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Experimental studies and modeling of clinoptilolite and vermiculite fixed beds for Mn^{2+}, Zn^{2+}, and Cr^{3+} removal

V.J. Inglezakis[a], M.A. Stylianou[b], M. Loizidou[c], A.A. Zorpas[d,*]

[a]*School of Engineering, Chemical Engineering Department, Nazarbayev University, Astana, Republic of Kazakhstan, Tel. +7 7172 706534; email: vasileios.inglezakis@nu.edu.kz*
[b]*Department of Civil & Environmental Engineering, NIREAS-International Water Research Center, Subsurface Research Laboratory, University of Cyprus, Nicosia, Cyprus, Tel. +357 2289 2214; email: stylianou.a.marinos@ucy.ac.cy*
[c]*School of Chemical Engineering, Unit of Environmental Science and Technology (UEST), National Technical University of Athens, Athens, Greece, Tel. +30 210 7723285; email: mloiz@chemeng.ntua.gr*
[d]*Faculty of Pure and Applied Science, Environmental Conservation and Management, Cyprus Open University, P.O. Box 12794, 2252 Latsia, Nicosia, Cyprus Tel. +357 23743440; emails: antoniszorpas@yahoo.com, antonis.zorpas@ouc.ac.cy*

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ABSTRACT

In the present study, batch and fixed bed experiments were conducted in order to compare clinoptilolite and vermiculite for the removal of Mn^{2+}, Zn^{2+}, and Cr^{3+} from aqueous solutions under the same experimental conditions. Ion-exchange equilibrium is examined by use of batch equilibrium isotherms, distribution coefficients, and maximum exchange levels (MEL). Fixed bed experiments were conducted, and breakthrough curves and operational capacity were determined. Furthermore, diffusion coefficients were estimated by use of simplified fixed bed models. Concerning the comparison of the two minerals, in all experiments, for both batch (distribution coefficients and MEL) and fixed bed (breakthrough points and operating capacity (OC)), vermiculite showed better performance than clinoptilolite for all metals. Vermiculite selectivity series derived from batch distribution coefficients as well as in fixed beds is $Cr^{3+} > Zn^{2+} > Mn^{2+}$ and is the same for clinoptilolite for liquid-phase equilibrium at relative concentration of $X < 0.2$. For more concentrated equilibrium solutions, the clinoptilolite selectivity changes for Cr^{3+} and remains the same for the other two metals, i.e. $Zn^{2+} > Mn^{2+} > Cr^{3+}$. MEL are 14.4–26.9 mg/g and 34.2–43.6 mg/g for clinoptilolite and vermiculite, respectively, and OC is found to be 3.6–7.9 mg/g and 12.8–29.3 mg/g for clinoptilolite and vermiculite, respectively, 25–75% lower than MEL. The application of the simplified fixed bed model is successful for Zn in both minerals and Cr^{3+}-vermiculite system. For Cr^{3+}-clinoptilolite system, the model is not applicable due to the sigmoidal shape of the isotherm while for Mn, the model fails in low concentrations for both minerals, and it seems to

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*Corresponding author.

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approach experimental data only for $X > 0.2–0.3$. Solid-phase diffusion coefficients were estimated to be in the order of magnitude of 10^{-8} cm^2/s for clinoptilolite and 10^{-9} cm^2/s for vermiculite.

Keywords: Clinoptilolite; Vermiculite; Heavy metals; Ion-exchange; Fixed beds reactors

1. Introduction

Industrial and, in lesser extent, municipal wastewater contain considerable heavy metal content and, therefore, treatment is required prior to disposal in natural environment [1]. The presence of these metals in the environment is of major concern as they are not biodegradable and tend to accumulate in living organisms and through food chain, threat the environment and human life. The removal of metal ions from aqueous solutions can be achieved by several processes such as precipitation, liquid-liquid extraction, reverse osmosis, adsorption, and ion-exchange. Most of the treatment processes used in practice are either non-effective to achieve the required stringent disposal standards or economically unsustainable. Hence, in recent years, the removal of metal ions using natural minerals as zeolites and clays has been one of the most popular and economically attractive methods.

The exchange of ions between a liquid phase and a porous solid is called ion exchange. Clays and zeolites are extensively used in ion-exchange processes due to their low cost, worldwide abundance, high exchange capacity, and selectivity properties [1,2]. Zeolites are hydrated aluminosilicate minerals that belong to the class of minerals known as "tectosilicates" with a cage-like structure that offers large internal and external surface areas for ion exchange. Clinoptilolite is the most abundant natural zeolite and its characteristic morphology includes an open structure of easy access, formed by open channels of 8–10 membered rings. These channels are occupied by ions such as Na^+, K^+, Ca^{2+}, and Mg^{2+} that can be exchanged with other metal ions such as manganese, chromium, and zinc. Vermiculite is typical phylosilicate 2:1 clay rich in magnesium. It consists of tetrahedral–octahedral–tetrahedral sheets. These magnesium ions are the result from the substitution of tetravalent silicon by trivalent aluminum in the tetrahedral layer of the vermiculite sheet, and furthermore, from the negative charge that is generated on the layer, hydrated magnesium is adsorbed on the tetrahedral layer between the sheets to maintain electro neutrality. Magnesium ions can be easily cation exchanged, which contribute to the high cation exchange capacity of vermiculite [3].

Most ion-exchange processes, both at the laboratory and plant scale, are performed in fixed beds. A solution is passed through a bed of ion-exchanger material where its composition is modified by ion-exchange or sorption. The composition of the effluent and its change with time depends on the properties of the ion exchanger, the composition of the feed, and the operating conditions. The curve representing the cation-exit concentration vs. time (or effluent volume) is called breakthrough curve and is used to characterize the process [4]. A significant number of papers has been published on fixed bed studies for the removal of heavy metals by clinoptilolite [4–9] and few papers on vermiculite [3,10–12]. Several fixed bed models have been applied on clinoptilolite and vermiculite fixed beds, but only few are using reliable diffusion-based models [5,6,10]. It is true that the vast majority of fixed bed models used in the related literature is kinetic-based and they make use of phenomenological pseudo-first or second order chemical reaction-like equations, which from physical meaning point of view are problematic as ion-exchange and adsorption are not chemical reactions but diffusion-driven processes. Furthermore, in order to interpret and model fixed bed data batch reactors, data are needed, a fact that in a number of publications is overlooked. Finally, there are few studies on the comparison of clinoptilolite and vermiculite; Cu^{2+}, Ni^{2+}, Zn^{2+}, and Pb^{2+} removal from aqueous solutions [3,11,12] and Mn^{2+} and Fe^{3+} from drinking water [8,13]. However, these studies address only small number of parameters in either batch or fixed bed operations.

In the present study, batch and fixed bed experiments were conducted in order to compare clinoptilolite and vermiculite for the removal of Mn^{2+}, Zn^{2+}, and Cr^{3+} from aqueous solutions under the same experimental conditions. Ion-exchange equilibrium was examined by use of batch equilibrium isotherms, distribution coefficients, and maximum exchange levels (MEL). In fixed beds breakthrough curves, operational capacity and diffusion coefficients were estimated by use of simplified fixed bed models. According to the authors' knowledge, very few, if any, studies include all experimental measurements included in the paper as both materials comparison and fixed bed modeling are based on a large number of experiments; three metals, two materials, two different modes of operation resulting in the evaluation of four different parameters, namely MEL, Langmuir equilibrium constant, operational capacity, and solid-phase diffusion coefficient (24 values in total). Is notable that full equilibrium curves are provided for both materials and all metals (6 curves) and full breakthrough curves (6 in total). Such extended comparison has not been made so far in the related literature but the value of the paper goes beyond this as it offers a detailed experimental protocol which can be easily replicated for different ion-exchange and adsorption systems. In this framework, pitfalls found in the related literature are explained and directions are provided for their avoidance.

