

EXPERIMENTAL STUDIES ON FLUIDIZED AND FIXED BED REACTORS FOR THE REMOVAL OF HEAVY METALS FROM AQUEOUS SOLUTIONS

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Abstract

In the present study the use of natural zeolite as filling agent 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 Mn²⁺, Zn²⁺ and Cr³⁺ uptake by natural clinoptilolite, using the same critical experimental conditions in order the results to be comparable: particle size (90-180 μm), volumetric flow rate of 12.48 BV/h, total normality of 0.01N, 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 Mn²⁺ and Zn²⁺ 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 (0-5BV) in comparison to the fixed bed experiments (10 BV) for all metals. Comparing the two processes under the same critical conditions (particle size and residence time), it is concluded that fixed bed operation exhibits better results than the fluidized bed. 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.

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].

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].

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 to 0.30 mm) for the removal of Cu, Ni and Zn [18; 14]; 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 nickel, lead and zinc from aqueous solutions [21]. The most relevant published study is the use of clinoptilolite fluidized 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 same critical experimental conditions in order the results to be comparable: 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 0.01N and initial pH value equal to 4 and ambient temperature (25°C) (table 1). The experimental setup is shown in Figures 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_0) 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 ($H_f=21.8\text{cm}$). A septum was placed close to H_f ($A=24\text{cm}$) so as to sample with a syringe. Samples of 10mL 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 versus 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
Hf (cm)	21,8	20
V (ml)	331,31	62,8
Q (ml/min)	68,9	13,06
Q (ml/h)	4134	783,61
Q (BV/h)	12,48	12,48

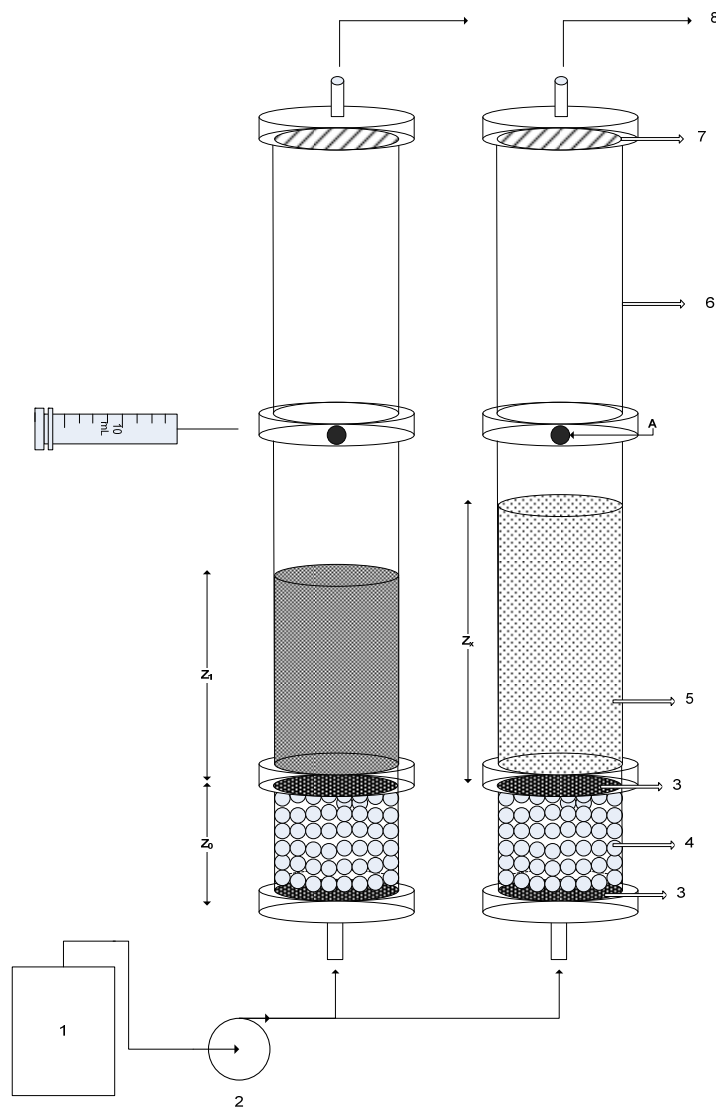


Figure 1. The experimental setup for fluidization runs: (1) metal solution tank; (2) peristaltic pump; (3) stainless steel sieve and filter; (4) calming section filled with glass beads - $Z_0=8\text{cm}$; (5) natural material bed ($Z_1=15\text{ cm}$); (6) plexiglass column; (7) filter; (8) outlet; (A)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

