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Comparison of Mn, Zn, and Cr removal in fluidized- and fixed-bed reactors by using clinoptilolite

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ABSTRACT

Natural minerals are used as sorbents in ion-exchange processes due to their high exchange capacity and their relatively low cost. In the present study the use of natural zeolite as filling medium in fixed- and fluidized-bed reactors for the removal of heavy metals from aqueous solutions is investigated. The major objective is to compare the removal efficiency of heavy metals by the two processes—fluidized and fixed bed. Fixed and fluidized bed experiments were conducted in order to examine the Mn^{2+}, Zn^{2+}, and Cr^{3+} uptake by natural clinoptilolite, using the same critical experimental conditions: particle size (90–180 μm), volumetric flow rate of 12.48 BV/h, total normality of 0.01 N, initial pH value equal to 4, and ambient temperature (25˚C). The fluidized bed process was conducted in an experimental 50 cm long plexiglass column of 4.4 cm internal diameter and fixed bed experiments in 70 cm long plexiglass columns of 2 cm internal diameter. The fluidized bed breakthrough curves for Mn^{2+} and Zn^{2+} are very similar with Cr to give the best results in terms of removal efficiency. In fixed bed the breakthrough curves are similar for all three metals, with Cr exhibiting slightly lower removal efficiency. Furthermore, the breakthrough points are shifted to the left (0–5 BV) in comparison to the fixed bed experiments (10 BV) for all metals. Comparing the two processes, it is concluded that fixed bed operation exhibits better results than the fluidized bed most probably due to better hydrodynamic conditions in the former.

Keywords: Zeolite; Fluidized bed; Fixed bed; Heavy metals; Ion-exchange

1. Introduction

Natural zeolites are extensively used in ion-exchange and adsorption processes due to their low cost, worldwide abundance, high exchange capacity, and selectivity properties [1,2]. The use of fluidized-bed reactors [3,4] for the removal of heavy metals from aqueous solutions has not been systematically studied in the related literature in contrast with the extensive use of fixed-bed and batch reactors [5–10].

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Fluidization is the operation by which fine solids are transformed into a fluid-like state through contact with a gas or liquid. In most liquid–solid systems, as the velocity is increased, the motion of the particles becomes more vigorous, whereas the bed density at a given velocity is the same in all sections of the bed. This is called particulate fluidization and its characteristic is the large but uniform expansion of the bed at high velocities. Fluidized beds are used in both catalytic and non-catalytic systems and several applications are found in wastewater treatment and particular in aerobic and anaerobic treatment of municipal and industrial wastewaters. Finally, in much lesser extent they are used in liquid–solid adsorption and ion-exchange processes [11–17]. In the typical case, in fluidized beds the particle size used is much smaller than in fixed beds and thus the uptake rates are higher leading, in general, to higher efficiency. In the present study, the experimental conditions are selected in order to eliminate the effect of particle size the aim being the comparison of the two reactors in terms of flow conditions, i.e. flow quality (hydrodynamic behavior). This is important as in fluidized beds could suffer from flow non-idealities, as channeling, leading to lower efficiency than the expected one.

Despite the large number of fixed bed studies, applications of natural zeolites such as clinoptilolite in fluidized-bed reactors for the removal of heavy metals from aqueous solutions are not reported in the literature. The use of other materials for the removal of heavy metals are reported such as sand (with a diameter of 0.15–0.30 mm) for the removal of Cu, Ni, and Zn [14,18]; chelating resin for the removal of Cu, Ni, Co, and Zn [19]; and synthetic zeolites such as zeolite A for the removal of copper [20] and zeolite Baylith WE984 for nickel, lead, and zinc from aqueous solutions [21]. The most relevant published study is the use of clinoptilolite fluidizated bed for the removal of NH_4 from aqueous solutions [14].

This study aims to represent the first results concerning the removal of heavy metals from aqueous solutions with natural zeolite (clinoptilolite) as adsorbent and furthermore to compare the removal efficiency of heavy metals from fluidized beds to fixed-beds reactors.