2. Materials and methods

2.1. Samples and characterization

Two different natural minerals were used in this study, zeolite (clinoptilolite, 0–5 mm) and vermiculite (0–5 mm). Zeolite was supplied by S&B Industrial Minerals SA and vermiculite by IGME (Institute of Geology & Mineral Exploration–Greece). Clinoptilolite and vermiculite were crushed and milled into powder (<90 μm), for further analysis. The elemental composition of the materials was obtained through XRF analysis with the use of an ARL Advant XP sequential XRF (Table 1). The specific surface area and the pore characteristics for both materials were measured volumetrically by physisorption of N_2 at normal boiling point temperature (77 K) in a static mode using Nova-2000 6.11 Quantachrome BET-porosimeter instrument (Fig. 1). As is evident from pore size distribution results, both materials exhibit a maximum at about 25 Angstroms. The BET surface area and porosity is 28.64 m^2/g and 16.3% for clinoptilolite and 20.82 m^2/g and 6.1% for vermiculite, respectively.

Table 1
Chemical composition of mineral samples

	Zeolite (w/w) %	Vermiculite (w/w) %
SiO_2	70.1	47
Al_2O_3	12.0	16.6
Fe_2O_3	0.727	12.3
CaO	3.04	0.575
MgO	0.765	21.6
Na_2O	0.304	–
TiO_2	0.113	0.922
K_2O	3.31	0.350
LOI[a]	9.45	–

[a] LOI: mass loss upon firing at 1,100°C.

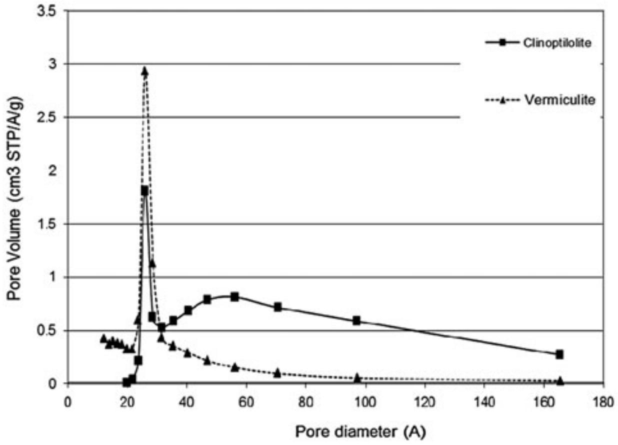

Fig. 1. Pore size distribution of clinoptilolite and vermiculite (BET analysis).

2.2. Batch experiments

Equilibrium studies were conducted as follows. Measured quantities of clinoptiloite or vermiculite (0.1–14 g) were added to vessels containing measured volume of Mn^{2+}, Zn^{2+}, or Cr^{3+} solution (100 mL) of normality 0.01 N. Every 10–20 d the solution was analyzed for metal concentrations until no further uptake from the minerals was observed. Total sampling volume was 2% of the total solution volume. The exchange temperature was kept constant during the batch reaction time at 25°C. All chemicals used were analytical grade reagents and high- purity deionized water. pH was initially adjusted to avoid precipitation during all ion-exchange experiments at 4 using HNO_3. MEL studies were conducted by repeated batch equilibrations as follows: a measured quantity of clinoptilolite or vermiculite (0.2–0.8 g) was added in a vessel containing measured volume of metal cation solution (100 mL) at an initial concentration of 0.01 N and an initial pH of 4. Every 3 d the solution was analyzed for metal concentration and then replaced with fresh solution until no further uptake from the zeolite was observed. The samples were analyzed for heavy metal cations by atomic absorption spectrometry (Perkin-Elmer model 2380 spectrophotometer). All experiments were performed in triplicate and the average standard deviation was 5%.

For the purposes of simplified fixed bed modeling, Langmuir equilibrium equation is used. The empirical constant (La) is related to the particular system under investigation and is obtained from batch experiments by use of the following equation [14]:

$$\frac{q_e}{Q_M} = \frac{K \cdot C_e}{1 + K \cdot C_e} \tag{1}$$

where q_e is the solid-phase concentration in equilibrium with liquid-phase concentration C_e, Q_M is the ultimate sorptive capacity and K is an equilibrium constant. In an ion-exchange system, ultimate sorptive capacity could be viewed as the upper limit of actual zeolite capacity. According to the relevant terminology and definitions, this upper limit is called real exchange capacity (REC) [15]. REC refers to the amount of the actual exchangeable cations of the zeolite, measured by ion-exchange methods, and is a characteristic constant of the ion exchanger independent of the experimental conditions. The total charge of the exchangeable (removable) cations is equal to the active negative charge of the zeolite structure. It should be mentioned that REC is rarely achieved in ion-exchange systems involving natural materials due to several reasons outlined in the related literature [15].

The dimensionless form of Langmuir equation is

$$Y = \frac{X}{\mathrm{La} + (1 - \mathrm{La}) \cdot X} \tag{2}$$

where $\mathrm{La} = \frac{1}{1+K \cdot C_o}$, $Y = \frac{q_e}{q_{\max}}$ and $X = \frac{C_e}{C_o}$.

where $q_{\max}$ is the solid-phase concentration in equilibrium with the initial (maximum) concentration C_o. For an ion-exchange system, $q_{\max}$ corresponds to the MEL, measured by use of repeated batch equilibrations in batch experiments. The parameter La is also called separation factor and La = 0 for irreversible, La < 1 for favorable, La = 1 for linear, and La > 1 for unfavorable isotherm type. Extensive analysis on zeolite capacity and experimental methods for the estimation of MEL are provided elsewhere [15].

MEL-normalized equilibrium curves should be used with caution. As mentioned above, REC refers to the amount of the actual total amount exchangeable cations of the solid phase and is a characteristic constant of the ion exchanger [15]. MEL, on the other hand, depends on the temperature and normality. MEL and REC could be equal for "ideal" ion-exchange systems, i.e. systems where complete exchange is achieved, which is not the case of zeolites [15]. While MEL-normalized equilibrium curves are useful for equilibrium modeling and derivation of thermodynamic properties, selectivity series is better investigated either by REC-normalized equilibrium curves or by use of distribution coefficients [15–17]. The distribution coefficient (λ_i, mL/g), for cation (i) is defined by [16]:

$$\lambda_i = \frac{C_{s \cdot i}}{C_{l \cdot i}} \tag{3}$$

where $C_{s \cdot i}$ and $C_{l \cdot i}$ are the solid and liquid cation concentrations in (mg/g) and (mg/mL), respectively. In general, the selectivity series derived from MEL-normalized equilibrium curves agree with those derived from distribution coefficients but the latter method is preferred [7,15,16].

2.3. Fixed bed experiments

Fixed bed experiments were conducted in order to examine the Mn^{2+}, Zn^{2+}, and Cr^{3+} uptake by clinoptilolite and vermiculite, using the same experimental conditions. Mineral samples were used in the same mean granular size of 0.250–1 mm (mesh size). Metal solutions were passed through the packed column at a relative volumetric flow rate of 10 BV/h (where BV is the volume of liquid equal to the volume of the empty bed), under a total normality of 0.01 N and initial pH value equal to 4 and ambient temperature (25°C). The ion-exchange process was conducted in 0.7 m long plexiglass columns of 0.02 m internal diameter (Fig. 2) (V_{bed} = 216.6 mL, H_{bed} = 0.69 m, M_c = 215 g (clinoptilolite), M_v = 253 g (vermiculite). The solution was introduced at a constant volumetric flow rate (Q) and