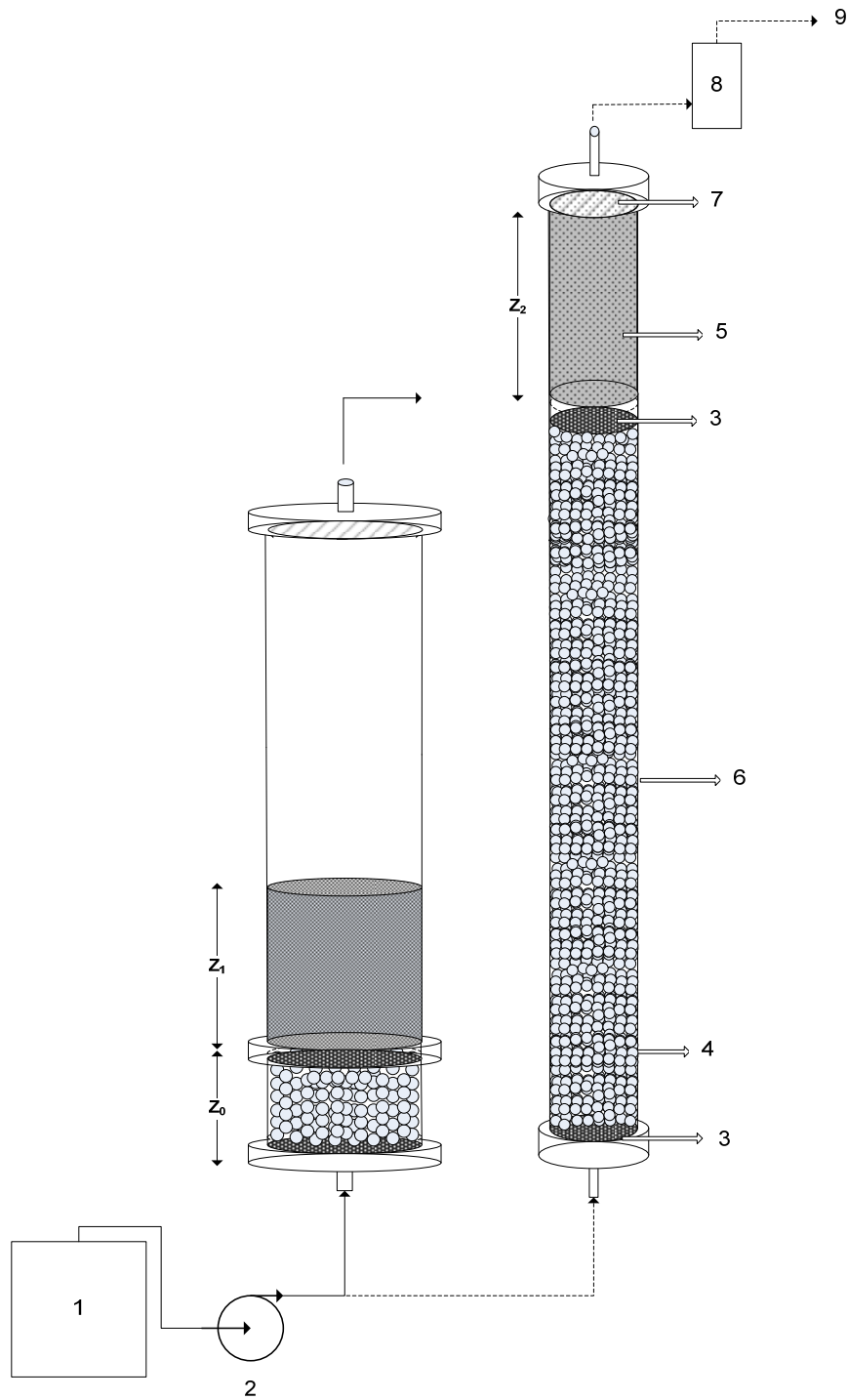


Figure 2. The experimental setup for fluidization and fixed bed runs: (1) metal solution tank; (2) peristaltic pump; (3) stainless steel sieve and filter; (4) calming section filled with glass beads; (5) natural material bed; (6) plexiglass column; (7) filter; (8) outlet; (9) measure

3. Results and Discussion

The removal efficiency of zeolite for the three investigated