



Treatment of underground water in open flow and closed-loop fixed bed systems by utilizing the natural minerals clinoptilolite and vermiculite

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ABSTRACT

Iron and manganese are found naturally in several soil and rock minerals while in the same time they are used as raw material in steel manufacture and products. Both metals can reach ground water reserves easily by rain or other means and while surface water does not usually contain high concentrations of iron or manganese because the oxygen-rich water enables both minerals to settle out as sediments, in anaerobic conditions, like in ground water deposits, iron and manganese are reduced to their soluble oxidation states Fe^{2+} and Mn^{2+} . The problem of groundwater contaminated with these metals has become evident the last decades and several methods have been tested in the related literature. Ion exchange and adsorption are inexpensive and simple methods, especially when natural minerals are used, as zeolites and clays, however, the relevant studies of simultaneous removal of Fe and Mn from natural samples in the literature are few. In the present study natural clinoptilolite (zeolite) and vermiculite (clay) are utilized for simultaneous removal of Fe and Mn from underground water samples in open flow and closed loop fixed bed systems. A closed loop fixed bed system is a fixed bed with recycling of liquid phase and thus, is a type of batch process. Vermiculite exhibited higher removal levels than clinoptilolite for both Fe and Mn. For both materials Fe removal is higher than Mn. In the closed loop fixed bed system after 24 h of treatment and 2 g/100 ml solid to liquid ratio, Fe and Mn removal levels reach 100% and 75% for vermiculite and 82% and 30% for clinoptilolite, respectively. Pretreatment of groundwater by precipitation increases removal of Fe and the system could reach 100% removal for clinoptilolite as well. Finally, results show that under the same operational conditions, closed loop fixed bed system is more promising for groundwater treatment than batch system.

Keywords: Drinking water; Manganese; Iron; Clinoptilolite; Vermiculite; Closed loop; Fixed beds

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1. Introduction

Iron and manganese are found naturally in several soil and rock minerals, the main ones are hematite (Fe_2O_3) and pyrolusite (MnO_2), used as raw material in steel manufacture. Iron and manganese reach ground water by rain, surface and waste water filtration dissolving minerals from soil strata, iron may also be present as a result of the use of iron coagulants or the corrosion of steel and cast iron pipes during ground water extraction and distribution [1]. Water percolating through soil and rock dissolves iron and manganese, and these minerals subsequently enter groundwater supplies. Surface water does not usually contain high concentrations of iron or manganese because the oxygen-rich water enables both minerals to settle out as sediments. In anaerobic conditions, like in ground water deposits, iron and manganese are reduced to their soluble oxidation states Fe^{2+} and Mn^{2+} , but they are oxidized to the insoluble oxidation states Fe^{3+} and Mn^{4+} in aerobic conditions (when ground water is pumped), readily these chemical species hydrolyses to form highly insoluble compounds such as $\text{Fe}(\text{OH})_3$ and MnO_2 , the first has a reddish-brown color and the second has a brownish-black appearance [1]. Concentrations of Mn from natural processes are low but can range up to 1.50 mg/l or higher. Levels in freshwater typically range from 1 to 200 $\mu\text{g}/\text{l}$ [2]. Sources of pollution, rich in organic matter (e.g., runoff from landfills, composts, brush or silage piles, or chemicals such as gasoline), can add to the background level by increasing Mn release from soil or bedrock into groundwater [3]. From a toxicological point of view, it is known that manganese exposure damages the nervous system functions, even it can cause an irreversible Parkinson-like syndrome known as manganism [2].

The United States Environmental Protection Agency has set the secondary maximum contaminant level for iron at 0.3 mg/l for drinking water, while World Health Organization sets a maximum acceptable drinking water concentration for iron and manganese of 0.3 and 0.1 mg/l, respectively [1,4]. The respective levels set out in the European Union by the Directive 98/83/EC of 1998, are 0.2 ppm for Fe and 0.05 ppm for Mn. According to a report published by the European Commission in 2007, Fe and Mn are among the parameters that most often cause non-compliance at a European level. In particular, out of 17 Member States, non-compliance for Fe and Mn was reported for 13 of them (76.5%) [5].