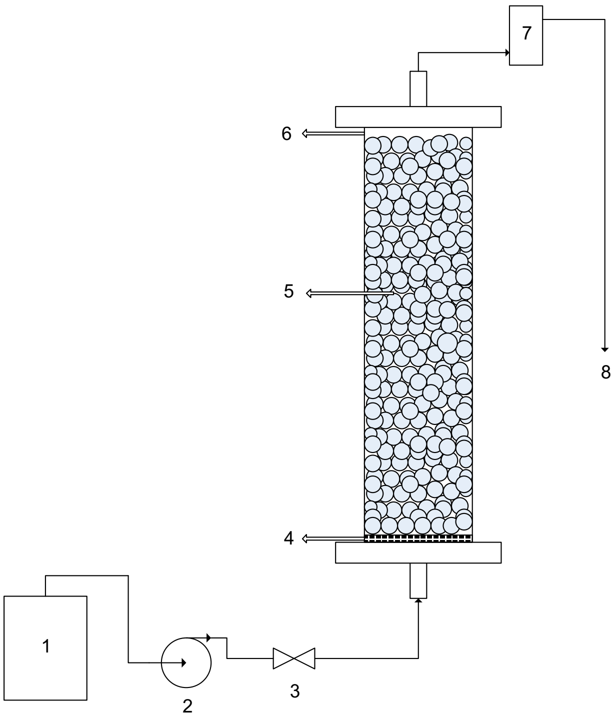

Fig. 2. The experimental setup for adsorption runs: (1) metal solution tank; (2) peristaltic pump; (3) valve; (4) plastic sieve; (5) natural material bed; (6) plexiglass column; (7) samples collector; and (8) outlet.

concentration (C), using a peristaltic pump in up-flow mode in order to assure complete wetting of the mineral particles. Liquid samples were withdrawn at the exit of the bed at specific time intervals, acidified with HNO_3 at pH 2 and analyzed for heavy metal cations. By plotting the exit metal concentration vs. time, the breakthrough curves were obtained. All experiments were performed in triplicate and the average standard deviation was 5%.

2.4. Fixed bed modeling

Details on the fixed bed modeling for adsorption/ion-exchange are provided elsewhere [18,19]. In order to use simplified models, the following assumptions should be met:

1. Plug flow. This assumption holds only if the bed Peclet number is greater than 100. Generally, in up-flow operation the quality of the flow is better, especially in low velocities. Peclet number correlations for materials that are frequently used in adsorption and ion-exchange systems in wastewater treatment applications, as for zeolites and similar particles of irregular shape, are provided elsewhere [20,21].
2. Constant pattern condition. With a favorable isotherm and a mass-transfer resistance or axial dispersion, the concentration front approaches a constant pattern, which is an asymptotic shape beyond which the wave will not spread. Practically, the constant pattern assumption holds if the equilibrium is favorable and under high residence times, i.e. deep bed and low superficial velocity.

Simplified models, under the above assumptions, have been proposed and analyzed in the related literature and are in the form of either arithmetic or analytical solutions [19]. For solid diffusion control the following dimensionless parameters are defined [14]:

$$\Lambda = \frac{\rho_b \cdot q_{\max}}{C_o} \qquad T = \frac{t - \left(\frac{V_o \varepsilon}{Q}\right)}{\left(\frac{\Lambda \cdot V_o}{Q}\right)} \qquad N_s = \frac{15 \cdot D_s \cdot \Lambda \cdot V_o}{r_p^2 \cdot Q} \tag{4}$$

where t is time, V_o is the total bed volume, ε is the bed voidage, Q is the volumetric flow rate, ρ_b is the bed density, r_p is the particles average radius, D_s is the solid-phase diffusion coefficient, $q_{\max}$ is the operating capacity (OC), which should be evaluated from bed data in fixed bed experiments, N_s is the number of transfer units, T is the throughput parameter, and Λ is the partition ratio. The operating ion-exchange capacity in (mg/g) is calculated using [18]:

$$q_{\max} = \frac{C_o \cdot V_T - \int_0^T C \cdot dV}{\rho_b \cdot V_o} \tag{5}$$

where V_T is the total effluent volume at time (T), when the exit concentration is equal to the inlet concentration. The following equations are approximate solution of fixed bed model under the constant pattern and plug flow assumption for favorable Langmuir isotherm, linear driving forces, and solid diffusion control [14]:

$$N_s \cdot (T - 1) = \frac{1}{\Psi_S} \cdot \left[\frac{\mathrm{La} \cdot \ln(\mathrm{X}) - \ln(1 - \mathrm{X})}{1 - \mathrm{La}} - 1\right] \tag{6}$$

where the kinetic parameter (Ψ_S) is calculated using: $\Psi_S = \frac{0.894}{1 - 0.106 \cdot La^{0.5}}$.

3. Results and discussion

3.1. Batch experimental results

In Figs. 3–5, the equilibrium curves and distribution coefficients for each metal in the two minerals derived in batch experiments are provided. As is evident, all isotherms are favorable, with the exception of Cr^{3+}-clinoptilolite (sigmoidal) and Mn^{2+}-vermiculite (linear). Sigmoidal Cr^{3+} isotherms and favorable isotherms for Zn^{2+} and Mn^{2+} on clinoptilolite have been reported elsewhere as well [7,22–25]. The equilibrium curves are used for the estimation of Langmuir parameter (La). MEL and La are provided in Table 2. In order to easily compare the two different minerals, equilibrium curves and distribution coefficients for all metals for each mineral are provided in Figs. 6 and 7.

Available literature capacity data exist for clinoptilolite, for example, 4.22 mg/g for Mn^{2+}, 5.82–7.12 mg/g for Cr^{3+}, and 3.08–21.2 mg/g for Zn^{2+} and for vermiculite 23.40–24.08 mg/g for Zn^{2+} [7,8,11,22,25,26]. Comparison of experimental capacity data from different studies should be used with caution as relevant definitions and experimental techniques vary widely in the related literature [15]. In the present study, only reliable MEL data measured, according to widely accepted experimental methods, are presented.

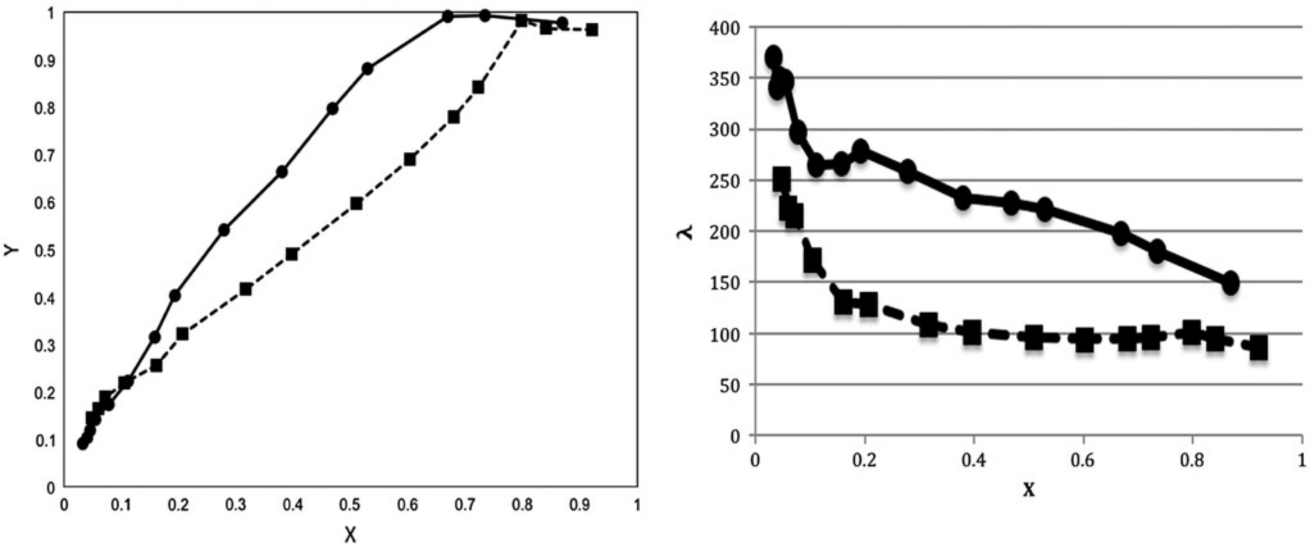

Fig. 3. Zn^{2+} equilibrium curves (left) and distribution coefficients (right). Clinoptilolite is marked with dashed line and square points and vermiculite in solid line and cyclic points.