metals in the fluidized columns is showed in Figure 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.

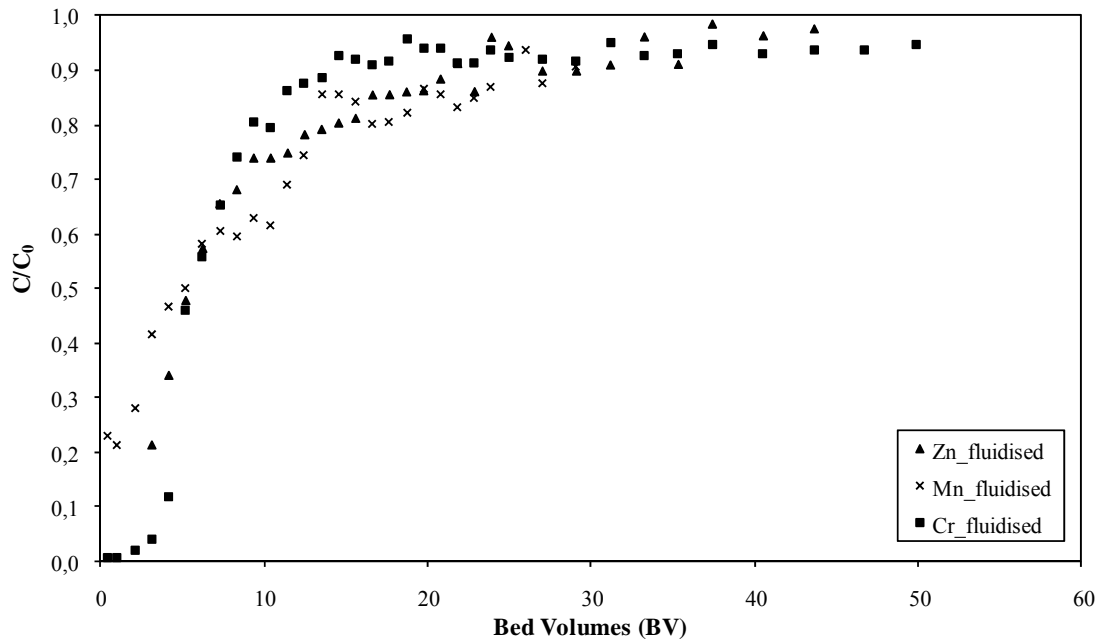


Figure 3. Experimental data of fluidization.

The removal efficiency of zeolite for the three investigated metals in the fixed bed runs is showed in Figure 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 (0-5BV) in comparison to the fixed bed experiments (10 BV).