The biological removal of iron and manganese by Fe–Mn oxidizing bacteria is gradually replacing the conventional physicochemical treatments [1,6]. Furthermore, ion exchange and adsorption are inexpensive and simple methods, especially when natural minerals are used, as zeolites and clays. Zeolites are naturally

occurring hydrated aluminosilicate minerals containing cations which are exchangeable with certain cations in solutions, such as lead, cadmium, zinc, and manganese. Vermiculite is typical clay and consists of tetrahedral–octahedral–tetrahedral sheets. As in the case of zeolites, vermiculite contains magnesium ions that can be easily cation-exchanged with other cationic species such as copper, which partly contribute to the high cation-exchange capacity of vermiculite [7]. As in the case of all natural minerals, is very difficult to conclude in one single universal selectivity order and the general trend is $\text{Pb} > \text{NH}_4 > \text{Cd} \approx \text{Cu} \approx \text{Fe} \geq \text{Zn} > \text{Mn}$ for clinoptilolite and $\text{Ni} > \text{Cr} \approx \text{Zn} \approx \text{Cu} \approx \text{Pb} > \text{Mn}$ for vermiculite. However, these series should be used with great caution as they might be different from study to study. In several occasions the natural minerals are modified to be transformed to their Na-rich form. This process is commonly termed as “pretreatment” and in general has a positive effect on the operations performance. Clinoptilolite, vermiculite, peat moss, slow sand filters and other natural materials have been found to have high heavy metals adsorption capacity, including Fe. Concerning manganese removal it was found that, for instance, Namontmorillonite has an adsorption capacity equal to 3.22 mg/g, dolomite equal to 2.21 mg/g, marble equal to 1.20 mg/g, quartz equal to 0.06 mg/g, clinoptilolite equal to 4.22 mg/g and granular activated carbon equal to 2.54 mg/g [3].

However, the relevant studies of simultaneous removal of Fe and Mn from natural samples in the literature are few. The work of García-Mendieta et al. of 2009 is on zeolite clinoptilolite but synthetic aqueous solutions are used [1]. Zeolite clinoptilolite and vermiculite are studied by Inglezakis [8]. In that research, natural clinoptilolite and vermiculite as well as their Na-forms are used for simultaneous removal of Fe (1.5 ppm) and Mn (0.5 ppm) from underground water samples for solid mass to water volume ratio of 1–4 g/100 ml and treatment duration of $t = 2\text{--}48$ h. Vermiculite exhibited higher removal levels than clinoptilolite for both Fe and Mn. In general, Fe removal is higher than Mn for vermiculite and the opposite holds for clinoptilolite. In particular, Fe and Mn removal levels are between 88–94% and 65–100% for vermiculite and 22–90% and 61–100% for clinoptilolite, respectively. The experimental results showed that the maximum permissible concentrations according to the EU legislation can be achieved [8].

Water treatment by ion exchange and adsorption is frequently taking place in fixed beds which is a continuous flow operation. A closed loop fixed bed system (CLFB) is a fixed bed with recycling of liquid phase and thus, is a type of batch process. With closed loop operation, continuous recycling of the effluent

results in elevated solid/liquid contact while the inlet concentration gradually decreases. Besides, the final product comes up in batches at large time intervals. In fact, closed loop operation is a practice of using fixed beds, which are typically engaged in open flow (semi-batch) operation, in a continuous flow process simulating batch operation [9,10]. Moreover, this set-up is expected to combine some advantages of both operation types to make an ion-exchange (or sorption) process more prolific. With the material grains trapped within the bed limits, the liquid product is free of dust particles and the maneuvers concerning bed evacuation and refilling are quite simple. At the same time, recycling of the liquid phase raises contact time allowing the system to come closer to final equilibrium and better advantage is taken of the ion-exchange capacity of the solid material, thus boosting the effectiveness of the process per solid mass unit. The fact that continuous flow of the solution around the solid particles can diminish resistance to mass transfer by means of reducing the boundary layer thickness of the grains and enhancing ion conduction within the bulk flow is a non-negligible asset, too. In brief, a closed loop operated fixed bed involving high flow rates will simulate a continuous stirring batch system.