2. Materials and methods

Zeolite (clinoptilolite) samples used in the experiments were provided by S&B Industrial Minerals S.A. (Greece) and it was used in a particle size of 90–180 μm. Fluidized and fixed bed experiments were conducted using the following experimental conditions: relative volumetric flow rate of 12.48 BV/h (where BV is a 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) (Table 1). The experimental conditions are selected in order to eliminate the effect of particle size.

The aim being the comparison of the two reactors in terms of flow conditions, i.e. flow quality (hydrodynamic behavior). The experimental setup is shown in Figs. 1 and 2.

The fluidization process was conducted in an experimental 50 cm long plexiglass column of 4.4 cm internal diameter. The column consists of a calming entry section of length of 8 cm filled with glass beads of mean radius of 2.1 mm, covered with stainless steel sieve and a 40 μm filter, in order to homogenize and evenly distribute the liquid flow before it reaches the zeolite bed section. An identical filter was placed on the top of the column, so as to prevent small particles escaping the column. The zeolite initial bed height (H_o) was set to 15 cm. The metal solutions were introduced at a constant volumetric flow rate using a peristaltic pump in up-flow mode. Flow rate was increased and the expanded bed height was recorded ($H_f = 21.8$ cm). A septum was placed close to H_f ($A = 24$ cm) so as to sample with a syringe. Samples of 10 mL were taken for measuring heavy metal content and solution pH and conductivity.

Fixed bed experiments were conducted in 70 cm long plexiglass columns of 2 cm 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.

Table 1
Column experimental parameters

	Fluidized bed	Fixed bed
D (cm)	4.4	2
A (cm^2)	15.20	3.14
H (cm)	21.8	20
V_b (ml)	331.36	62.8
Q (ml/min)	68.9	13.06
Q_{rel} (BV/h)	12.48	12.48
ε (–)	0.715	0.585
ρ_b (g/ml)	0.605	0.88

