid water pollution. There are numerous sources of industrial effluents leading to heavy metal discharges apart from the mining and metal related industries. Heavy metal pollution frequently results from the industrial use of organic compounds containing metal additives in the petroleum and organic chemical industries, e.g. textile mill products (Cr), organic chemicals (Cr, Pb), petroleum refining, pulp industries and fertilizers (Cr, Cu, Pb), iron and steel manufacturing plants (Fe) [1].

Zeolites are well known materials for the removal of heavy metals such as cadmium, lead, cobalt and nickel [2–4]. Ion exchange by zeolites is considered to be one of the main processes for the removal of toxic metals from solutions [2–8]. Removal of  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Pb}^{2+}$  has been studied in beds containing sepiolite, chabazite-phillipsite zeolitic tuff and activated carbon, resulting in satisfactory re-

moval of these metals [2]. Effective removal of  $\text{Fe}^{2+}$ ,  $\text{Pb}^{2+}$  and  $\text{Cr}^{3+}$  by chabazite and phillipsite and of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  by clinoptilolite and phillipsite have also been reported [4,6–8].

The influence of the experimental conditions, i.e. volumetric flow rate, solution concentration, particle size and chemical modification of the original material on exchange rates is theoretically expected and experimentally verified in several studies for removal of metals and other cations using several materials. For instance, recovery of uranium adsorbed on slurry was examined by using a column packed with an ion exchange membrane, the recovery of copper from liquid streams by using a chelating resin and the adsorption of lead and cadmium by activated carbon [9–11].

However, few data are available for clinoptilolite columns and the influence of experimental conditions is not experimentally verified, as research is mainly performed in batch mode systems [12–16]. Especially for clinoptilolite packed beds, the related research is focused on ammonia removal [17–19]. Column operation is different from that of a batch system due to the continuous flow of the solutions through packed particles. From a practical point of view, the influence of operating conditions on the process deduced by ex-

\* Corresponding author. Fax: +30-210-77-23-155.

E-mail address: lenag@chemeng.ntua.gr (H. Grigoropoulou).

periments in fixed beds is more representative than that obtained in batch systems, because kinetics in beds is influenced by the whole equilibrium curve and diffusion rates in the material. In practical applications it is critical to know the degree of influence of each operational parameter on the operation performance, or, in other words, a quantitative representation of this influence is a valuable engineering tool.

The present study aims to assess the ability of natural and modified clinoptilolite for the treatment of solutions containing heavy metals, namely  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  and establish the selectivity series of clinoptilolite for these metals, under a wide range of experimental conditions. The effects of volumetric flow rate, solution concentration, exchanger particle size and chemical modification of the natural sample on the removal efficiency in column operation mode are also examined and the degree of influence of each examined experimental parameter is investigated.

## 2. Experimental

### 2.1. Heavy metal solutions

All chemicals used were analytical grade reagents. Stock solutions of metals were prepared in a concentration range of 0.005–0.02 N using nitric salts dissolved in deionized water. Initial pH adjustment was applied in order to avoid precipitation during ion exchange experiments. Values near to the initial ones for each metal solution were applied, namely 4 for lead and copper, 2 for iron and 3 for chromium using  $\text{HNO}_3$ .

### 2.2. Ion exchange material

Clinoptilolite is a low cost zeolite found worldwide in high amounts. The mineral used was collected from a deposit in the northern part of Greece. It was ground and then sieved to different fractions, of which 1.4–1.7, 1.18–1.4 and 0.8–1 mm were used in the study, after being thoroughly washed with water in order to eliminate dust eventually present.

The following two samples were used:

*CLIN-1*: Natural clinoptilolite. BET surface area was measured by  $\text{N}_2$  porosimetry (Sorptomatic 1900 Carlo Erba Instruments) and was found to be  $25 \pm 5 \text{ m}^2/\text{g}$ . Measured particle density was 2.1 g/mL.

*CLIN-2*: Modified sample. A  $\text{Na}^+$ -rich sample was prepared according to the following procedure: 25 Bed Volumes—BV—(6.3 L) of 0.73 M NaCl solution were introduced into a 2.1 cm diameter and 70 cm long column, packed with CLIN-1, at 45 °C. Upward flow rate was 25 BV/h (105 mL/min). The pH of the pretreatment solution was 7.5. After pretreatment, the material was washed in situ using 10 BV (2.5 L) of water. These experimental conditions were found to be sufficient for

the improvement of ion exchange properties of clinoptilolite as described elsewhere [20].