CLFB is studied for ammonium removal from a wastewater resulted after homogenization and anaerobic digestion of a mixture of wastes and wastewater from animal processing units and sewage sludge, by using natural zeolite clinoptilolite [11]. The CLFB system, under the same experimental conditions and relative flow rate of 2.56 BV/h, reached a removal of almost 22% higher than the equivalent batch system. The study concluded that CLFB is offering an alternative to conventional continuous flow open fixed bed systems. The advantage of this kind of operation is that the available capacity of material could be highly utilized by passing the liquid phase repeatedly from the fixed bed, leading it to almost complete saturation. This kind of operation however, could be useful for relatively high concentration and small volumes of waste and in systems that there is no need for continuous flow of the waste (batch treatment cycles) [11].

In the present study natural groundwater is treated in open flow and closed loop fixed bed operations for

the simultaneous removal of Fe and Mn from natural groundwater samples by use of natural minerals, namely a zeolite (clinoptilolite) and a clay (vermiculite). The contribution of the paper in the related literature is dual and coincides with the goals of the study; (a) the use of an alternative operational scheme (closed loop fixed bed) which is compared to the classic open flow fixed bed and batch operations, and (b) the simultaneous removal of Fe and Mn from natural samples.

2. Materials and methods

2.1. Minerals and water samples

A zeolite-rich sample from the volcanic tuffs of the Skaloma area, Thrace, Greece, was used as a natural zeolite sample. In a previous work [12], the main mineral constituent was determined and characterized as “heulandite type-II”, an intermediate type of the isomorphous series heulandite–clinoptilolite end members. Significant amounts of mordenite were found to contribute to the mineral structure as a secondary zeolitic phase. The other clay mineral involved in the present work was an exfoliated vermiculite sample coming from the same region. The chemical composition of the materials was determined by XRF (X-ray fluorescence) method (Table 1). Furthermore, the specific surface area (SSA) and the pore characteristics for the solid materials were measured by N₂ adsorption at 77 K using an Autosorb-1 Quantachrome nitrogen porosimeter with krypton upgrade (BET analysis). Prior to any use, the mineral samples were ground and sieved to particle size of 0.84–1.0 mm, homogenized, thoroughly washed with deionized water to remove dust and dried overnight at 105°C. Finally, the bulk density is measured experimentally and is found to be 0.96 ± 0.01 and 0.15 ± 0.01 g/ml for zeolite and vermiculite, respectively.

The potentially potable groundwater sample used in this work came from Greece, Peloponnese region, Lakonia county, Neapolis city, Lakkos site, drill NA6. All physical and chemical analyses in water were made according to standard methods [13]. In particular, the concentration of metal ions (Fe, Mn, Ca and Mg) was measured by atomic absorption spectroscopy (AAS), using a Perkin Elmer Model 2380 spectrophotometer.

Table 1
Chemical analysis of clinoptilolite and vermiculite

Oxide (%w/w)	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	MgO	CaO	Na ₂ O	K ₂ O	LOI
Clinoptilolite	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

LOI: Loss on ignition at 1100°C.

Dissolved oxygen (DO) is measured by membrane electrode method (APHA 4500-O G), acidity (pH) by electrometric method (APHA 4500-H+) and conductivity (S) by electrode method (APHA 2510 B). Finally, total solids (TS) is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature (105°C). Total solids includes total suspended solids (TSS), the portion of total solids retained by a filter (2.0 µm), and total dissolved solids (DS), the portion that passes through the filter. The relevant methods are detailed in the section 2540 of APHA.

