

Removal of Cu(II) in fixed bed and batch reactors using natural zeolite and exfoliated vermiculite as adsorbents

Marinos A. Stylianou*, Vasilis J. Inglezakis, Konstantinos G. Moustakas,
Simos Ph. Malamis, Maria D. Loizidou

*Unit of Environmental Science and Technology, School of Chemical Engineering,
National Technical University of Athens, 9, Heroon Polytechniou Str., Zographou Campus,
157 73 Athens, Greece
Tel. +30-210-772 2334/3108; Fax +30-210-772 3285; email: marstyl@central.ntua.gr*

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Abstract

The ability of natural zeolite (clinoptilolite) and exfoliated vermiculite to remove copper from aqueous solutions was studied in fixed bed column and batch reactors. The effect of agitation speed (0, 100, 200, 400 rpm), temperature (25, 45, 60°C), and particle size [2.5–5.0 mm, dust (<0.25 mm)] and solution pH (1.00–4.00) on the removal of heavy metals was studied. Fixed bed experiments were conducted, using three different volumetric flow rates of 5–7–10 BV (Bed Volumes)/h, under an initial normality of 0.01 N (317.7 mg/L), at initial pH of 4.00 and ambient temperature (25°C). Vermiculite was found to be more effective for the removal of copper in batch mode reactors under all the tested conditions, while the removal efficiency follows the order: vermiculite > clinoptilolite dust > clinoptilolite 2.5–5.0 mm. The removal of Cu(II) using vermiculite reached 67.6%, at ambient temperature and at the agitation speed of 400 rpm, while it was approximately 42.5% at 60°C with no agitation. The highest removal level in the case of clinoptilolite use reached the percentage of 37.3% at the temperature of 60°C without agitation; the same removal efficiency was obtained at ambient conditions with an agitation speed of 400 rpm. Clinoptilolite dust is found to be more efficient than granular clinoptilolite under all the conditions that were tested. Agitation and temperature also affect the uptake of the specific ions. Finally, the acidity of the aqueous solution influences the removal of copper by minerals. In column studies, the decrease of the flow rate resulted in the increase of the removal efficiency.

Keywords: Ion exchange; Copper; Clinoptilolite; Vermiculite

*Corresponding author.

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1. Introduction

The increasing levels of toxic metals that are discharged to the environment as industrial wastes, represent a serious threat to human health, living resources and ecological systems. Although there are many sources of heavy metals, specific industrial sectors are at present those, which mostly contribute to environmental pollution with these toxic metals [1]. Mining wastes and acid mine drainage contribute significant quantities of dissolved copper to effluent streams. Other sources are fertilizer manufacturing, petroleum refining, paints and pigments, steel works, foundries, electroplating and electrical equipment, brass, etc. Although copper is an essential element, acute doses cause metabolic disorders. Inhalation of copper produces symptoms similar to those of silicosis and allergic contact dermatitis. Chronic copper poisoning causes hemolytic anemia, neurological abnormalities and corneal opacity [2].

Among various available treatment processes for the removal of heavy metals, such as precipitation, phytoextraction, ultrafiltration and reverse osmosis, ion exchange is considered to be a cost effective method provided that low cost ion exchangers, such as zeolites and clays, are used [3].

Zeolites are naturally occurring hydrated aluminosilicate minerals. They belong to the class of minerals known as “tectosilicates” [4]. The structure of zeolites consists of the three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, while the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cations (Na, K, or Ca). These cations are exchangeable with certain cations in solutions, such as lead, cadmium, zinc, and manganese [3]. Vermiculite is typical clay [5,6] and consists of tetrahedral–octahedral–tetrahedral sheets. The two tetrahedral silicate layers are

bonded together by one octahedral magnesium hydroxide-like layer and the structure is often referred to as 2:1 phyllosilicate. When tetravalent silicon is substituted by trivalent aluminum in the tetrahedral layer of the vermiculite sheet, a negative charge is generated on the layer and, thus, hydrated magnesium is adsorbed on the tetrahedral layer between the sheets to maintain electro neutrality. These magnesium ions can be easily cation-exchanged with other cationic species such as copper, which partly contribute to the high cation-exchange capacity of vermiculite [7]. Vermiculite can adsorb heavy metals via two different mechanisms: (1) through cation exchange at the planar sites, resulting from the interactions between metal ions and negative permanent charge (outer-sphere complexes) and (2) through the formation of inner-sphere complexes through Si–O– and Al–O– groups at the clay particle edges. Both mechanisms are pH dependent but the latter is particularly influenced by pH because in acid conditions ($\text{pH} < 4$) most silanol and aluminol groups on edges are protonated [8].