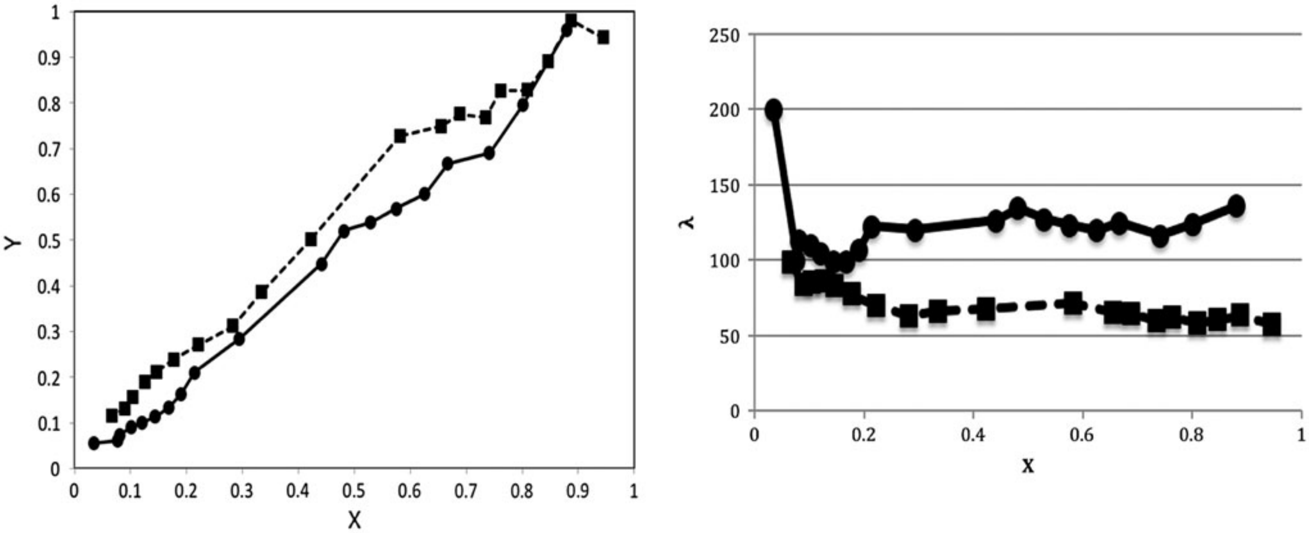

Fig. 4. Mn^{2+} equilibrium curves (left) and distribution coefficients (right). Clinoptilolite is marked with dashed line and square points and vermiculite in solid line and cyclic points.

Vermiculite selectivity series derived from distribution coefficients is $Cr^{3+} > Zn^{2+} > Mn^{2+}$ and is the same for clinoptilolite for $X < 0.2$. For more concentrated solutions, the selectivity changes for Cr and remains the same for the other two metals, i.e. $Zn^{2+} > Mn^{2+}$. The preference of clinoptilolite to Zn^{2+} than Mn^{2+} is reported in many studies and is well established and is probably explained by the higher hydrated diameter of Mn^{2+} [22–24]. Selectivity order deduced from MEL is $Zn^{2+} > Mn^{2+} > Cr^{3+}$ for both minerals, with the exception of $Mn^{2+} \cong Cr^{3+}$ in vermiculite. The difference of selectivity series derived by MEL and distribution coefficients is not surprising and has been noted elsewhere as well [7]. MEL values should be used with caution when comes to selectivity series derivation; in this case MEL and distribution coefficients derive the same selectivity series for Zn^{2+} and $Mn^{2+,}$ but not for Cr^{3+}.

Furthermore, as is evident by examining the distribution coefficients and MEL levels, vermiculite

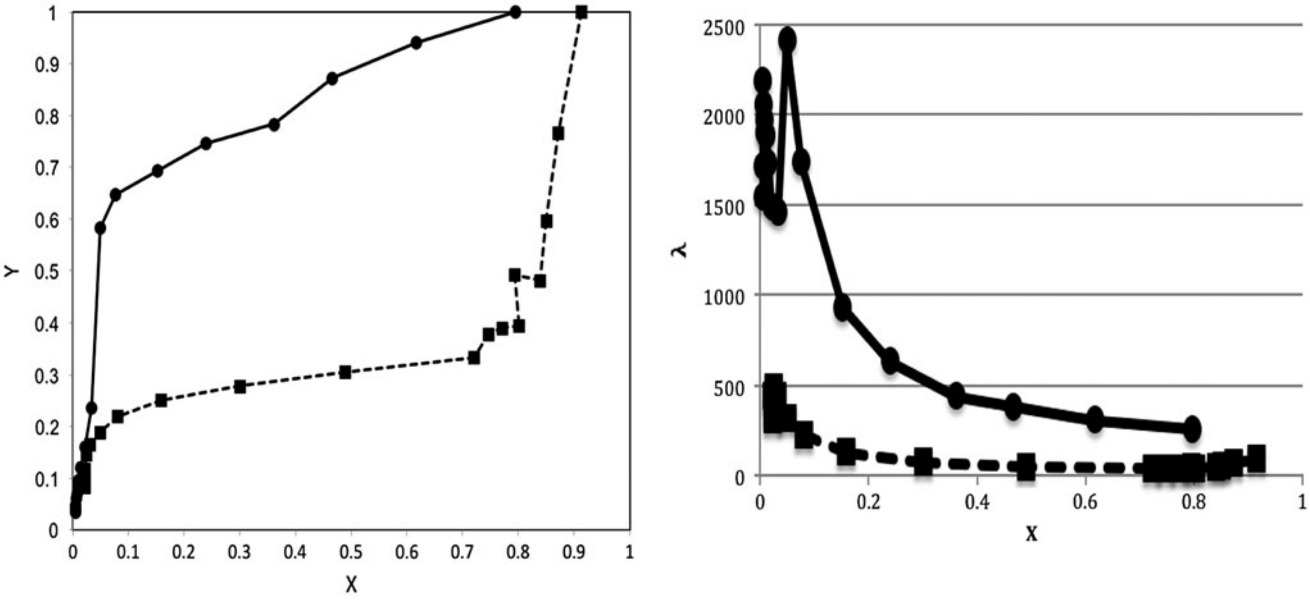

Fig. 5. Cr^{2+} equilibrium curves (left) and distribution coefficients (right). Clinoptilolite is marked with dashed line and square points and vermiculite in solid line and cyclic points.

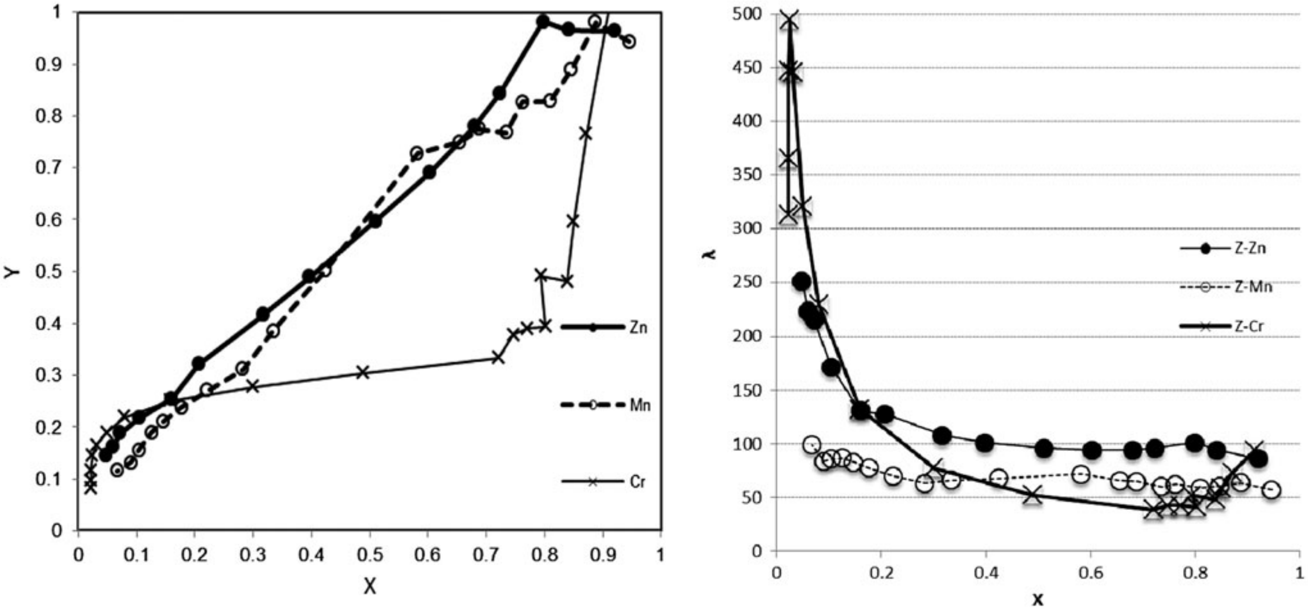

Fig. 6. Clinoptilolite equilibrium curves (left) and distribution coefficients (right).