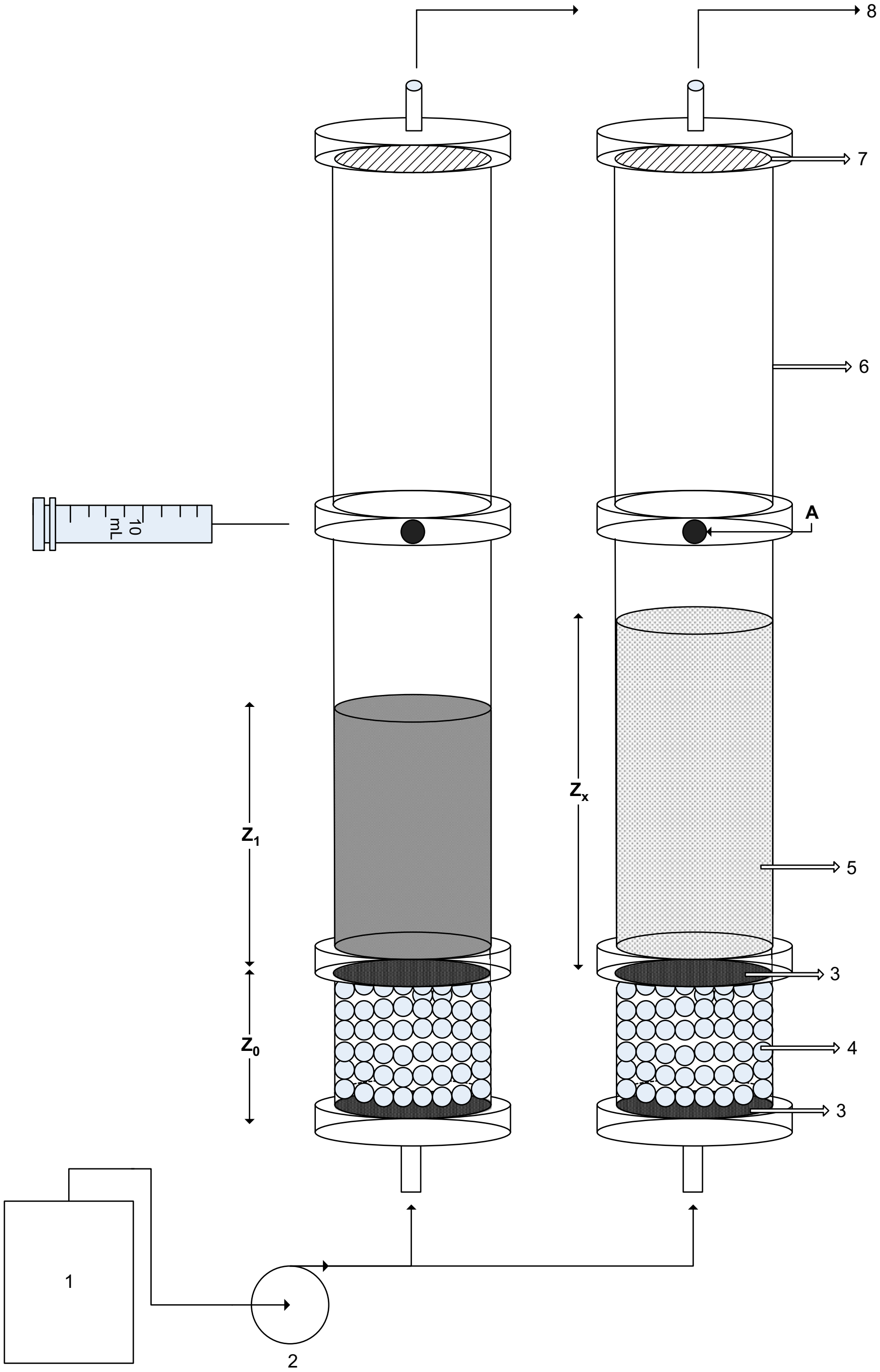

Fig. 1. The experimental setup for fluidization runs: (1) metal solution tank; (2) peristaltic pump; (3) stainless steel sieve and filter; (4) calming section filled with glass beads —$Z_0 = 8$ cm; (5) natural material bed ($Z_1 = 15$ cm); (6) plexiglass column; (7) filter; (8) outlet; (A) septum for sampling with a syringe; (Z_x) fluidization height.

3. Results and discussion

The removal efficiency of zeolite for the three investigated metals in the fluidized columns is showed in Fig. 3. It can be seen that fluidized bed gives very similar breakthrough curves for Zn and Mn with an early breakpoint, with the concentration reaching almost immediately the level of 20%. In contrast, the results are much better for Cr which exhibits an S-shaped breakthrough curve and a breakpoint of about 5 BV.