Batch mode and column studies have been performed by researchers to examine heavy metal adsorption onto clinoptilolite [1,4,9–17] and vermiculite [7,8,18–20]. Panayotova [17] reported that in experiments that were conducted batchwise, the optimum wastewater to zeolite ratio in order to remove copper ions from wastewater is 100:1 and the optimum pH value of water to be treated is 5.5–7.5. Experimental work also showed that zeolite with finer particles has a higher uptake capacity. Erdem et al. [3] studied the removal of heavy metal cations by zeolite in batch method experiments and, according to equilibrium studies, the selectivity sequence was found to be $\text{Co}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Mn}^{2+}$. Cincotti et al. [15] examined sardinian natural clinoptilolites to evaluate their adsorption for copper, cadmium, lead and zinc, as well as ammonium removal. The natural material was either used without any pre-treatment or once converted into the sodium form. Equilibrium

data for each species and the natural material was obtained. Breakthrough experiments of lead solutions were performed and showed that 5% breakpoint resulted to be equal to 250 BV (Bed Volumes). Blanchard et al. [16] reported that wastewater containing heavy ions, such as Pb^{2+} , Zn^{2+} , Cu^{2+} besides NH_4^+ ions, can be treated effectively by filtration on clinoptilolite columns. The order of efficiency was $\text{Pb}^{2+} > \text{NH}_4^+ > \text{Cd}^{2+}$, Cu^{2+} , $\text{Sr}^{2+} \geq \text{Zn}^{2+} > \text{Co}^{2+}$. Inglezakis et al. [21] examined the influence of clinoptilolite on solution acidity and the effect of acidity on the ion exchange process. Selectivity determination demonstrated that for two-component and four-component solutions, the ion exchange capacity followed the order: $\text{Pb}^{2+} > \text{Fe}^{3+} > \text{Cr}^{3+} \geq \text{Cu}^{2+}$. On the other hand, selectivity in single metal solutions where acidity was not adjusted followed the order $\text{Pb}^{2+} > \text{Cr}^{3+} \geq \text{Fe}^{3+} \approx \text{Cu}^{2+}$. Seaborn and Jameson [18] used exfoliated vermiculite as an ion exchange medium for the removal of transition metal ions from dilute aqueous solutions. They showed that divalent ions are preferred to trivalent ones and the order of the breakthrough time was $\text{Ni}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} \geq \text{Cr}^{3+}$. Fonseca et al. [19] investigated vermiculite as an exchanger for heavy cations, as a function of time of reaction, pH and cation concentration. Malandrino et al. [8] studied the sorption behavior of vermiculite with respect to different heavy metals as a function of pH and in the present of different ligands. They showed that adsorption of metal ions on vermiculite decreases with decreasing pH and increasing ionic strength.

This paper presents results on the ability of natural zeolite (clinoptilolite) and vermiculite

(clay) to remove Cu^{2+} from aqueous solutions. The effect of the particle size of the minerals, agitation speed, and temperature were examined during batch experiments. Furthermore, the optimum pH values of the aqueous solutions to be treated were investigated. Finally, the effect of flow rate on breakthrough point was investigated for up-flow operation in packed beds of clinoptilolite. The effect of both vermiculite and zeolite for the removal of copper in aqueous solutions has not been studied. Furthermore, there is a gap in the literature concerning the variety of operating conditions, which this work aims to fill.