Prior to any treatment, the water is not suitable for human consumption because of its high Fe and Mn content. A number of experiments were conducted with pretreated water samples. The pretreatment procedure was as follows. The tank containing the proper amount of water was vigorously shaken for 1–2 min and then was kept still, at room temperature and in the absence of light, for 24 h, thus being used as a small natural precipitation tank. Then, with a peristaltic pump, the upper 2/3 of the water were smoothly transferred to another vessel. This fraction was evidently less colorful, containing much less suspended solids than its precedent. All preliminary measurements concerning the properties of both natural and pretreated groundwater are summarized in Table 2.

It is evident that the precipitation pretreatment had no effect on the Mn concentration. This was expected since, under anaerobic conditions, Mn normally occurs in the Mn²⁺ oxidation state [14]. Oxidation of Mn²⁺ at pH<9.5 and in the absence of CO₃²⁻ ions is an extremely slow reaction [15]. On the contrary, in the presence of dissolved oxygen, the soluble Fe²⁺ ions are oxidized to Fe³⁺ which precipitate as hydrated Fe₂O₃, forming particles that can also adsorb other species from the aqueous phase [16,17]. The consumption of dissolved oxygen for the formation of Fe₂O₃ is evidenced by a decrease in the DO value from 80% to 66%. Also, the fact that the decrease in TS, DS and TSS values is not proportional to the removal of Fe indicates that other compounds are dragged down to the residue. The pH and specific electric conductivity values are

acceptable for human consumption for both natural and pretreated samples. The total solids concentration, on the other hand, is slightly exceeding the maximum acceptable for human consumption value of 500 mg/l even after precipitation.

2.2. Fixed bed experiments

A cylindrical column of 71 cm height and 2.1 cm diameter was used as a fixed bed reactor. Fiber filters at the bottom and at the top were applied to prevent any particle movement due to gravity or bulk flow. Glass spheres of 1 mm diameter were used to adjust the fixed bed volume, smoothing the transition between different flow regimes and, acting as pre-bed, to enhance the homogeneous flow distribution. Tight packing and a bed height/bed diameter ratio >15 were also implemented in an attempt to eliminate the effect of non-ideal flow phenomena such as axial dispersion and channeling. All vessels, tubes and other equipment that came in contact with the aqueous phase were made from polymers (PTFE, Tygon, PVC, PE and PP) that have minimum interaction with metallic cations [18,19].

The fixed bed experiments were conducted in two operation modes, namely open flow and closed loop. The open flow operation mode refers to the typical semi-batch set up, with continuous flow of the liquid-to-be-treated through the bed, the outlet being considered as the final product of the process. In the closed loop operation mode (Fig. 1), with continuous flow from a vessel through the bed and the outlet being led back to the vessel for a certain number of cycles (or time period), the process turns batchwise. In either case, upflow operation was selected in order to eliminate channeling effects and to achieve better wetting of the particles [20]. To avoid bubble formation, the bed experiments were initiated at minimal flow speed with persistent tapping at the outer sidewall of the column. Before reuse, all parts coming in contact with the aqueous phase were thoroughly washed with 1N HNO₃ solution and deionized water, successively. All experiments were conducted at room temperature (21–26°C).

Table 2

Fe, Mn, Ca and Mg concentration, pH, specific electric conductivity (SEC), dissolved oxygen (DO), total suspended solids (TSS), dissolved solids (DS) and total solids (TS) of natural and pretreated groundwater samples

Samples	Fe	Mn	Ca	Mg	TSS	DS	TS	DO [%sat]	pH	SEC [µs/cm]
	[mg/l]									
Natural	4.1	1.35	54	33	8.30	528	544	80	7.1	805
Pretreated	0.90	1.35	–	–	1.48	515	517	66	6.9	860