In Table 1 the results of the chemical analysis of natural and modified clinoptilolite, performed by SEM/EDS measurements (Jeol Scanning Microscope—6100) are presented (% , w/w).

According to the chemical analysis, the theoretical or maximum exchange capacity of the material is  $2.62 \pm 0.26 \text{ meq/g}$ , calculated as the sum of Mg, Ca, K and Na which are considered to be exchangeable. The ratio Si/Al is 4.29 (mol/mol) and the corresponding ratio of  $(\text{Na} + \text{K})/\text{Ca}$  is 1. The chemical composition and the ratio Si/Al, generally ranging from 4 to 5.5, are typical for clinoptilolite [21]. From Table 1 it is obvious that the modified sample is enriched in  $\text{Na}^+$  ions with mainly  $\text{Ca}^{2+}$  and some  $\text{K}^+$  cations being removed from the natural clinoptilolite during the pretreatment procedure.

### 2.3. Fixed bed experiments

Ion exchange in fixed beds has been described in several studies [13,22–26]. As the feed passes through the bed, the ion exchange zone moves downstream and, in due course, reaches the exit. When the concentration of the effluent reaches 5–10% of the influent, the flow is stopped. This point is commonly referred in the related literature as “breakthrough point” or “breakpoint”, and is fixed accordingly to the needs of the operation. Since only the last portion of the fluid proceeded has this concentration level, the average fraction of solute removed from the beginning until the breakpoint is generally very high [13,25]. In the present study, the “breakpoint” is set at 10% and the total volume of the treated solution until this point ( $V_{\text{BR}}$ , expressed in terms of Bed Volumes) is used as a measure of the operation’s removal efficiency.

The ion exchange process is conducted in 70 cm long plexiglass columns of 2.1 cm internal diameter. The solutions are introduced at a constant volumetric flow ( $Q$ ) and concentration ( $C$ ), using a peristaltic pump, in upflow mode, in order to assure complete wetting of the particles (diameter  $d$ ). The exchange temperature was  $27 \pm 1 \text{ }^\circ\text{C}$ . In Table 2 the experimental conditions are presented.

Table 1  
Chemical analysis of clinoptilolite samples

Oxide	Natural	Modified
$\text{SiO}_2$	$63.6 \pm 1.6$	$62.4 \pm 1.2$
$\text{Al}_2\text{O}_3$	$12.1 \pm 0.9$	$14.3 \pm 0.1$
$\text{Na}_2\text{O}$	$1.2 \pm 0.3$	$2.5 \pm 0.3$
$\text{K}_2\text{O}$	$1.7 \pm 0.8$	$1.2 \pm 0.1$
$\text{CaO}$	$3.5 \pm 0.4$	$1.4 \pm 0.2$
$\text{MgO}$	$1.6 \pm 0.2$	$1.8 \pm 0.1$
$\text{FeO}$	$2.0 \pm 1.2$	$2.5 \pm 1.0$
$\text{H}_2\text{O}^a$	$14.0 \pm 0.5$	$14.0 \pm 0.5$

<sup>a</sup> Water was measured separately by complete dehydration of the material.

Table 2  
Experimental conditions for ion exchange of heavy metals on clinoptilolite

Run	$Q$ (BV/h) <sup>a</sup>	$C$ (N)	$d$ (mm)	Sample
1	5	0.01	1.18–1.4	CLIN-1
2	10	0.01	1.18–1.4	CLIN-1
3	15	0.01	1.18–1.4	CLIN-1
4	5	0.02	1.18–1.4	CLIN-1
5	5	0.01	1.18–1.4	CLIN-1
6	5	0.005	1.18–1.4	CLIN-1
7	5	0.01	0.8–1	CLIN-1
8	5	0.01	1.18–1.4	CLIN-1
9	5	0.01	1.4–1.7	CLIN-1
10	5	0.01	1.18–1.4	CLIN-2

Duplicate experimental runs with standard error  $11.4 \pm 3\%$ .

<sup>a</sup> One Bed Volume is equal to the volume of empty column (0.25 L).

All experiments were carried out for four metals:  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$ . The range of the operating variables examined is within the general limits used in practical applications, according to the related literature [4,6,8,17,27–29].

Liquid samples were withdrawn at the exit of the bed at specific time intervals, depending on the flow rate and acidified with  $\text{HNO}_3$  at pH 2. Then, the samples were analyzed for heavy metal cations by atomic absorption spectrometry (Perkin Elmer model 350B spectrophotometer).