2. Materials and methods

2.1. Materials

Two different minerals were used in order to examine the removal of Cu^{2+} from aqueous solutions. Natural zeolite (clinoptilolite) and vermiculite (clay) were supplied by S&B Industrial Minerals S.A and I.G.M.E. (Institute of Geology & Mineral Exploration). Clinoptilolite was ground and then sieved to different fractions of which the fraction of 2.5–5.0 mm and dust were used for this study. Vermiculite was used in dust form having a size <0.25 mm. The chemical composition of the materials used was determined through XRF and wet chemical analysis (for oxides: XRF on fused beads containing $\text{Li}_2\text{B}_4\text{O}_7$ flux, LOI: mass loss upon firing at 1100°C) (Table 1). The cation exchange capacity (CEC) of clinoptilolite was 188.40 meq/100 g. The respective value for vermiculite was 120.65 meq/100 g (NH_4AC method).

Table 1
Chemical analysis of minerals (%w/w)

	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI
Zeolite	70.08	11.72	0.14	0.67	0.71	3.18	0.55	3.50	9.45
Vermiculite	37.35	12.32	0.30	4.84	25.64	3.26	0.06	0.29	15.28

Table 2

Various parameters tested on the ion exchange of Cu on clinoptilolite granular, clinoptilolite dust and vermiculite in batch mode experiments

Parameters tested	Temperature (°C)	Time interval (min)	Agitation (rpm)	Solution pH
Particle size	25	1–3–5–10–20–45–120	–	4.00
Temperature	25–45–60	10–45–120	–	4.00
Agitation	25	5–10–20–45–120	0–100–200–400	4.00
Acidity	25	10–45–120	–	1.00, 2.00, 3.00, 4.00

The minerals were used without any chemical pre-treatment. The samples were washed and air-dried at 80°C and then kept in desiccators. Solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ 0.01 N (0.005 mol/L or 317.7 ppm Cu) was prepared using analytical grade reagent and high-purity deionised water. The pH was initially adjusted at 4 to avoid precipitation during all ion exchange experiments using nitric acid (HNO_3).

2.2. Batch experiments

The ion exchange of Cu^{2+} on clinoptilolite 2.5–5 mm, clinoptilolite dust and vermiculite dust was examined in batch mode experiments. A measured quantity of mineral (2 g) was added to a vessel containing measured volume of Cu^{2+} solution (100 mL). The initial copper concentration in the solution was 317.7 mg/L. Different parameters were tested (Table 2) and the solutions were analyzed after a specified time interval. The experiments were repeated for each different period of time in order to avoid sampling during experiment (one experiment for each time interval). The final pH was recorded in order to check for precipitation.

In order to check the effect of acidity on copper uptake by the minerals, initial pH value was adjusted by adding HNO_3 at 4.00, 3.00, 2.00 and 1.00. Since the aim of this work is to investigate the effects of acidity on the ion-exchange process only, lower values are not used, as clinoptilolite structure breaks down in highly

acidic solutions. This process known as dealumination, takes place at acidity values typically lower than 1 [21,22]. Furthermore, higher pH values were not tested as precipitation of $\text{Cu}(\text{OH})_2$ occurs at $\text{pH} > 5.75$ for an influent Cu concentration of 317.7 ppm.

The concentrations of metal ions were measured by atomic absorption spectroscopy (AAS), using a Perkin Elmer Model 2380 spectrophotometer.

2.3. Fixed bed experiments

Fixed bed experiments were conducted in order to examine the Cu^{2+} uptake by natural clinoptilolite [2.5–5 mm], using three different volumetric flow rates of 5–7–10 BV/h (where BV is a volume of liquid equal to the volume of the bed), under a total normality of 0.01 N and an initial pH value of 4.00 and at ambient temperature (25°C). The ion exchange process was conducted in 0.7 m long plexiglass columns of 0.02 m internal diameter. The solution was introduced at a constant volumetric flow rate (Q) and concentration (C), using a peristaltic pump in up-flow mode, in order to assure complete wetting of the zeolite particles. Liquid samples were withdrawn at the exit of the bed at specific time intervals, depending on the flow rate, acidified with HNO_3 at pH 2 and analyzed for heavy metal cations. By plotting the exit metal concentration vs. time, the breakthrough curves can be obtained.

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 that passes through the bed has this concentration level, the average fraction of solute removed from the beginning until the breakpoint is generally very high [23]. In the present study, the “breakpoint” is set at 10% and the total volume of the treated solution until this point (V_{BR} , expressed in terms of Bed Volumes) is used as a measure of the removal efficiency of the operation.