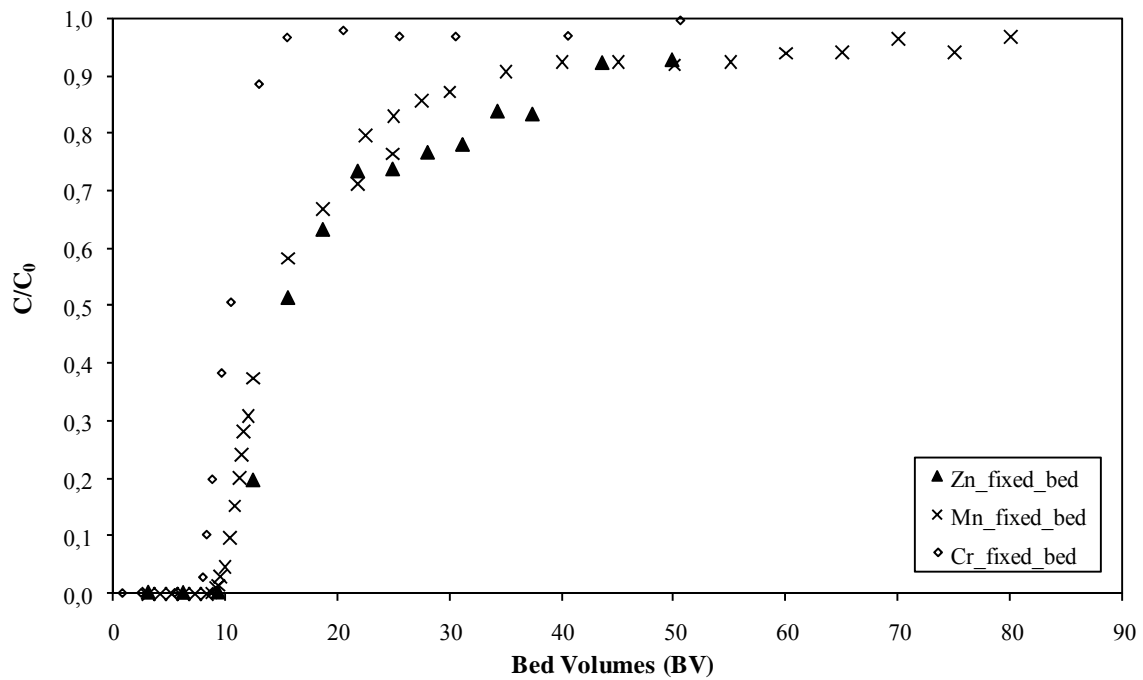


Figure 4. Experimental data of fixed bed reactors.

Comparing the two processes (Figure 5-7) under the same conditions (particle size and residence time), it is concluded that fixed bed operation has better results than the fluidized bed. In fixed beds, the zeolite continues removal of metal ions for a longer period, and by extension, purification of larger quantities of the aqueous solution of the metal. As mentioned above, the two reactors are operating under the same contact time and particle size. Thus, the equilibrium behavior and solid phase mass transfer rates are expected to be the same [25, 26]. Furthermore, the reactors operate approximately under the same particle Reynolds number ($Re_p = 0.01$) and thus the external mass transfer rate is possible to be 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 [25, 26]. Thus, taking into account that the fixed bed is operating under upflow conditions which ensures close-to-ideal flow [27], 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.

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 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 [22, 23]. Another configuration is the use of anaerobic fluidized bed reactors (AFBR) with natural zeolite as support for treating high-strength distillery wastewater (COD removal) [24]. However, this configuration is different as zeolite is primarily used as support media for the immobilization of microorganisms 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 fluidised 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 fluidised beds, utilising water and air as fluidisers, resulted in inferior results compared to those of fixed 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 latter is prone to clogging problems. The use of fluidized beds for clogging avoidance is also mentioned elsewhere for Anaerobic Fluidized bed reactors (AFBR) [24].