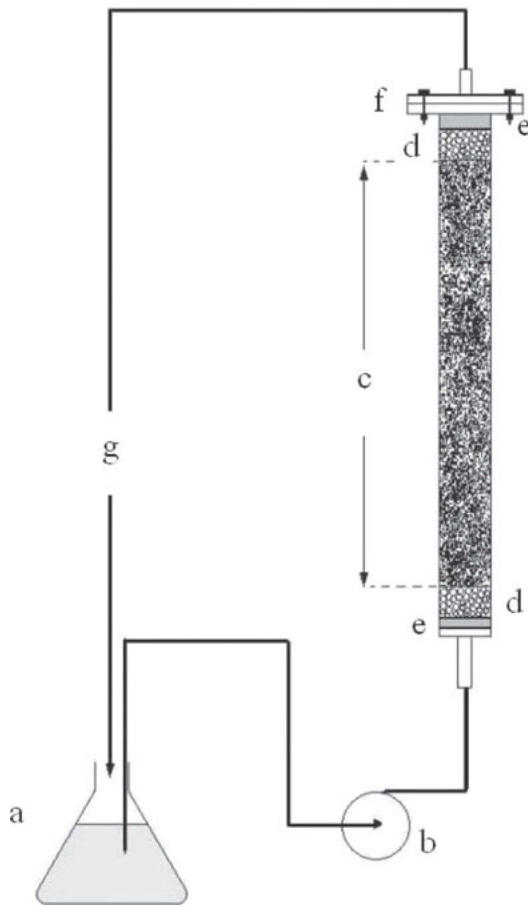


Fig. 1. Fixed bed operating in closed loop mode: (a) feed tank (b) peristaltic pump (c) fixed bed height (part of the column containing the clay particles) (d) glass particles (e) fiber filters (f) flange (g) outlet returning to feed tank.

In general, in liquid–solid adsorption and ion exchange open fixed beds operation comparisons between different fixed beds are made by using the same relative volumetric flow rate Q_{rel} (BV/h), which is equal to the ratio of the volumetric flow rate (Q) and the void bed volume (V). This, in turn means that the comparisons are made on the basis of the same residence time τ (h) provided that the bed voidage (ϵ) remains constant:

$$\tau = \frac{\epsilon \cdot V}{Q} = \frac{\epsilon}{Q_{rel}} \quad (1)$$

In other cases, the comparisons are made on the basis of the same hydraulic load (or pollutant load), which is the liquid load per solid mass (L , $m^3/h \cdot kg$) is defined as:

$$L = \frac{Q}{M} = \frac{Q}{V \cdot \rho_b} = \frac{Q_{rel}}{\rho_b} = \frac{1}{\tau \cdot \rho_b} \quad (2)$$

In the occasion where the bulk density (ρ_b , kg/m^3) is the same between different fixed beds by keeping the same residence time, the hydraulic load is kept constant as well. However, for fixed beds of materials of different bulk density, by keeping the same residence time, the hydraulic load is much lower for the heavier material. In other words, the heavier material has to cope with lower liquid volume and thus pollutant load per unit time. Consequently, the comparison between materials of different bed density under the same residence time is in favor of the heavier material. On the other hand, by keeping the same hydraulic load the residence time is different in the beds and is lower in the bed of the heavier material. Consequently, the comparison between the materials under the same hydraulic load is in favor of the lighter material. In the present experiments one more complication is that vermiculite expands in the fixed bed and as particle density varies is difficult to measure the bed voidage. This means that residence time cannot be accurately estimated. Thus, inevitably, the comparison of the materials is done for the same hydraulic load.

In the case of a closed loop fixed bed and batch mode operations the comparisons between different materials are made under the same solid/liquid ratio, which is the fixed bed solid mass/total liquid volume ratio (SL, kg/m^3):

$$SL = \frac{M}{V_{tot}} = \frac{V \cdot \rho_b}{V_{tot}} \quad (3)$$

where V_{tot} = the total liquid volume to be treated. Finally, the number of total loops (R) in a CLFB operation is calculated as follows:

$$R = \frac{Q \cdot t}{V_{tot}} \quad (4)$$

where t = the total operation duration. The residence time τ (h) in the closed loop fixed operation is not linked to the solid/liquid ratio, as is the case between residence time and hydraulic load in open fixed bed operation. Thus, in principle, solid/liquid ratio and residence time can be kept the same for different materials. However, as mentioned above, the variation of vermiculite particle density makes it difficult to say whether the residence time has a specific value. The result is that even if the same relative flow rate is used the residence time is different as the materials do not exhibit the same bed voidage. As it will be experimentally proven, the lower residence time (higher flow rate) has the opposite effects in a CLFB system in comparison to an open flow fixed bed operation.