The samples were analyzed for heavy metal cations by AAS (Perkin Elmer model 2380 spectrophotometer).

3. Results and discussion

3.1. Effect of particle size of the minerals on the uptake of copper

The time-dependent behavior of Cu^{2+} adsorption was measured by varying the equilibrium time between the adsorbate and adsorbent in the range of 1–120 min. The percentage removal of Cu^{2+} from aqueous solution as a function of contact time (without agitation, $T = 25^\circ\text{C}$) indicates that higher removal of Cu^{2+} was observed in the case of vermiculite. Furthermore, clinoptilolite dust was found to be more efficient than granular clinoptilolite (Fig. 1).

Comparisons between materials showed that the % removal of Cu^{2+} from the aqueous solution follows the order:

vermiculite > clinoptilolite dust > clinoptilolite
2.5–5.0 mm.

Although clinoptilolite was found to have a higher CEC than vermiculite, in the experiments

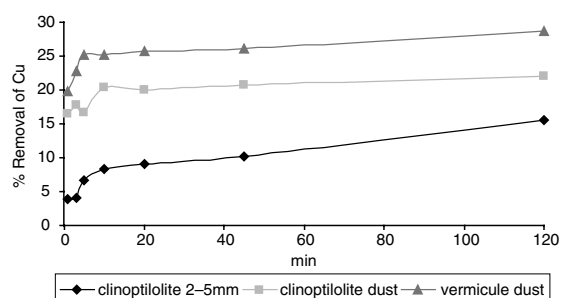


Fig. 1. Percentage removal of copper as a function of contact time ($T = 25^\circ\text{C}$, without agitation).

conducted it was found that vermiculite is more effective in removing Cu^{2+} than clinoptilolite. Furthermore, the dust form of the minerals is found to be more efficient than the granular form; this is attributed to the increasing availability and accessibility of the ion exchange centers. An exchange or an adsorption site is characterized by its availability and its accessibility with respect to the incoming ion. In the dust form minerals, the availability of ion exchange centers is almost the same to the greater granules because the mineral has practically the same concentration of active sites, while accessibility is easier since the diffusion paths become shorter. Availability is straightforwardly related to the equilibrium behavior of the ion exchange system (available site is the one that can be occupied by the incoming ion). Accessibility is related to the kinetic behavior of the ion exchange system: it expresses the ease of movement of the specific cation within the pores leading to this site. The availability and the accessibility of an exchange site depend not only on the characteristics of the site, but also on the specific incoming cation [24].

3.2. Effect of temperature on the uptake of copper

An increase in Cu^{2+} removal from the aqueous solution with a raise in temperature was observed. Vermiculite was found to be more effective,