### 3. Results and discussion

#### 3.1. Effect of volumetric flow rate

The effect of volumetric flow rate is examined for CLIN-1 particles of 1.18–1.4 mm and concentration of 0.01 N (runs 1–3). Typical experimental breakthrough curves are shown in Fig. 1 and the effect of volumetric flow rate on  $V_{\text{BR}}$  is shown in Fig. 2.

As it can be seen removal efficiency is favored by lower volumetric flow rates in the region 5–10 BV/h, while this is not true for higher flow rates. The increase in removal efficiency however is not proportional to the flow rate and, furthermore, depends on the specific cation. By lowering the volumetric flow rate from 15 to 5 BV/h  $V_{\text{BR}}$  is increased by a factor near to 3–3.5, for all metals studied.

A range of flow rates between 5 and 15 BV/h was used for ammonia removal using natural and modified clinoptilolite [17]. By changing the flow rate from 10 to 5 BV/h,  $V_{\text{BR}}$  increased by a factor of 1.34 (34%), while 15 BV/h was considered too high to achieve high ammonia removal rates. Similar results have been obtained elsewhere for the same operation where decreasing the flow rate from 13.33 to 6.67 BV/h the breaking point ( $C/C_0 = 3\%$ ) increased by a factor near to 1.6 [19]. For  $\text{Cu}^{2+}$  exchange on Na-clinoptilolite, at flow rates between 7.5 and 22.5 BV/h,  $V_{\text{BR}}$  was slightly influenced by flow rate and increased by a factor of 1.24 (24%) lowering the flow rate from 22.5 to 7.5 BV/h [28]. The volumetric flow rate of 12 BV/h was proposed for a satisfac-

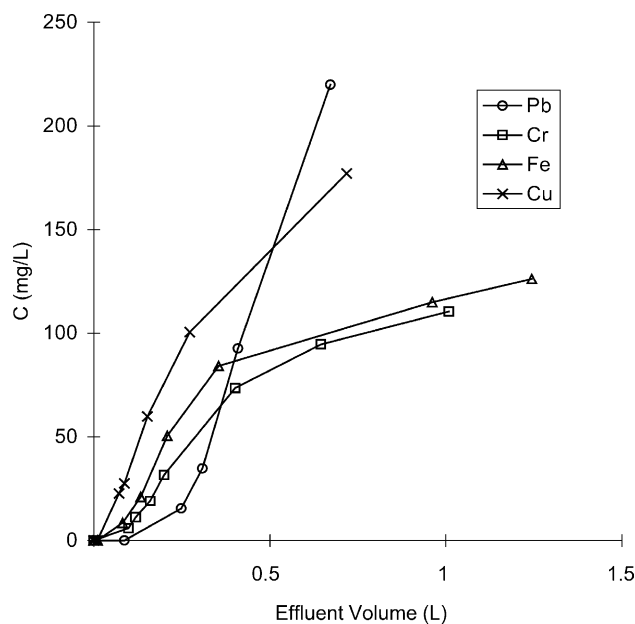


Fig. 1. Typical experimental breakthrough curves for the ion exchange of heavy metals on natural clinoptilolite ( $C = 0.01$  N,  $Q = 5$  BV/h,  $d = 1.18$ – $1.4$  mm).

tory exchange of Pb, Cd, Cu, Zn, Co and ammonium ions using clinoptilolite. However, no comparative data, for the examined flow rates, were presented [6,27].

According to the present study, higher flow rates than 15 BV/h should be avoided since breakthrough would occur faster and with less sharpened boundaries ( $V_{\text{BR}}$  is limited between 1.1 and 1.8 BV for  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  and only for  $\text{Pb}^{2+}$  is relatively high, reaching 5.1 BV). Lower than 5 BV/h flow rates are expected to be beneficial on removal efficiency, leading however to practically too high retention times. Consequently, 5 BV/h is considered to be a reasonable flow rate, resulting in  $V_{\text{BR}}$  between 3.4 and 6.1 BV for  $\text{Cu}^{2+}$ ,  $\text{Cr}^{3+}$  and  $\text{Fe}^{3+}$  and 14 BV for  $\text{Pb}^{2+}$ .