3. Results and discussion

3.1. Open flow experiments with natural groundwater

The operational conditions for these experiments are summarized in Table 3. The vermiculite bed density is nearly 6.5 times lower as compared to the zeolite sample and thus, in order to compare the different minerals, under the same hydraulic load (L), (Q) and thus (Q_{rel}) in the vermiculite bed was kept ~ 6.5 times lower than that of the zeolite bed. As is clear, this operational arrangement is in favor of vermiculite as the lower (Q_{rel}) means higher residence time, which in general enhances the performance of a fixed bed.

Samples were taken from the fixed bed outlet at regular intervals and the c/c_0 values (namely the ratio of outlet to inlet concentration) were plotted against total effluent volume (measured in void bed volumes, BV) to yield the breakthrough curves presented in Figs. 2 and 3. From Figs. 2 and 3, it can be concluded that both minerals achieved very low Mn uptake performance, as 70% of the Mn content is present at the very first outflow samples, the Mn concentration still being excessively high (~ 0.95 mg/l). Zeolites are known as ion-exchangers with relatively low selectivity towards Fe ions [21,22] and very low selectivity towards Mn [23]. The uptake of transition metals in non-acidic environment is hindered by the formation of large complexes,

Table 3
Open flow experiments with natural groundwater sample:
Operational conditions

Material	Bed height [cm]	Solid mass [g]	Q_{rel} [BV/h]	Q [ml/min]
Zeolite	35	111	185	375
Vermiculite	35	17.3	28	56

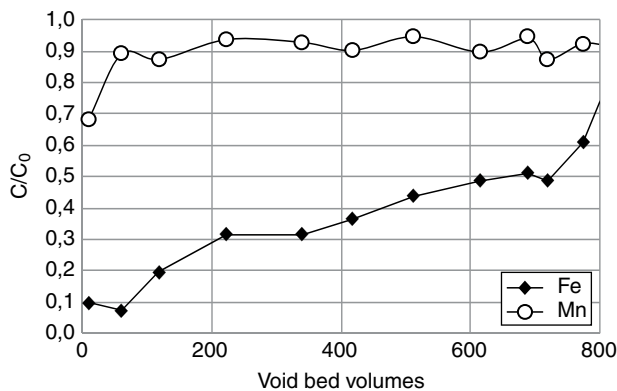


Fig. 2. Open flow experiment in zeolite fixed bed.

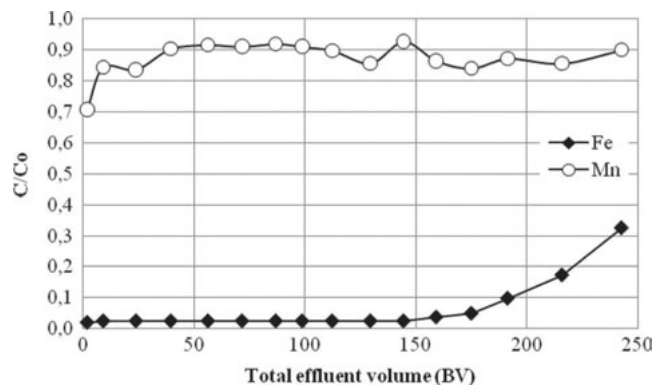


Fig. 3. Open flow experiment in the exfoliated vermiculite fixed bed.