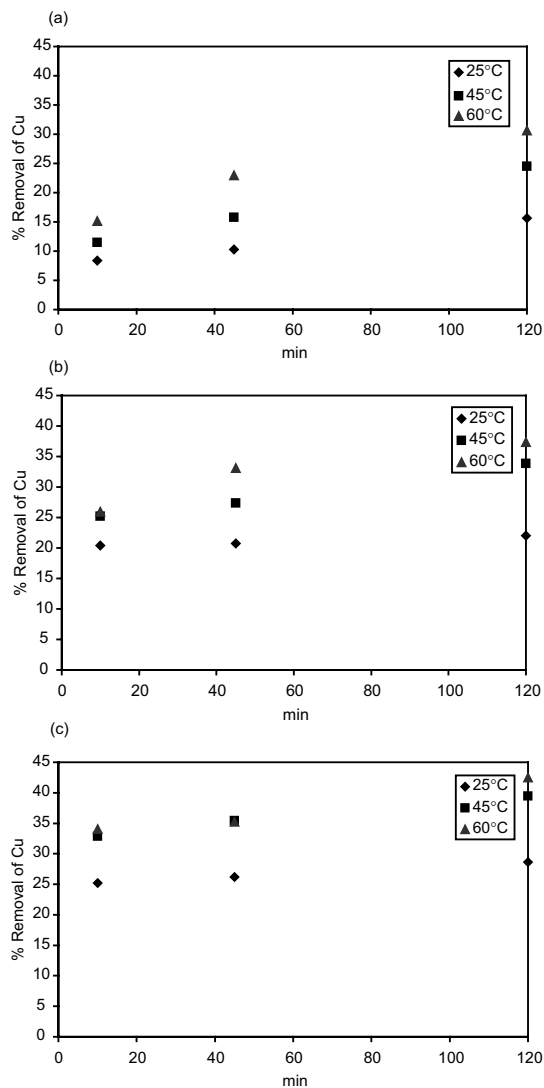


Fig. 2. Percentage removal of copper for (a) clinoptilolite 2.5–5.0 mm, (b) clinoptilolite dust and (c) vermiculite as a function of temperature.

reaching 39.5 and 42.5% removal at the temperatures of 45 and 60°C respectively (Fig. 2 (c)). Clinoptilolite dust seems to be more effective than clinoptilolite 2.5–5.0 mm at 45°C (33.9% > 24.5%) and at 60°C (37.4 > 30.6) (Fig. 2(a) and (b)).

As far as the effect of the temperature on the adsorption process is concerned, the metal uptake is favored at higher temperatures, since

higher temperatures activate the metal ions for enhancing adsorption at the coordinating sites of the minerals [25]. Also, it is mentioned that cations move faster when temperature increases. Potential explanations for this are that specific or electrostatic interactions become weaker and the ions become smaller, since solvation is reduced [24].

3.3. Effect of agitation on the uptake of copper

Experimental results regarding the effect of agitation speed (0, 100, 200, 400 rpm) are presented. It is clear that agitation is found to be appropriate for maximum adsorption of Cu^{2+} from the minerals. The removal of Cu^{2+} using vermiculite reaches 67.6% at 400 rpm (Fig. 3 (c)). On the other hand, the highest removal level achieved by clinoptilolite is found to be 37.3% (for the dust form) (Fig. 3(a) and (b)).

The effect of agitation speed was examined at agitation speeds of 0–100–200–400 rpm. Agitation speed above 500 rpm was not examined, because the suspension was not homogeneous [7]. It is obvious that agitation increased copper removal from aqueous solutions. This is due to the fact that Cu^{2+} , through their transportation to the solid phase, meets resistance at the liquid phase, through the boundary layer. The motion induced through the agitation of suspensions during experiments leads to a decrease of the boundary layer thickness and to a consequent decrease of the transportation resistance of copper ions. This increases the transfer rate of the ions and, thus, the adsorption rate of the minerals.

3.4. Effect of acidity on the uptake of copper

The pH of the aqueous solution is an important variable, which controls the adsorption of the metal at the solid–water interfaces as well as the ion exchange of cations. The influence of pH on the adsorption of Cu(II) on vermiculite and clinoptilolite (granular and dust) was examined in the pH range of 1.00–4.00. It is observed that