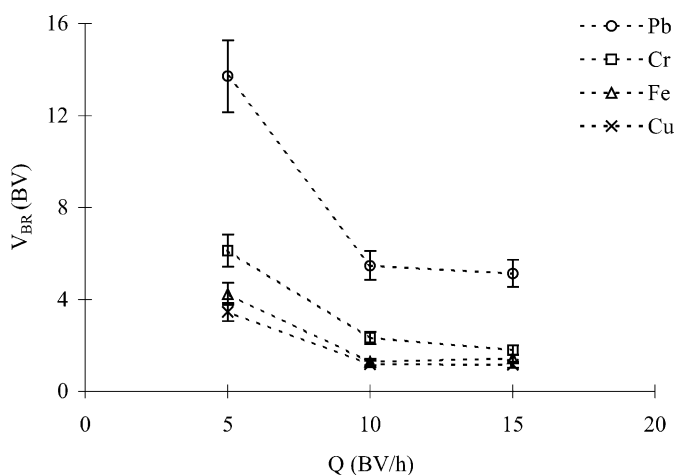


Fig. 2. Effect of volumetric flow rate on breakpoint for the ion exchange of heavy metals on natural clinoptilolite ( $C = 0.01$  N,  $d = 1.18$ – $1.4$  mm). Total volume of treated solution until breakpoint ( $V_{\text{BR}}$ ) is expressed in terms of Bed Volumes.

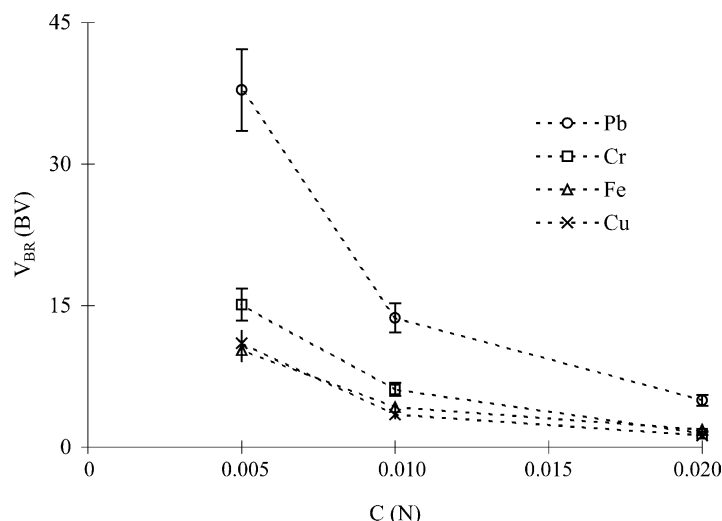


Fig. 3. Effect of concentration on breakpoint for the ion exchange of heavy metals on natural clinoptilolite ( $Q = 5$  BV/h,  $d = 1.18$ – $1.4$  mm).

Lower flow rates result in high residence times in the column. It is well known that because of the relatively slow loading kinetics of zeolites, relatively long residence times are needed [30]. In actual column operation, any volume element of the solution is in contact with a given layer of the bed for only a limited period of time, usually insufficient for attainment of equilibrium. Thus the failure of attaining local equilibrium results in lower uptake of cations from the incoming solution [13].

However, some side effects of low flow rates may be serious in bench-scale operations. In the present study, upflow operation was chosen in order to assure complete wetting of the material. In downflow mode, complete wetting of the material is not always possible and specially designed liquid distributors should be used [31]. Generally, by lowering the flow rate, the liquid holdup of the bed is lowered and liquid maldistribution may have serious effects upon the effectiveness of the process [20,32]. At low liquid holdup values, a portion of the material is not well wetted and thus not active during the process, remaining unused, while due to maldistribution, some portion of the liquid is traveling along the column through preferential paths (channeling) and leaves the bed essentially without treatment [33]. In a clinoptilolite ion exchange study [17] a decrease of 40% in process effectiveness was observed in large columns compared to smaller ones, under the same operational conditions, e.g. downflow operation and flow rate of 5–7.5 BV/h. The difference was attributed to the channeling. Furthermore, upflow mode resulted in a more effective use of clinoptilolite compared with downflow, under the same conditions [28].

### 3.2. Effect of concentration

The effect of solution concentration on  $V_{BR}$  is examined for 1.18–1.4 mm particle size and 5 BV/h volumetric flow rate (runs 4–6) and the results are reported in Fig. 3.