such as $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ [24], which are mechanically filtered by the narrow micropore zeolite system. Vermiculite, on the other hand, is supposed to show generally higher selectivities for divalent cations and Mn^{2+} , in particular, is amongst the most favorably ion-exchanged transition metals [25,26]. Moreover, the open flow experiments comprise a dynamic process, the results (breakthrough data) relying not only on equilibrium, but on kinetics as well. From this point of view, exfoliated vermiculite is expected to perform better, since it is a sheer mesoporous material and ion transfer to and from the active centers encounters little resistance [27,28]. Natural clinoptilolite does have a secondary mesoporous structure (with average pore diameter typically between 30 and 50 Å) but the active centers for ion-exchange primarily lie in the primary micropore structure [29]. BET analysis showed that clinoptilolite exhibits higher surface area and porosity than vermiculite, 28.64 m^2/g and 16.3% and 20.82 m^2/g and 6.1%, respectively. The surface area difference is small but in any case, ion exchange is not influenced by the available area but by the available exchange sites. Besides, the active centers of vermiculite are fully accessible while, in clinoptilolite, many active centers can be practically non-accessible due to pore clogging [30]. In fact, experimentally measured values of total ion-exchange capacity of vermiculite samples can reach up to 260 meq/100 g [31], the respective values for natural clinoptilolites ranging from 100 to 200 meq/100 g [32,33]. Although these facts these differences are not confirmed by the breakthrough curves for Mn removal in Figs. 2 and 3, as both minerals exhibited more or less the same behavior towards Mn.

Vermiculite and zeolite exhibited totally different behavior towards Fe during the open flow experiments. According to Fig. 2, the performance of zeolite in removing Fe from the aqueous phase is very poor. Instead, vermiculite took up major quantities of Fe and the breakthrough curve (Fig. 3) lied under the threshold

of $c/c_0 = 0.05$ —which stands for the maximum acceptable for human consumption concentration of 0.2 mg/l—for 175 void bed volumes (6.25 h). Another issue is that during the experiments precipitation of Fe^{3+} occurred at the bottom section (close to the inlet) and a film of red-brownish residue, obviously $\text{Fe}(\text{OH})_3$, started to cover the grains and stick on the inner surface of the column. It is possible that the upflow motion of already formed $\text{Fe}(\text{OH})_3$ or Fe^{3+} complexes incorporations was efficiently constrained in the small voids between the grains with the aid of gravity. With time, the residue would pile up. In the vermiculite bed, with the volumetric flow set at 56 ml/min, the residue was relatively undisturbed. In the zeolite bed, the flow speed was 6.5 times higher and parts of the residue were irregularly swept along, reaching the outlet. So, the breakthrough curves in Figs. 2 and 3 are representing a combination of ion-exchange, precipitation and mechanical sweeping. At low speed, the process seems efficacious, with the objective being the reduction of the Fe concentration. But in order to study the process and to extract information useful for scale-up and large-scale applications, it is preferable to pre-treat the groundwater so that all Fe content of the solution fed to a fixed bed operation occurs as dissolved ions. Besides, lowered concentrations at the inlet are usually beneficial in fixed bed operations, as the overall performance can be greatly increased by achieving lower outlet concentrations for longer time periods [34–37].

Apart from Fe and Mn concentrations, pH and specific electric conductivity were also monitored at the bed outlet but only minor fluctuations around the starting values were noticed. It is observed that the specific electric conductivity values were practically unchanged during the whole procedure, which implies that the basic mechanism for the Fe and Mn ions uptake was ion-exchange. Ion-exchange, in contrast to sorption, is a stoichiometric process: the Fe and Mn ions that were retained by the natural minerals were exchanged with other cations (typically Mg^{2+} for vermiculite and Mg^{2+} , Ca^{2+} , Na^+ and K^+ for zeolite) of equal electric charge as a total [38,39]. The mobilities of these ions are close in value to those of Fe^{2+} and Mn^{2+} [7]. The specific electric conductivity of a solution is essentially given by

the concentrations and mobilities of the charge carriers (electrons or ions). Thus, it is normal that substitution of Fe and Mn ions by equivalent Mg^{2+} , Ca^{2+} , Na^+ and K^+ ions has no serious effect on the specific electric conductivity of the solution. Moreover, it can be deduced that the total of the Fe^{3+} ions that precipitated during the experiments had already been in this oxidation state but remained in the bulk of the solution as suspended solids or were transferred in the bed because of the pump suction. Otherwise, if oxidation of Fe^{2+} had occurred during the experiments, a subsequent decrease in the ions content would have been evidenced by a decline in SEC values. Indeed, periodical dissolved oxygen measurements showed that no oxygen was consumed during the experiments, as the inlet and outlet DO values were similar and remained constant throughout the whole process.