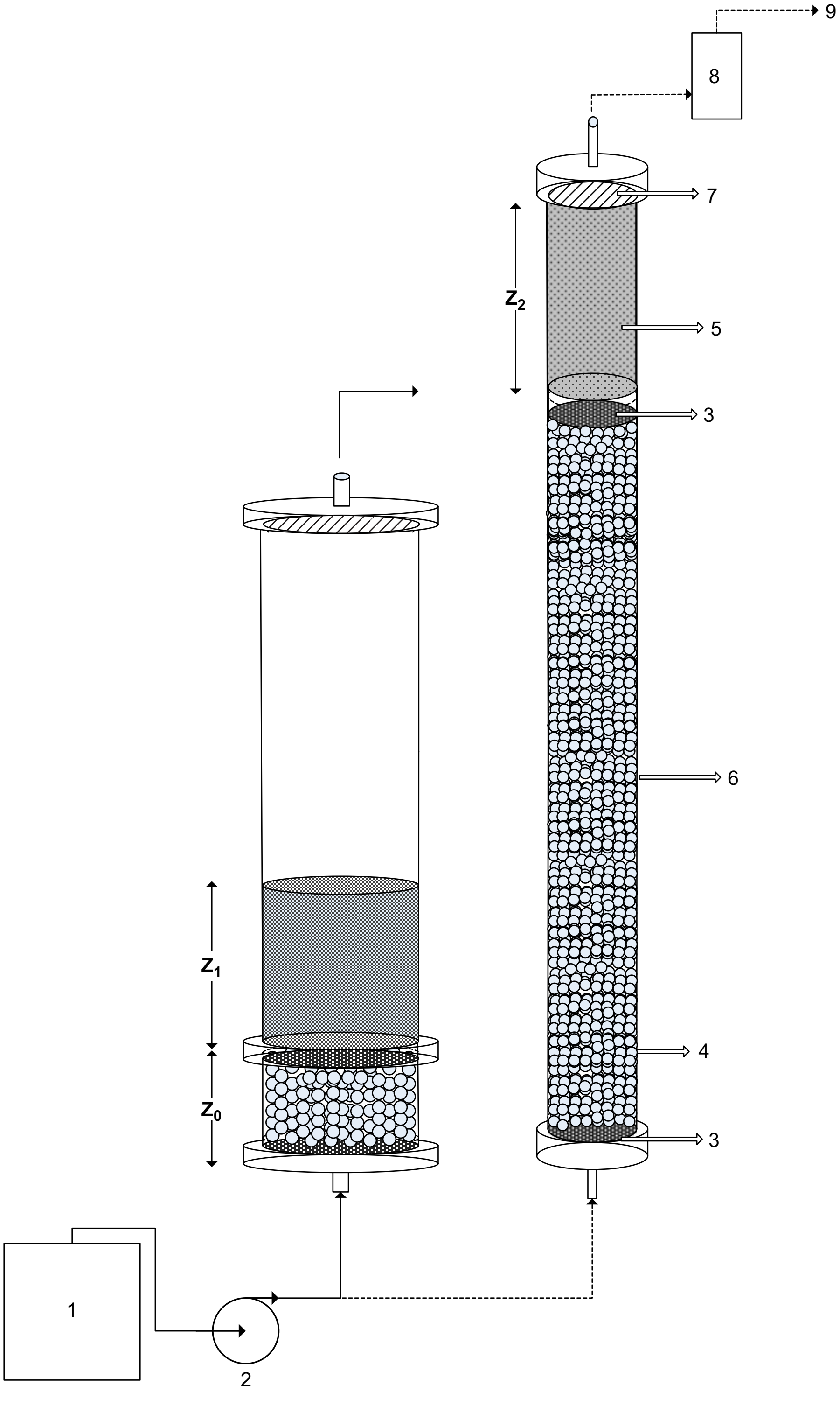

Fig. 2. The experimental setup for fluidization and fixed bed runs: (1) metal solution tank; (2) peristaltic pump; (3) stainless steel sieve and filter; (4) calming section filled with glass beads; (5) natural material bed ($Z_2 = 20$ cm); (6) plexiglass column; (7) filter; (8) outlet; (9) measure.

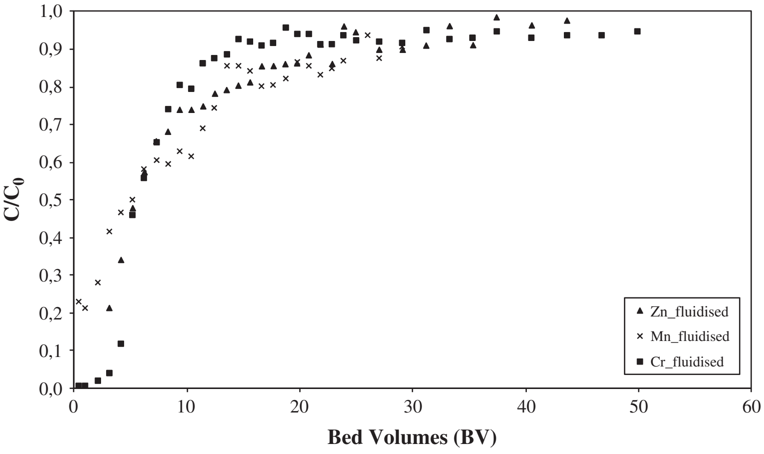

Fig. 3. Experimental data of fluidization.