exhibits better results than clinoptilolite for all metals. According to other studies, vermiculite performed better than clinoptilolite for Mn^{2+}, Fe^{3+}, and Cu^{2+} in batch systems [3,13]. The opposite was observed for Pb^{2+} removal, confirming the widely known high selectivity of clinoptilolite for Pb^{2+} [12]. As mentioned above, selectivity series is better investigated either by REC-normalized equilibrium curves or by use of distribution coefficients [15,16]. Although MEL-normalized equilibrium curves provide the same selectivity series, there are exceptions. Characteristic example is Mn^{2+}, for which, while MEL-normalized equilibrium curves demonstrate a higher selectivity in clinoptilolite, distribution coefficients (and MEL values) show

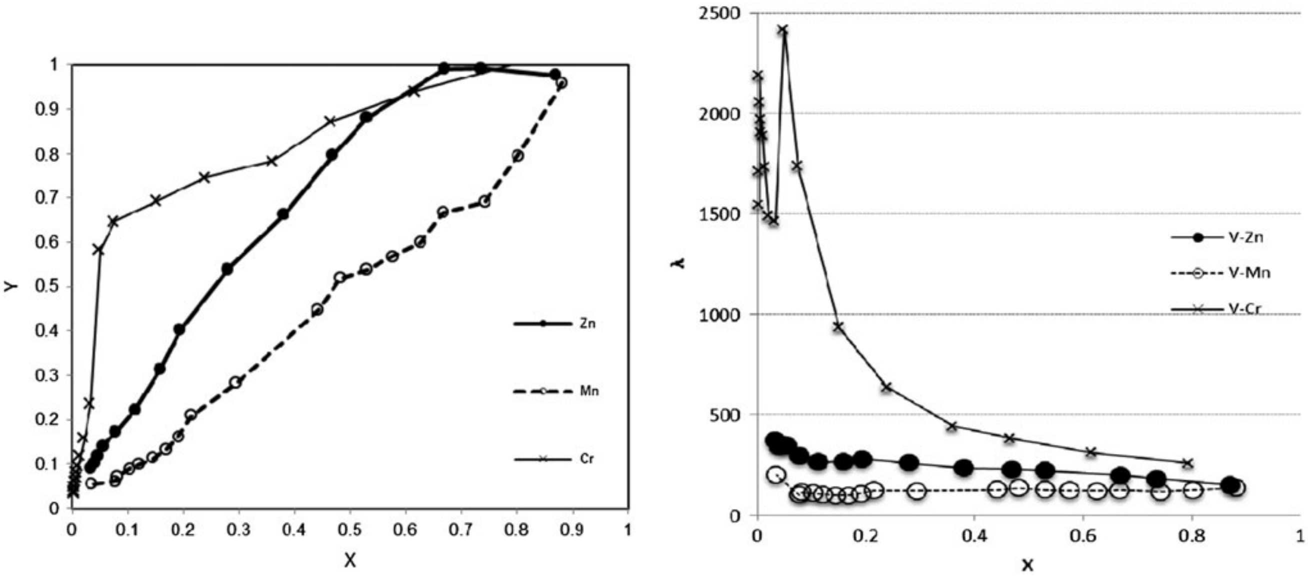

Fig. 7. Vermiculite equilibrium curves (left) and distribution coefficients (right).

Table 2
Batch experimental results

	Zn^{2+}		Mn^{2+}		Cr^{3+}	
	MEL (mg/g)	La	MEL (mg/g)	La	MEL (mg/g)	La
Clinoptilolite	26.9	0.63	15.8	0.68	14.4	N/A
Vermiculite	43.6	0.33	34.2	0.99	35.0	0.12

higher selectivity for vermiculite. Obviously, distribution coefficient is a safer way to derive selectivity series.

3.2. Fixed bed experimental results

The use of clinoptilolite and vermiculite as packing material in fixed bed experiments was examined in the same experimental conditions, and the results for Mn^{2+}, Zn^{2+}, and Cr^{3+} uptake are shown in Figs. 8 and 9. Fig. 8 is in logarithmic scale, in order, the differences between metals to be easily identified. It should be noted that from practical point of view, the most interesting part of the breakthrough curve is the first part up to the breakpoint, typically up to 10% relative exit concentration, which is the point where the operation is stopped at a desired low exit concentration of the pollutant.

Analyzing the results for each mineral separately, it can be seen that selectivity for low exit concentrations (breakthrough point) confirm the selectivity order derived from the distribution coefficients, which is $Cr^{3+} > Zn^{2+} > Mn^{2+}$. The situation is somewhat more complicated in Cr^{3+}-clinoptilolite case, where distribution coefficients show the same selectivity series for low concentrations while for higher concentrations Cr^{3+} becomes the less preferred cation. However, this change occurs at about $X = 0.2$ and probably this is the reason of agreement of batch and fixed bed selectivity series at low concentrations. In all cases, the OC is 25–75% lower than MEL, with the difference to depend on the specific metal and mineral. Similar results have been presented for Pb^{2+}, Cu^{2+}, Fe^{3+}, and Cr^{3+} uptake by clinoptilolite, where the OC was only a portion of the MEL, around 20–50%, depending on the specific metal and flow rate [7]. Similar OC values have been reported for Cr^{3+} on clinoptilolite 1.7–3.09 mg/g and for Zn^{2+} and Mn^{2+} on vermiculite, 23.40 and 26.78 mg/g, respectively [7,27,28].

Operating capacity values confirm the selectivity order derived from MEL experiments, which is $Zn^{2+} > Mn^{2+} > Cr^{3+}$ for both minerals, with the

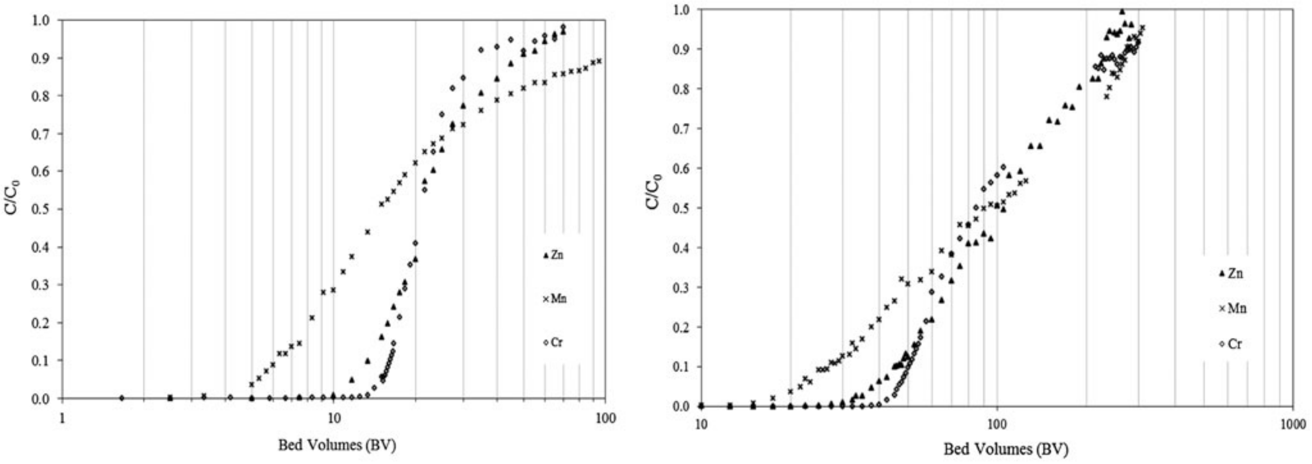

Fig. 8. Breakthrough curves for clinoptilolite (left) and vermiculite (right).