Table 3

Dilution ratios and corresponding  $V_{BR}$  ratios for the exchange of heavy metals on natural clinoptilolite

Dilution ratio	Pb	Cr	Fe	Cu
2	2.8	3.5	2.4	3
4	7.6	10	5.6	9

It can be seen that the dilution of the solutions is leading to an increase of the total volume treated. If the dilution ratio were equal to the ratio of the corresponding  $V_{BR}$  volumes, then dilution would not be of practical use. The corresponding ratios are defined as follows:

$$\text{dilution ratio} = \frac{C_0}{C_1} \quad (1)$$

$$V_{BR} \text{ ratio} = \frac{V_{BR,1}}{V_{BR,0}} \quad (2)$$

where subscript 0 refers to the maximum concentration and the corresponding  $V_{BR}$  and subscript 1 to the concentration of the diluted solution and the corresponding  $V_{BR}$ . In Table 3 dilution ratios and the corresponding  $V_{BR}$  ratios are presented for the experimental data on Fig. 3.

It is evident that dilution leads to an increase in  $V_{BR}$ , the magnitude of which depends on the specific metal exchanged. This finding can be attributed to the increase of selectivity in ion exchange by dilution of the solutions [13]. The valences of the exchanging cations have a strong effect on ion exchange equilibrium and thus on the removal efficiency of any type of ion exchange process. This behavior is commonly referred as “concentration-valency effect” [13,16]. It is theoretically known that in cases where the exchanging ions are not of equal valence, the equilibrium is a function of the total concentration and, for higher concentrations, is shifted to favor pickup of the lower charged

cations and consequently to exclude higher charged cations from the solid phase [13,34]. In the present study the heavy metals are exchanged with the cations initially present in the zeolite, namely  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , it is therefore expected that ion exchange will be favored by dilution.

Similar results have been obtained in the case of adsorption. The effect of concentration was examined in adsorption studies of lead and cadmium by activated carbon, under a volumetric flow rate of 20 BV/h and concentration between  $10 \times 10^{-3}$  and  $50 \times 10^{-3}$  g/L. Lowering the concentration by a factor of 5 the BV treated until breakpoint ( $C/C_0 = 3\%$ ) was increased by a factor of about 2 [11].

### 3.3. Effect of particle size

The effect of particle size on  $V_{\text{BR}}$  is examined for concentration of 0.01 N and volumetric flow rate of 5 BV/h (runs 7–9) and the results are shown in Fig. 4.

It can be seen that lowering the particle size from 1.4–1.7 to 0.8–1 mm,  $V_{\text{BR}}$  is increased by a factor near to 2 in all cases. The effect of particle size on ion exchange of ammonium ions in clinoptilolite packed beds has been studied elsewhere. Decreasing the particle size from 1.6–4.6 to 0.5–1 mm the breaking point ( $V_{\text{BR}}$ ) increased by a factor near to 2 [17].

The dependence of the performance on particle size is leading to the conclusion that diffusion (either particle or film) is the rate-limiting step of the overall ion exchange [13]. It is well known that by decreasing the particle size, the performance of adsorption and ion exchange processes is improved [13,23]. However small particle sizes result in high flow resistance of the column and should be avoided.

According to the basic theory of adsorption and ion exchange and for particle-diffusion-controlled ion exchange, the exchange rate is proportional to  $\bar{D}/d^2$  [13]. Since particle size ( $d_p$ ) is supposed to influence neither the equilibrium state nor the diffusion coefficient ( $\bar{D}$ ) of a specific cation,

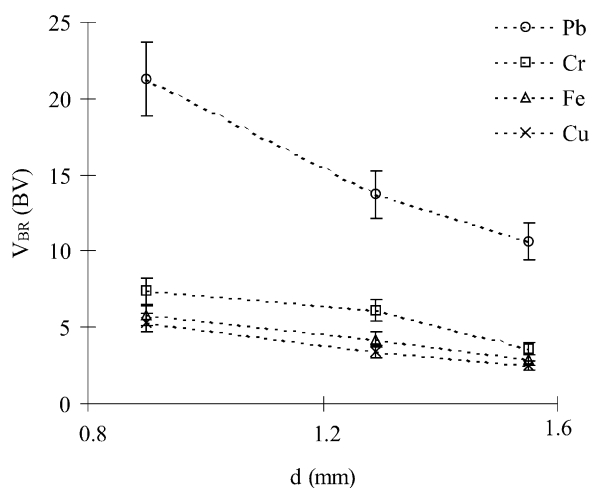


Fig. 4. Effect of particle size on breakpoint for the ion exchange of heavy metals on natural clinoptilolite ( $C = 0.01$  N,  $Q = 5$  BV/h).