The removal efficiency of zeolite for the three investigated metals in the fixed bed runs is showed in Fig. 4. In fixed bed the breakthrough curves are similar for all three metals, with Cr exhibiting slightly lower removal efficiency. Furthermore, fluidized bed breakthrough point is shifted to the left (0–5 BV) in comparison to the fixed bed experiments (10 BV).

In column operations two basic operational parameters are the residence time (τ) and the duty (L). The residence time is the contact time:

$$\tau = \varepsilon \cdot \frac{V_b}{Q} = \frac{\varepsilon}{Q_{\text{rel}}} \tag{1}$$

where (ε) is the bed porosity, (V_b) is the bed volume, and (Q_{rel}) is the relative flow rate (BV/h). The duty, also termed as loading, is the ratio of treated volume to adsorbed mass, expresses the workload that the column has to undertake (under the same inlet pollutant concentration):

$$L = \frac{V_{\text{eff}}}{M} = \frac{Q \times t}{\rho_b \times V_b} = \frac{Q_{\text{rel}} \times t}{\rho_b} = \frac{V_{\text{rel}}}{\rho_b} \tag{2}$$

where (V_{eff}) is the effluent volume, (M) is the mass of the packing material, (t) is the operation duration, (V_{rel}) is the relative effluent volume expressed as bed volumes (BV), and (ρ_b) is the bed bulk density.

When using the same material and inlet pollutant concentration in different fixed beds the bed porosity and bulk density are the same. By using the same relative flow rate the residence time (τ) is the same while the comparison is typically made by plotting the exit concentration vs. the exit relative volume (BV), i.e. the comparison is made for the same load (L). However, when two different bed configurations and/or different packing materials are compared the bed porosity and bulk density are different. By using the same relative flow rate the residence time is different while the comparison of the operations should be made for the same load, not relative effluent volume. In the present study, by keeping the same relative flow rate the residence time is higher for the fluidized bed, which means that the later exhibits an advantage against fixed bed.

Comparing the two processes (Figs. 5–7) under the same relative volumetric rate, it is concluded that fixed bed operation has better results than the fluidized bed for Zn and Mn, i.e. for the same duty the fixed bed exit concentration is lower and by extension, it can process larger quantities of the solution. The differences are minimized for high exit concentration (>0.6–0.8). For Cr the difference is only apparent for low concentrations (<0.2) and the exit curves are essentially identical. This is despite the fact that the contact time in fluidized bed is higher. As the particle size is the same, the solid phase mass transfer rates are expected to be the same [22,23]. Furthermore, the reactors operate approximately under the same particle Reynolds number ($Re_p = 0.01$) and thus the external mass transfer rate is possibly higher in the fixed bed [11]. However, this is not expected to be the determining factor for the better performance of the fixed bed as heavy metals uptake by clinoptilolite is mainly controlled by the solid phase diffusion process [22,23]. Thus, taking into account that the fixed bed is operating under upflow conditions which ensures close-to-ideal flow [24], the efficiency of the fluidized bed is lower most probably due to hydrodynamic rather than mass transfer reasons, i.e. due to non-idealities leading in channeling and other flow-disturbing macro-phenomena.