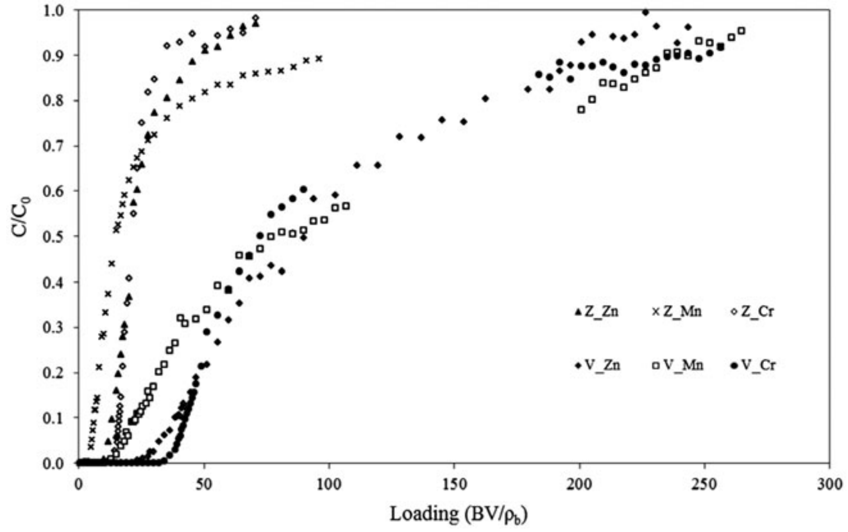

Fig. 9. Breakthrough curves for clinoptilolite (Z) and vermiculite (V).

exception of $Mn^{2+} \cong Cr^{3+}$ in vermiculite MEL values. Similar results were obtained for clinoptilolite in other experiments [7]. Fixed bed performance should be analyzed by combining full equilibrium curve, maximum solid-phase concentration, and kinetics. For example, while Cr^{3+} exhibits the lower capacity in both materials (MEL and OC), results in better performance in terms of breakpoint due to its much higher distribution coefficients and probably higher kinetic rates. On the other hand, when the interest focuses on the total loading of the fixed bed, capacity (MEL and OC) plays the first role. Concluding, in all experiments, both batch (distribution coefficients and MEL) and fixed bed (breakthrough points and OC), vermiculite showed better performance than clinoptilolite for all metals. According to other studies, vermiculite performed better than clinoptilolite for Mn^{2+} and Fe^{3+} removal from drinking water in fixed bed and closed-loop fixed bed systems [8].

From Fig. 9, it can be clearly seen that the two minerals give completely different breakthrough curves. The zeolite bed reaches 100% much sooner than that of vermiculite, thus, ion-exchange in a zeolite bed requires smaller bed volumes. Also, for completing the 90% of the ion-exchange process in a zeolite packed column, about 70–100 BV are required. Comparing this result to a vermiculite packed column is the latter requires approximately 300 bed volumes. Converting bed volumes into hours of experiment needed for the process, then for the zeolite are required 7–9 h, while for vermiculite ion-exchange process 30 h. This shows that vermiculite exhibits much better performance and removal continuous for a longer period and by extension purification of larger quantities of the aqueous solution of the metal is achieved.

It should be emphasized that when we use the same material in different fixed beds, the bed porosity (ε) and bulk density (ρ_b) are the same. By using the same relative flow rate (Q_{rel}), the residence time (ε/Q_{rel}) is the same while the comparison is typically made by plotting the exit concentration vs. the exit relative volume (V_{rel}), i.e. the comparison is made for the same load (V_{rel}/ρ_b) [9]. When two different packing materials are compared the bed porosity and bulk density may be different and thus, the residence time is different while the comparison of the materials' performance should be made for the same load, not relative effluent volume. In the present study, the correction on load was made (see Fig. 9). However, the correction on bed porosity, which influences residence time, was not made as vermiculite is expanding in water and bed porosity as well as particle density cannot be accurately measured.

3.3. Fixed bed modeling

The results of the simplified model application on experimental data are presented in Figs. 10–12 and Tables 3 and 4. The application of the model is clearly successful for Zn^{2+} in both minerals and Cr^{3+}-vermiculite system. For Cr^{3+}, the model is not applicable due to the sigmoidal shape of the isotherm while for Mn, the model totally fails in low concentrations and it seems to approach experimental data for $X > 0.2$–0.3.

The available fixed bed-derived diffusion coefficients are for clinoptilolite for Pb^{2+}, between 1.08 and 5.45×10^{-8} cm^2/s and for vermiculite for Ni^{2+}, Cu^{2+}, Zn^{2+}, Cr^{3+}, of the order of 10^{-9} cm^2/s [5,6,10]. These values are, in general, agreement with those presented in Table 4, with the exception of Mn^{2+} on vermiculite. Concerning diffusion coefficients measured in batch systems, there are no published data available for vermiculite while existing values of D_s for several cations as Na^+, Zn^{2+}, Pb^{2+}, Cu^{2+}, Fe^{3+}, and Cr^{3+} uptake by clinoptilolite are at least one order of magnitude lower, between 0.01 and 5.7×10^{-9} cm^2/s [6,11,16,29,30]. These results are in line with the related literature. Theoretically, for a specific ion-exchange or adsorption system, the equilibrium isotherm, ion-exchange capacity, and solid diffusion coefficient are independent of the experimental method used for their determination and independent of flow conditions. However, a number of experiments have shown that fixed bed and batch system experiments could result in different values, which on the top might be flow-depended [6]. Experience has shown that solid-phase capacity should be experimentally measured in fixed bed experiments (OC) and if

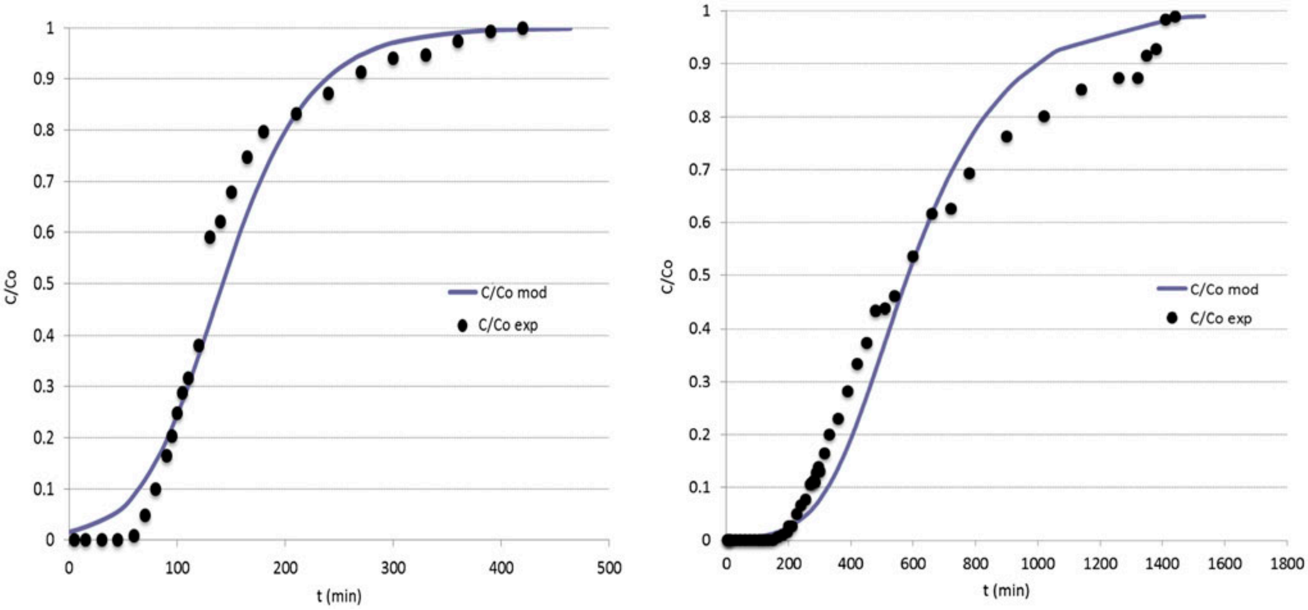

Fig. 10. Zn^{2+} experimental and model curves for clinoptilolite (left) and vermiculite (right).