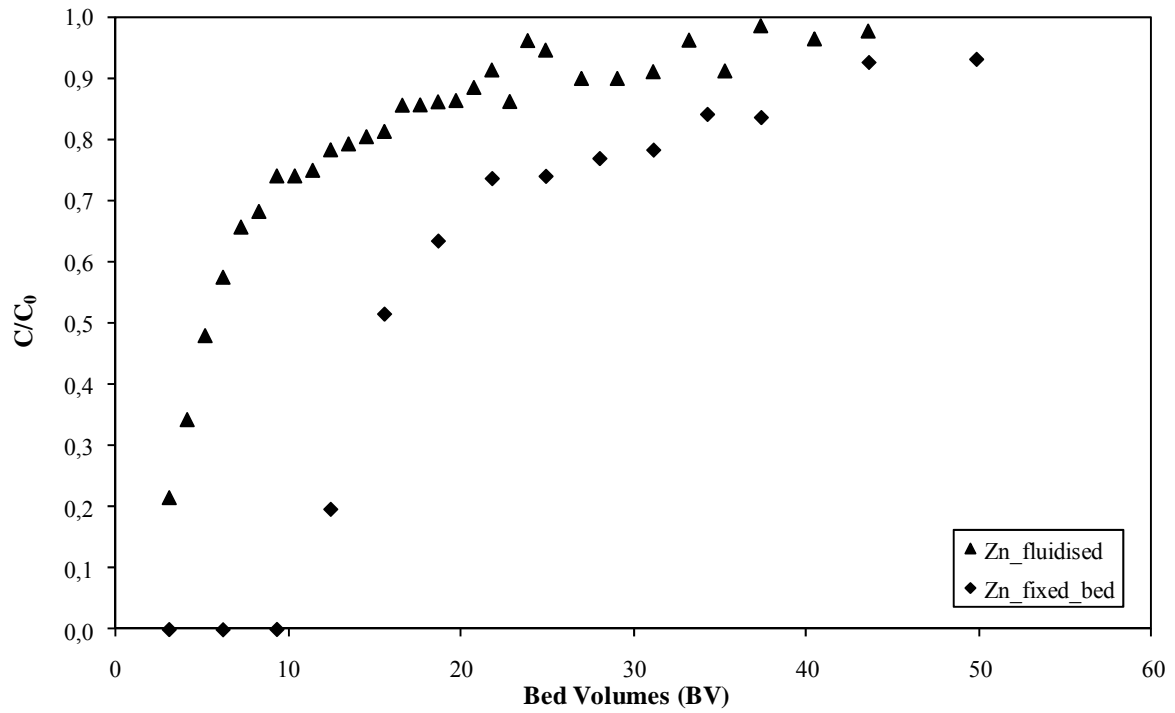


Figure 5. Breakthrough curves (12,48BV/h) fixed bed and fluidized experiments for Zn