higher rates should be observed for smaller particles. However, some exceptions have to be pointed out: it has been found that smaller particle sizes may exhibit lower rates, due to lower effective diffusion coefficients, resulting from structural problems or pore clogging [14,35,36]. Consequently, taking into account this exception, when comparing rates for particles with  $d_1$  and  $d_2$  ( $d_1 < d_2$ ) smaller particle might result in higher kinetics only if

$$\frac{\bar{D}_1}{d_1^2} > \frac{\bar{D}_2}{d_2^2} \Leftrightarrow \frac{\bar{D}_1}{\bar{D}_2} \left( \frac{d_2}{d_1} \right)^2 > 1 \quad (3)$$

According to the experimental data, since the ion exchange material was thoroughly washed before use, pore clogging is not expected to influence the diffusion coefficients which are considered to be constant irrespective of particles size. Then, with particle diffusion as the controlling step, the exchange rate should be increased by moving from 1.55 to 0.9 mm particles. Consequently,  $V_{\text{BR}}$  should be increased as it can be viewed as an indication of exchange rate, since it is well known that the shape of breakthrough curve (and thus the location of  $V_{\text{BR}}$ ) is influenced by the rate of ion exchange process.

### 3.4. Effect of ion exchanger modification

The effect of modification of natural clinoptilolite is examined for concentration of 0.01 N, volumetric flow rate of 5 BV/h and particle size of 1.18–1.4 mm (runs 1 and 10) and the results are reported in Fig. 5.

Fig. 5 shows that the modification of the natural sample is favorable, resulting in 32–100% higher breakpoint values, depending on the specific cation. The treatment of natural clinoptilolite with sodium chloride solutions was found to improve the effective exchange capacity, and therefore its performance for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Cu}^{2+}$  [7,15,20,29,37]. The improvement in the removal efficiency was attributed to the increase of easy removable  $\text{Na}^+$  ions in the zeolite structure. The effect of clinoptilolite pretreatment on ion exchange of ammonia ions in dilute solutions (20–25 mg/L), under vol-

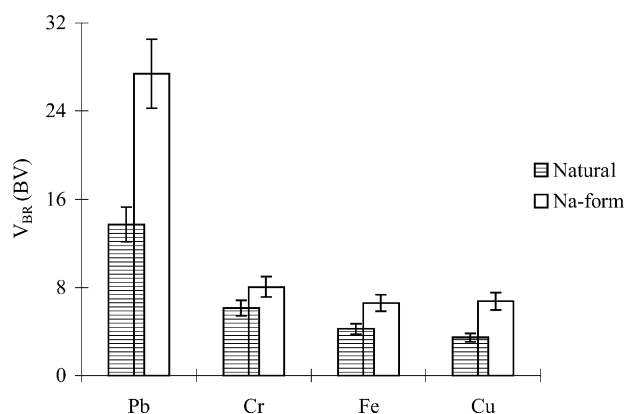


Fig. 5. Effect of the modification of the natural sample for the ion exchange of heavy metals ( $C = 0.01$  N,  $Q = 5$  BV/h,  $d = 1.18$ –1.4 mm).



umetric flow rate of 10–20 BV/h has been also investigated. The breaking point ( $C/Co = 10\%$ ) was increased by a factor of 1.43–1.73 (43–73%), compared to that of natural sample [17,18].

#### 4. Conclusions

The removal efficiency increases with decreasing flow rate, particle size and concentration and is improved by a factor of 2–10, depending on the specific metal and the examined parameter. The modification of the natural sample is favorable, leading to an increase of removal efficiency by 32–100%.

Since the metals used in the present study with different chemical and physical properties influenced in the same manner it can be qualitatively speculated that other heavy metals would be equally influenced.

Removal efficiency order (or selectivity series) is the same for all examined experimental conditions:  $Pb^{2+} > Cr^{3+} > Fe^{3+} \geq Cu^{2+}$ . This order could be explained by the fact that large and stable inorganic complexes may be mechanically excluded from the zeolitic structure by sieve action. It is well known that transition metals can form stable complexes due to their electronic structure [38].  $Fe^{3+}$ ,  $Cr^{3+}$  and  $Cu^{2+}$  can form stable complexes with water molecules, these complexes being charged and giving color to their solutions. The hydrated ions  $[Fe(H_2O)_6]^{3+}$ ,  $[Cu(H_2O)_4]^{2+}$  and  $[Cr(H_2O)_6]^{3+}$  or, more frequently,  $[Cr(H_2O)_5Cl]^{2+}$  are the corresponding stable species. On the other hand  $Pb^{2+}$  is forming a hydrated ion, but generally it has not the tendency to form strong complexes. This must be the reason for its preferential uptake by the ion exchanger, compared to the other metals.

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