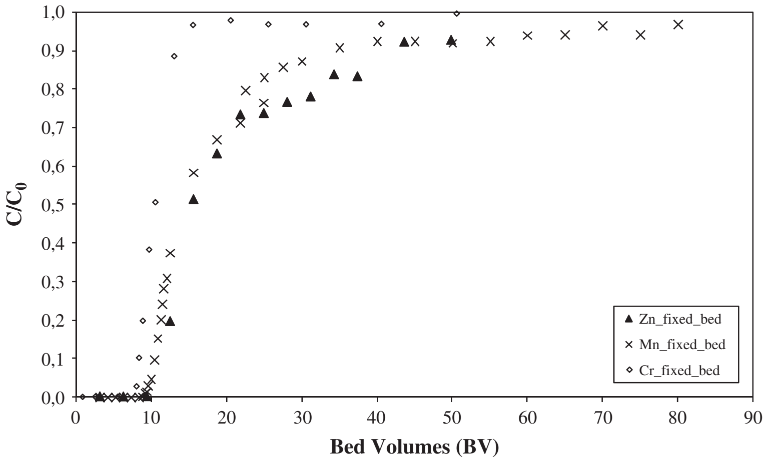

Fig. 4. Experimental data of fixed-bed reactors.

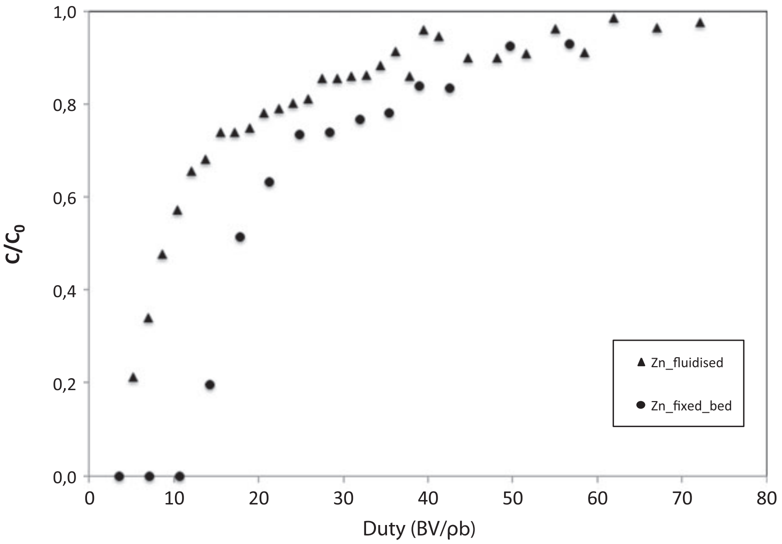

Fig. 5. Breakthrough curves of fixed bed and fluidized experiments for Zn.

Despite the extensive literature on fixed beds, applications of natural zeolites in fluidized-bed reactors for the removal of heavy metals from aqueous solutions are not reported. There are only fluidized beds studies for the removal of heavy metals by use of other materials such as sand, chelating resin, and synthetic zeolites such as zeolite A and Baylith WE984 [14,18,19,21]. Also, there are studies for the removal of heavy metals by zeolites but in bubble column (three-phase) not fluidized bed (two-phase) operation, where gas is used for rigorous agitation of the liquid–solid phase. A relevant example of the use of this kind of reactor is the zinc uptake by natural clinoptilolite [25,26]. Another configuration is the use of anaerobic fluidized bed reactors (AFBR) with natural zeolite as support for treating high-strength distillery wastewater (COD removal) [27]. However, this configuration is different as zeolite is primarily used as support media for the immobilization of micro-organisms and thus to retain the biomass in the reactor.

The most relevant publication is related to the removal of NH_4 from aqueous solutions by use of fluidized beds of clinoptilolite [14]. In particular, a series of fixed and fluidized bed ion-exchange column runs were conducted to identify the ability of natural clay minerals, sepiolite, and clinoptilolite, to remove ammonia from a contaminated drinking water reservoir [14]. The results showed that clinoptilolite fluidized beds, utilizing water and air as fluidizers, resulted in inferior results compared to those of fixed