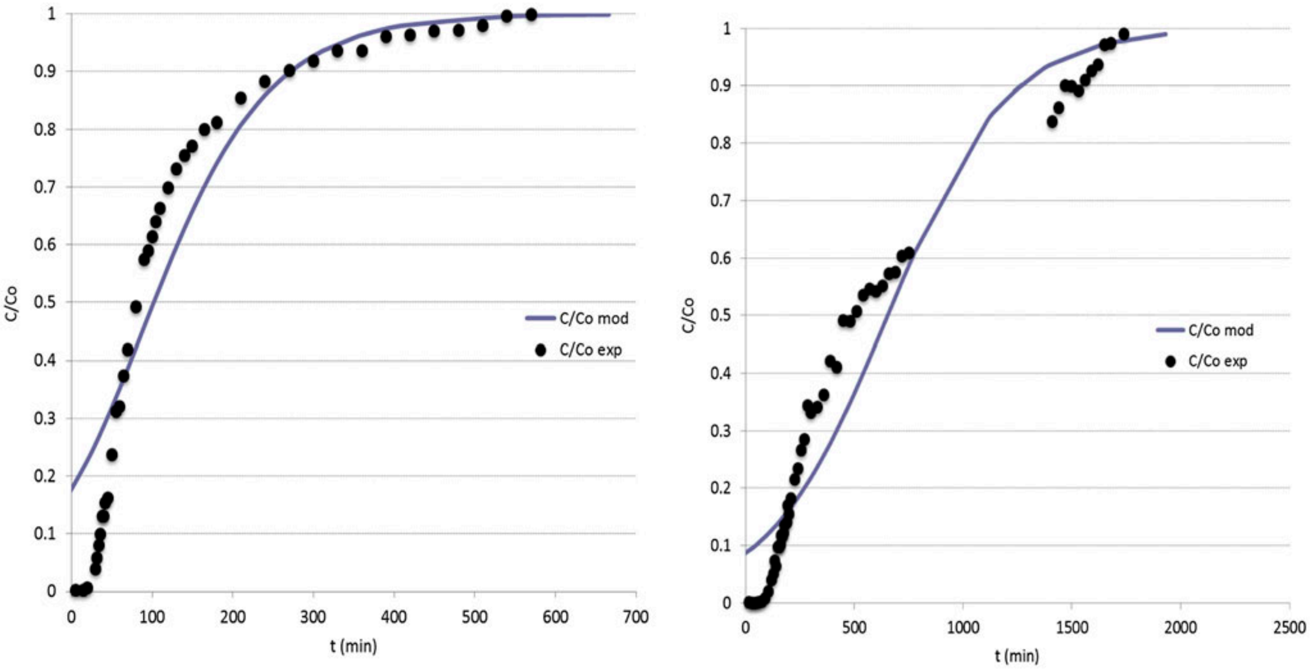

Fig. 11. Mn^{2+} experimental and model curves for clinoptilolite (left) and vermiculite (right).

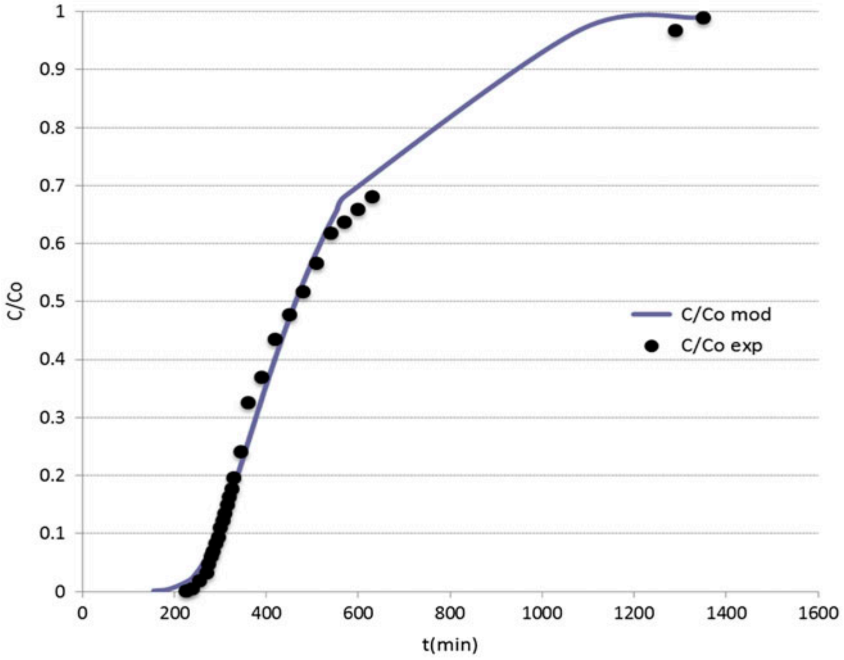

Fig. 12. Cr^{3+} experimental and model curves for vermiculite.

models are applicable, diffusion coefficients should be also determined in fixed bed apparatus (D_s). However, for equilibrium isotherms, it is more practical to be studied in batch reactor systems. In the case that such isotherms are used in fixed bed models, the equilibrium discrepancy (if exists) can be compensated by a different estimate for the solid diffusion coefficient [6].

Table 3
Fixed bed experimental results (OC, mg/g)

	Zn^{2+}	Mn^{2+}	Cr^{3+}
Clinoptilolite	7.9	4.9	3.6
Vermiculite	29.3	25.6	12.8

Table 4
Fixed bed modeling results (D_s, cm^2/s)

	Zn^{2+}	Mn^{2+}	Cr^{3+}
Clinoptilolite	6.2×10^{-8}	4.1×10^{-8}	N/A
Vermiculite	7.4×10^{-9}	3.9×10^{-7}	6.1×10^{-9}

Finally, is worthwhile to mention that most fixed bed models used in the related literature are kinetic-based and they make use of phenomenological pseudo-first or second order chemical reaction-like equations, which from physical meaning point of view are problematic as ion exchange and adsorption are not chemical reactions but diffusion-driven phenomena. The present study demonstrates the use of a simplified but meaningful diffusion-derived model which provides a significant parameter, namely the solid-phase diffusion coefficient.

4. Conclusions

Ion-exchange equilibrium is examined by use of batch equilibrium isotherms and distribution coefficients and fixed bed dynamic experiments for all metals and both minerals. Concerning the comparison of the two minerals, in all experiments, both batch (distribution coefficients and MEL) and fixed bed (breakthrough points and OC), vermiculite showed better performance than clinoptilolite for all metals. All isotherms are favorable, with the exception of Cr^{3+}-clinoptilolite (sigmoidal) and Mn^{2+}-vermiculite (linear). Vermiculite selectivity series derived from distribution coefficients is $Cr^{3+} > Zn^{2+} > Mn^{2+}$ and is the same for clinoptilolite for $X < 0.2$. For more concentrated solutions, the selectivity changes for Cr^{3+} and remains the same for the other two metals, i.e. $Zn^{2+} > Mn^{2+}$. MEL are 14.4–26.9 mg/g and 34.2–43.6 mg/g for clinoptilolite and vermiculite, respectively. Analyzing the fixed bed results, selectivity for low exit concentrations confirmed the selectivity order derived from the distribution coefficients. OC is found to be 3.6–7.9 mg/g and 12.8–29.3 mg/g for clinoptilolite and vermiculite, respectively, deriving the same selectivity as MEL values. In all cases, the OC is 25–75% lower than MEL, with the difference to depend on the specific metal and mineral. The application of the simplified fixed bed model is successful for Zn^{2+} in both minerals and Cr^{3+}-vermiculite system. For Cr^{3+}-clinoptilolite system, the model is not applicable due to the sigmoidal shape of the isotherm while for Mn^{2+}, the model totally fails in low concentrations and it seems to approach experimental data for $X > 0.2$–0.3. Solid-phase diffusion coefficients were estimated to be in the order of magnitude of 10^{-8} cm^2/s for clinoptilolite and 10^{-9} cm^2/s for vermiculite.