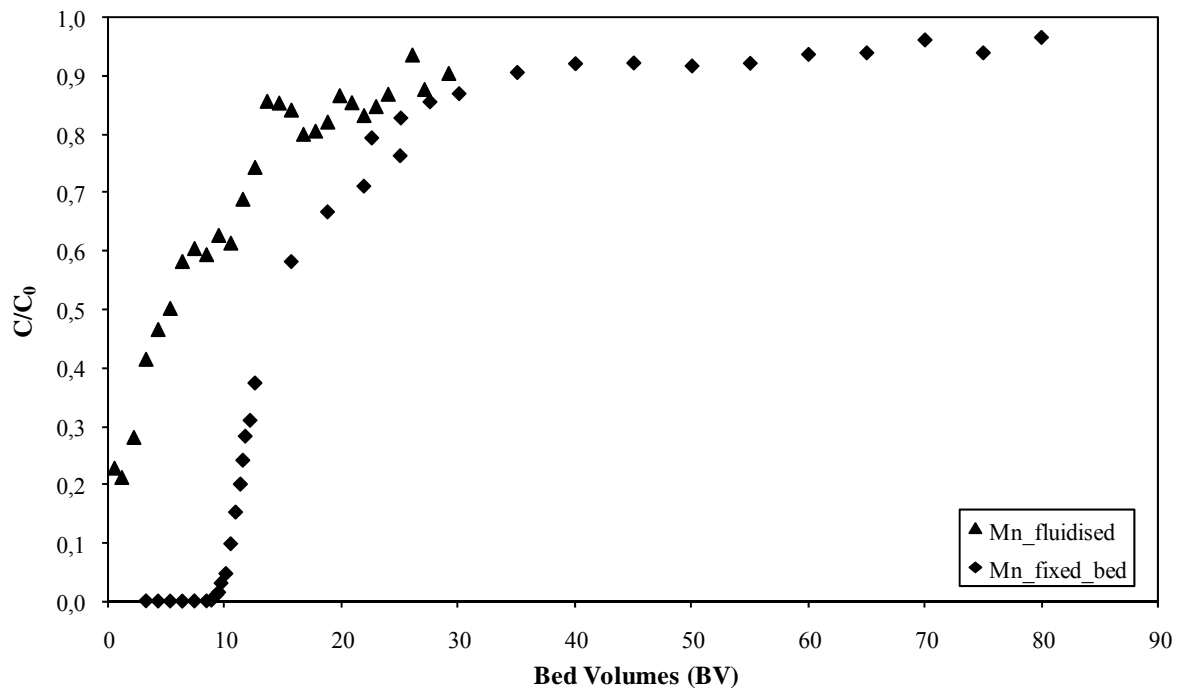


Figure 6. Breakthrough curves (12,48BV/h) fixed bed and fluidized experiments for Mn

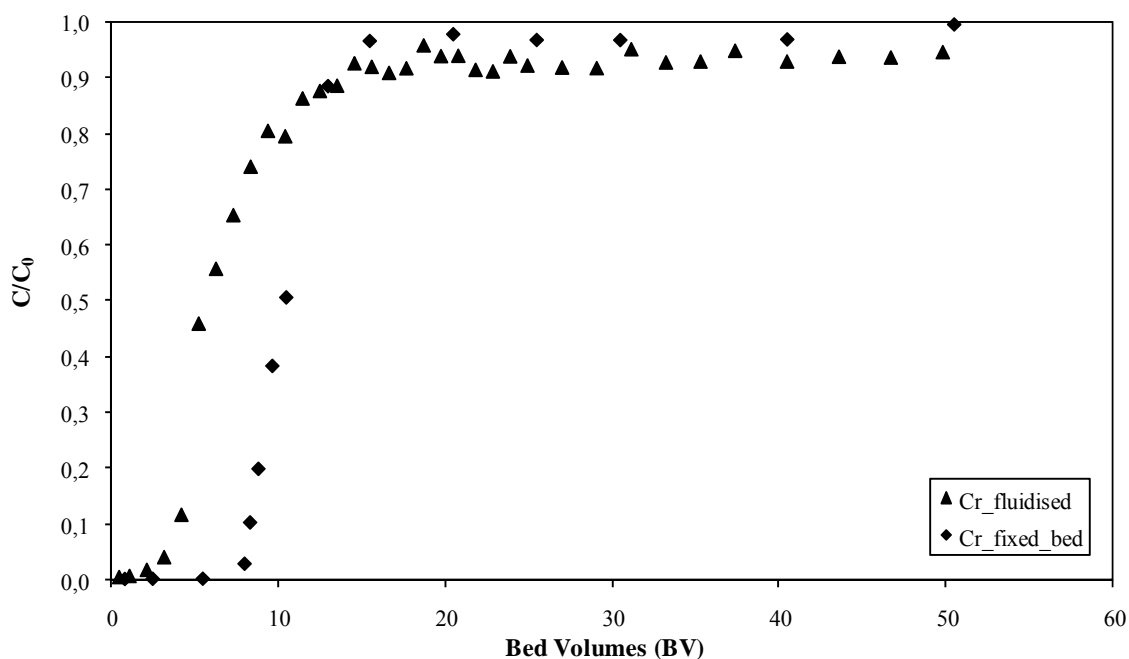


Figure 7. Breakthrough curves (12,48BV/h) fixed bed and fluidized experiments for Cr

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 experimental conditions in order the results to be comparable: 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 0.01N and initial pH value equal to 4 and ambient temperature (25°C). Comparing the two processes under the same conditions (particle size and residence time), it is concluded that fixed bed operation has better results than the fluidized bed. 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

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