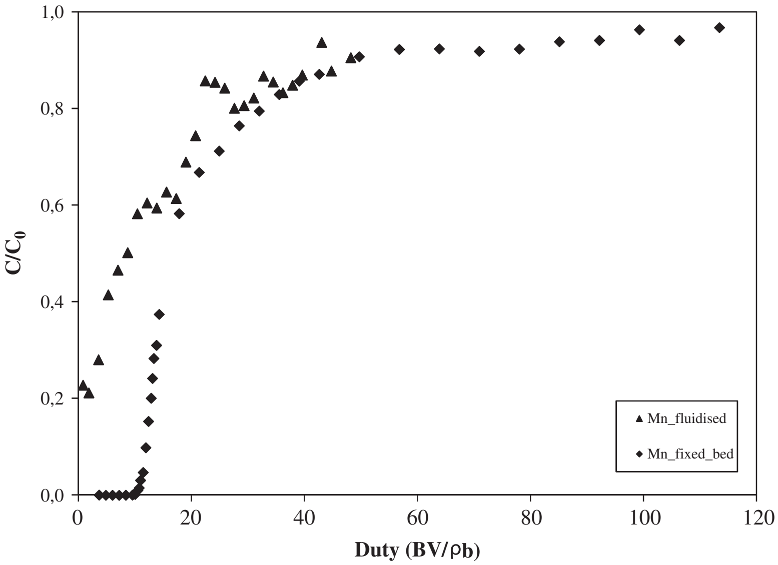

Fig. 6. Breakthrough curves of fixed bed and fluidized experiments for Mn.

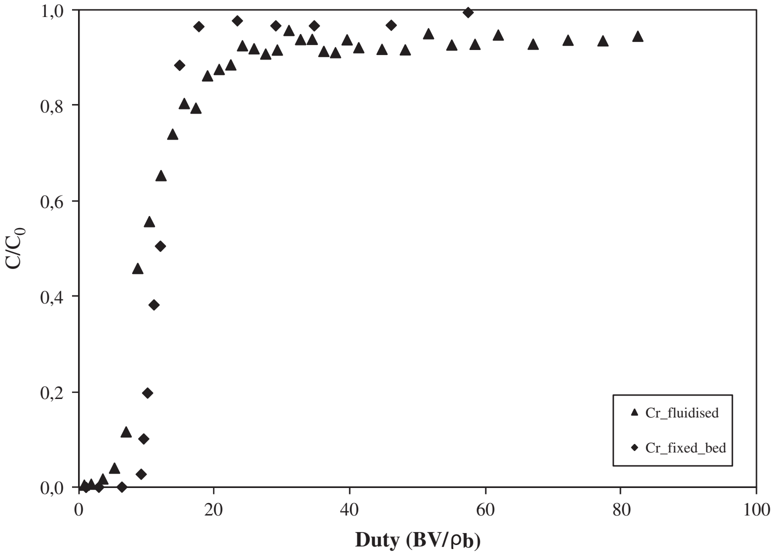

Fig. 7. Breakthrough curves of fixed bed and fluidized experiments for Cr.

bed runs. This was ascribed by the authors to the presence of ammonia in the circulating water and competition of exchangeable ions released in water and the ability of air to adsorb nitrogen.

It should be noted that in real conditions, wastewater might contain high concentrations of suspended solids and in this case the use of fluidized bed is expected to experience less operational problems in relation to the fixed bed as the later is prone to clogging problems. The use of fluidized beds for clogging avoidance is also mentioned elsewhere for AFBR [27].

4. Conclusions

In the present study, fixed and fluidized bed experiments were conducted in order to examine the Mn^{2+}, Zn^{2+}, and Cr^{3+} uptake by natural clinoptilolite (90–180 μm), using the same relative volumetric flow rate of 12.48 BV/h, under a total normality of 0.01 N and initial pH value equal to 4, and ambient temperature (25°C). Comparing the two processes, it is concluded that fixed bed operation has better results than the fluidized bed most probably due to better hydrodynamic conditions in the former. However, in real conditions, wastewater contain suspended solids and in this case the use of fluidized bed will lead to better results as in the fixed bed clogging problems are expected to occur.

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] D. Kunii, O. Levespiel, Fluidization Engineering, John Wiley and Son, New York, NY, 1969.

[4] V.J. Inglezakis, M.A. Stylianou, M. Loizidou, Hydrodynamic studies on zeolite fluidized beds, Int. J. Chem. Reactor Eng. 8(1) (2010) 1542–6580.