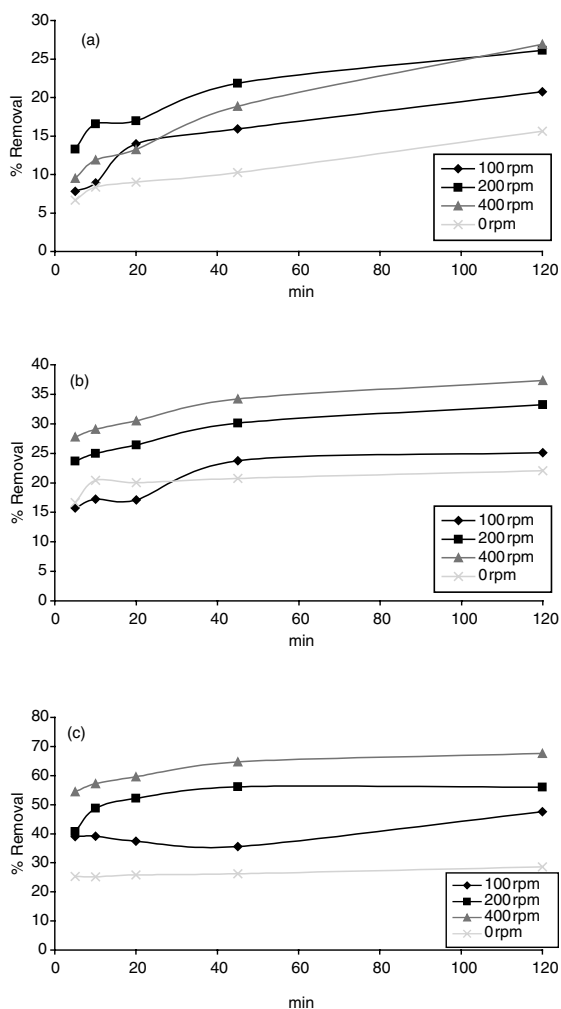


Fig. 3. Percentage removal of copper with agitation for (a) clinoptilolite 2.5–5.0 mm, (b) clinoptilolite dust and (c) vermiculite.

acidity influences the removal of Cu^{2+} by the minerals (Fig. 4 (a)–(c)). The increase of the pH of the solution from 1 to 4 increases the removal of copper. For all minerals, it can be seen that there is a decrease in the ion exchange capacity for pH 1–2. This decrease in the adsorption of Cu^{2+} probably reflects a reduction in the quantity of negative surface charges on the clay. H^+ cations should be considered as competitive ones in ion-exchange processes and, consequently, ion

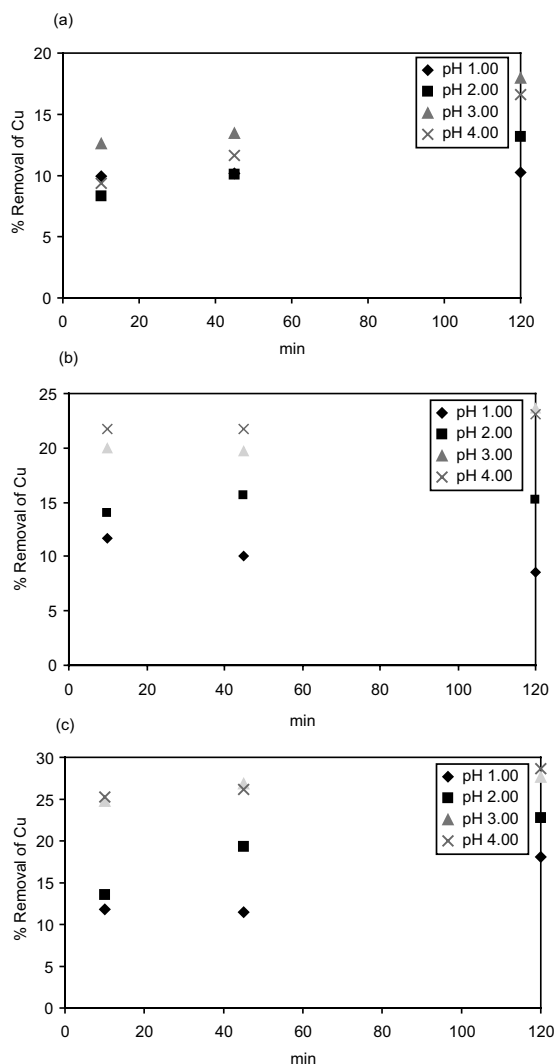
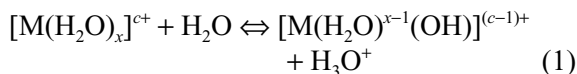


Fig. 4. Percentage removal of copper for (a) clinoptilolite 2.5–5.0 mm, (b) clinoptilolite dust and (c) vermiculite, in the pH range of 1.00–4.00.

exchange of metals is favored by high pH values, which should, however, be lower than the minimum pH of precipitation. However, low pH values may also have a beneficial effect as they influence the hydrolysis of the metals. Hydration is followed by hydrolysis, according to the following two-ray reversible reaction, giving acidic properties to heavy metal solutions. Consequently, at

decreasing pH the above equilibrium is shifted to the left and more highly charged metal complexes are formed, a fact which is beneficial for the exchange [21].