List of symbols

q_e	—	the solid-phase equilibrium concentration (mg/g)
q_{max}	—	solid-phase maximum concentration (mg/g)
C_e	—	liquid-phase equilibrium concentration (mg/mL)
C_o	—	initial liquid-phase concentration (mg/mL)
X	—	dimensionless (or relative) liquid-phase concentration
Y	—	dimensionless (or relative) solid-phase concentration
Q_M	—	the ultimate sorptive capacity (mg/g)
K	—	Langmuir equilibrium constant (dimensionless)
La	—	Langmuir empirical constant or separation factor (dimensionless)
REC	—	real exchange capacity (mg/g)
MEL	—	maximum exchange level (mg/g)
OC	—	operating capacity (mg/g)
V_o	—	total bed volume (mL)
V_T	—	total effluent volume at time (t) (mL)
ε	—	bed voidage (dimensionless)
Q	—	volumetric flow rate (mL/sec)
ρ_b	—	bed density (g/mL)
r_p	—	particles average radius (cm)
D_s	—	solid-phase diffusion coefficient (cm^2/s)
Λ	—	partition ratio (dimensionless)
T	—	throughput parameter (dimensionless)
N_s	—	number of transfer units (dimensionless)
Ψ_S	—	kinetic parameter (dimensionless)

References

[1] G.V. Tsitsishvili, T.G. Andronikashvili, G.M. Kirov, L.D. Filizova, Natural Zeolites, Ellis Horwood, New York, NY, 1992.

[2] F. Helfferich, Ion Exchange, Dover Publications, New York, NY, 1995.

[3] M.A. Stylianou, V.J. Inglezakis, K.G. Moustakas, S.Ph. Malamis, M.D. Loizidou, Removal of Cu(II) in fixed bed and batch reactors using natural zeolite and exfoliated vermiculite as adsorbents, Desalination 215 (2007) 133–142.

[4] M.A. Stylianou, M.P. Hadjiconstantinou, V.J. Inglezakis, K.G. Moustakas, M.D. Loizidou, Use of natural clinoptilolite for the removal of lead, copper and zinc in fixed bed column, J. Hazard. Mater. 143 (2007) 575–581.

[5] A. Cincotti, N. Lai, R. Orrù, G. Cao, Sardinian natural clinoptilolites for heavy metals and ammonium removal: Experimental and modeling, Chem. Eng. J. 84 (2001) 275–282.

[6] V. Inglezakis, H. Grigoropoulou, Modeling of ion exchange of Pb^{2+} in fixed-beds of clinoptilolite, Microporous Mesoporous Mater. 61 (2003) 273–282.

[7] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Equilibrium and kinetic ion exchange studies of Pb^{2+}, Cr^{3+}, Fe^{3+} and Cu^{2+} on natural clinoptilolite, Water Res. 36(11) (2002) 2784–2792.

[8] V.J. Inglezakis, K. Elaiopoulos, V. Aggelatou, A.A. Zorpas, Treatment of underground water in open flow and closed-loop fixed bed systems by utilizing the natural minerals clinoptilolite and vermiculite, Desalin. Water Treat. 39 (2012) 215–227.

[9] M.A. Stylianou, V.J. Inglezakis, M. Loizidou, Comparison of Mn, Zn, and Cr removal in fluidized- and fixed-bed reactors by using clinoptilolite, Desalin. Water Treat. 53(12) (2015) 3355–3362.

[10] D.J. Seaborn, G.J. Jameson, Some ion exchange properties of exfoliated vermiculite, Hydrometallurgy 2(2) (1976) 141–155.

[11] S. Malamis, E. Katsou, A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: Examination of process parameters, kinetics and isotherms, J. Hazard. Mater. 252–253 (2013) 428–461.

[12] V.J. Inglezakis, M. Stylianou, M. Loizidou, Ion exchange and adsorption equilibrium studies on clinoptilolite, bentonite and vermiculite, J. Phys. Chem. Solids 71(3) (2010) 279–284.

[13] V.J. Inglezakis, M.D. Doula, V. Aggelatou, A. Zorpas, Removal of iron and manganese from underground water by use of natural minerals in batch mode treatment, Desalin. Water Treat. 18 (2010) 341–346.

[14] R.H. Perry, D. Green, Perry's Chemical Engineers' Handbook, McGraw-Hill, International Editions, 1997.

[15] V. Inglezakis, The concept of "capacity" in zeolite ion exchange systems, J. Colloid Interface Sci. 281 (2005) 68–79.

[16] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Ion exchange studies on natural and modified zeolites and the concept of exchange site accessibility, J. Colloid Interface Sci. 275(2) (2004) 570–576.

[17] D. Caputo, F. Pepe, Experiments and data processing of ion exchange equilibria involving Italian natural zeolites: A review, Microporous Mesoporous Mater. 105 (2007) 222–231.

[18] V.J. Inglezakis, A. Zorpas, Fundamentals of ion exchange fixed beds, in: Inamuddin, M. Luqman (Eds.), Ion-exchange Technology: Theory, Materials and Applications, Springer, UK, 2012, pp. 121–161.

[19] V.J. Inglezakis, S.G. Poulopoulos, Adsorption, Ion Exchange and Catalysis, Design of Operations and Environmental Applications, first ed., Elsevier, Amsterdam, 2006.

[20] V.J. Inglezakis, Non ideal flow in liquid-solid fixed beds of irregular-shaped particles: A critical review, Int. J. Chem. React. Eng. 8 (2010) R3.

[21] V.J. Inglezakis, M. Lemonidou, H.P. Grigoropoulou, Liquid holdup and flow dispersion in zeolite packed beds, Chem. Eng. Sci. 56 (2001) 5049–5057.

[22] L. Mihaly-Cozmuta, A. Mihaly-Cozmuta, A. Peter, C. Nicula, H. Tutu, D. Silipas, E. Indrea, Adsorption of heavy metal cations by Na-clinoptilolite: Equilibrium and selectivity studies, J. Environ. Manage. 137 (2014) 69–80.

[23] T. Motsi, N.A. Rowson, M.J.H. Simmons, Adsorption of heavy metals from acid mine drainage by natural zeolite, Int. J. Miner. Process. 92 (2009) 42–48.

[24] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, J. Colloid Interface Sci. 280 (2004) 309–314.

[25] S.R. Taffarel, J. Rubio, On the removal of Mn^{2+} ions by adsorption onto natural and activated Chilean zeolites, Miner. Eng. 22 (2009) 336–343.

[26] S. Çoruh, The removal of zinc ions by natural and conditioned clinoptilolites, Desalination 225 (2008) 41–57.

[27] O. Abollino, A. Giacomino, M. Malandrino, E. Mentasti, Interaction of metal ions with montmorillonite and vermiculite, Appl. Clay Sci. 38 (2008) 227–236.

[28] M. Malandrino, O. Abollino, A. Giacomino, M. Aceto, E. Mentasti, Adsorption of heavy metals on vermiculite: Influence of pH and organic ligands, J. Colloid Interface Sci. 299 (2006) 537–546.

[29] I. Rodríguez Iznaga, V. Petranovskii, G. Rodríguez Fuentes, C. Mendoza, A. Benítez Aguilar, Exchange and reduction of Cu^{2+} ions in clinoptilolite, J. Colloid Interface Sci. 316(2) (2007) 877–886.

[30] A.E. Kurtoğlu, G. Atun, Determination of kinetics and equilibrium of Pb/Na exchange on clinoptilolite, Sep. Purif. Technol. 50(1) (2006) 62–70.