[5] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, Water Res. 18(12) (1984) 1501–1507.

[6] 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.

[7] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Ion exchange of Pb^{2+}, Cu^{2+}, Fe^{3+}, and Cr^{3+} on natural clinoptilolite: Selectivity determination and influence of acidity on metal uptake, J. Colloid Interface Sci. 261 (2003) 49–54.

[8] V.J. Inglezakis, M.A. Stylianou, D. Gkantzou, M.D. Loizidou, Removal of Pb(II) from aqueous solutions by using clinoptilolite and bentonite as adsorbents, Desalination 210 (2007) 248–256.

[9] 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(1–2) (2007) 575–581.

[10] 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.

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

[12] N. Epstein, Applications of liquid–solid fluidization, Int. J. Chem. Reactor Eng. 1 (2003) 1–6.

[13] C.I. Lee, W.F. Yang, C.I. Hsieh, Removal of copper (II) by manganese-coated sand in a liquid fluidized-bed reactor, J. Hazard. Mater. 114(1–3) (2004) 45–51.

[14] M.S. Celik, B. Ozdemir, M. Turan, I. Koyuncu, G. Atesok, H.Z. Sarikaya, Removal of ammonia by natural clay minerals using fixed and fluidized bed column reactors, Water Sci. Technol.: Water Supply 1(1) (2001) 81–88.

[15] R. Saravanane, D.V. Murthy, Application of anaerobic fluidized bed reactors in wastewater treatment: A review, Environ. Manage. Health 11(2) (2000) 97–117.

[16] M. Turan, H. Gulsen, M.S. Çelik, Treatment of landfill leachate by a combined anaerobic fluidized bed and zeolite column system, J. Environ. Eng. 131(5) (2005) 815–819.

[17] M. Pérez, L.I. Romero, D. Sales, Anaerobic thermophilic fluidized bed treatment of industrial wastewater: Effect of F:M relationship, Chemosphere 38(14) (1999) 3443–3461.

[18] P. Zhou, J.-C. Huang, A.W.F. Li, S. Wei, Heavy metal removal from wastewater in fluidized bed reactor, Water Res. 33(8) (1999) 1918–1924.

[19] P. Menoud, L. Cavin, A. Renken, Modelling of heavy metals adsorption to a chelating resin in a fluidized bed reactor, Chem. Eng. Process. 37(1) (1998) 89–101.

[20] M. Jovanović, N. Rajić, Ž. Grbavčić, B. Obradović, Zeolite in a fluidized bed reactor: Hydrodynamic and Cu(II) sorption studies, Proceedings of the Fifth Serbian-Croatian-Slovenian Symposium on Zeolites, Zlatibor, Serbia, 2013, pp. 128–131.

[21] E.M. Homem, M.G.A. Vieira, M.L. Gimenes, M.G.C. Silva, Nickel, lead and zinc removal by adsorption process in fluidised bed, Environ. Technol. 27 (2006) 1101–1114.

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

[23] V.J. Inglezakis, H.P. Grigoropoulou, Modeling of ion exchange of Pb^{2+} in fixed beds of clinoptilolite, Microporous Mesoporous Mater. 61(1–3) (2003) 273–282.

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

[25] W. Xu, L.Y. Li, J.R. Grace, Zinc removal from acid rock drainage by clinoptilolite in a slurry bubble column, Appl. Clay Sci. 50 (2010) 158–163.

[26] V. Vivacqua, W. Xu, G. Hébrard, L.Y. Li, J.R. Grace, Modeling of zinc adsorption onto clinoptilolite in a slurry bubble column, Chem. Eng. Sci. 100 (2013) 326–331.

[27] N. Fernández, S. Montalvo, R. Borja, L. Guerrero, E. Sánchez, Performance evaluation of an anaerobic fluidized bed reactor with natural zeolite as support material when treating high-strength distillery wastewater, Renewable Energy 33 (2008) 2458–2466.