3.5. Effect of volumetric flow rate

The effect of volumetric flow rate is examined for clinoptilolite particles of 2.5–5 mm and an initial solution concentration of 0.01 N. Typical experimental breakthrough curves are shown in Fig. 5 and the effect of volumetric flow rate on V_{BR} is shown in Fig. 6.

As it can be seen removal efficiency is favored by lower volumetric flow rates in the region 5–10 BV/h. 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 10 to 5 BV/h V_{BR} is increased.

According to the present study, higher flow rates than 10 BV/h should be avoided since breakthrough would occur faster and with less sharpened boundaries. Flow rates lower than 5 BV/h flow rates are expected to be beneficial on removal efficiency, leading however to practically too

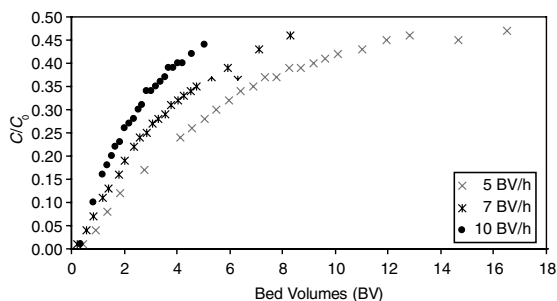


Fig. 5. Typical experimental breakthrough curves for the ion exchange of copper on natural clinoptilolite ($C = 0.01$ N, $Q = 5$ – 7 – 10 BV/h, $d = 2.5$ – 5 mm, breakthrough point = 10%).

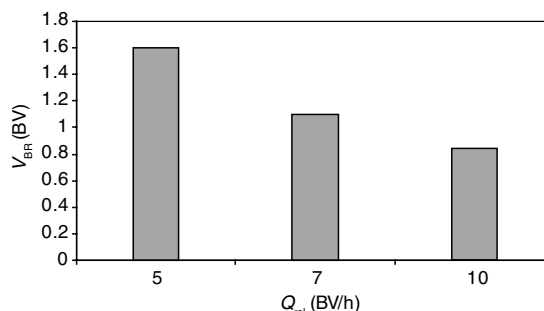


Fig. 6. Effect of volumetric flow rate on breakpoint for the ion exchange of copper on natural clinoptilolite ($C = 0.01$ N, $d = 2.5$ – 5 mm). Total volume of treated solution until breakpoint (V_{BR}) is expressed in terms of Bed Volumes.

high retention times. Consequently, 5 BV/h is considered to be a reasonable flow rate.

Lower flow rates result in high residence times in the column. It is well known that because of the slow loading kinetics of zeolites, relatively long residence times are needed. 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 [23].

However, some side effects of low flow rates may be serious in bench-scale operations. In the present study, up-flow 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. Generally, by lowering the flow rate, the liquid hold-up of the bed is lowered and liquid maldistribution may have serious effects upon the effectiveness of the process. At low liquid hold-up 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 [23].

4. Conclusions

This work has studied the effect of both vermiculite and zeolite in the removal of copper from solutions in batch reactors as well as in bed columns under a variety of operating conditions. In conclusion, the series of the tests performed in this work shows that

- Vermiculite was found to be the most effective mineral for the removal of Cu^{2+} in aqueous solutions, while granular clinoptilolite was the least effective one under all operating conditions. The % removal of copper follows the order: vermiculite > clinoptilolite dust > clinoptilolite 2.5–5.0 mm.
- The usage of vermiculite resulted in the removal of Cu^{2+} by 67.6% at ambient temperature and 400 rpm agitation and the respective removal was approximately 42.5% at 60°C without agitation. The highest removal level reached by clinoptilolite was 37.0%.
- High agitation speeds and high temperatures enhance the ion exchange processes by the minerals. The highest efficiencies were observed at high agitation speeds (400 rpm) at room temperatures and the second highest removal efficiencies were observed at high temperatures (60°C) with no agitation. At a future study it is interesting to examine the effect of combined high agitation speeds and temperatures.
- Acidity of the aqueous solutions also influences the removal of ions by the minerals. The pH value of 4.00 seems to give better results than lower pH values.
- In column studies the decrease of the flow rate resulted in the increase of the removal efficiency. However, there is a need to balance between very low flows which are not practicable and high flows that reduce removal efficiencies.

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