The pH at the outlet varied in the range 7.01–7.17. A reasonable explanation for the fact that the pH values at the outlet were practically equal to the starting value of 7.10 during these experiments is that the groundwater contained large amounts of Mg^{2+} and Ca^{2+} ions, as well as Na^+ and K^+ ions, part of which were, to a certain extent, ion-exchanged with the ion-exchangeable ions of the natural minerals, but these ions have similar dissolution and hydrolysis behavior [40]. The uptake of Mn^{2+} and Fe^{2+} should normally raise the pH value at the outlet, since these metallic ions are substituted by alkali and alkali earths [32,41]. But the Fe^{2+} and Mn^{2+} ion-exchange was too low and had no impact on the pH value, which was rather governed by the interaction of the Mg^{2+} , Ca^{2+} , Na^+ and K^+ ions between the minerals and the aqueous phase.

3.2. Closed loop experiments with natural groundwater

The operational conditions for these experiments are summarized in Table 4. In order to compare the minerals, the solid-to-liquid ratio (LS) is fixed at 1 or 2 g/100 ml and (Q_{rel}) was kept constant at 10 BV/h. It should be noted that the same relative flow rate is not equivalent to same residence time as the materials do not exhibit the same bed voidage.

Table 4
Closed loop experiments with natural groundwater sample: Operational conditions

Material	Bed height (cm)	SL (g/100 ml)	Solid mass (g)	Water volume (ml)	Q (ml/min)	R^a (–)
Zeolite	50	1	158	15.85	29	2.6
	52	2	165	8.23	30	5.1
Vermiculite	60	1	29.7	2.97	34	16.3
	46	2	22.8	1.14	26	31.2

^aFor operation duration of 24 h.

In Figs. 4 and 5, the c/c_0 values in the feed tank are plotted against time for all experiments conducted with natural groundwater in closed loop operation. It should be denoted that, during these experiments, formation of residue within the bed limits was not as intense as in the open flow experiments, being observable only at a relatively early stage, namely <2 h and 5–6 h for vermiculite and zeolite respectively. As time elapsed, the Fe concentration at the inlet decreased and Fe^{3+} dissolution became feasible, so the residue was gradually washed out.

Vermiculite was successful in taking up the Fe load of the natural groundwater without any pretreatment. After 24 h, the Fe content in the feed tank deteriorated to

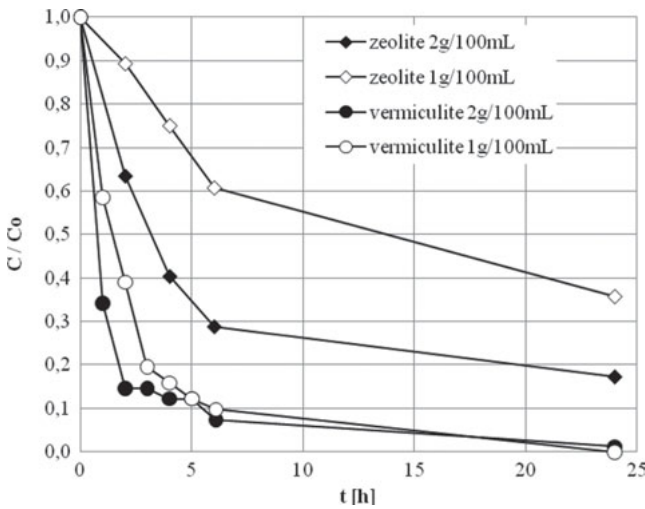


Fig. 4. Fe depletion using fixed beds in closed loop operation to treat natural groundwater.

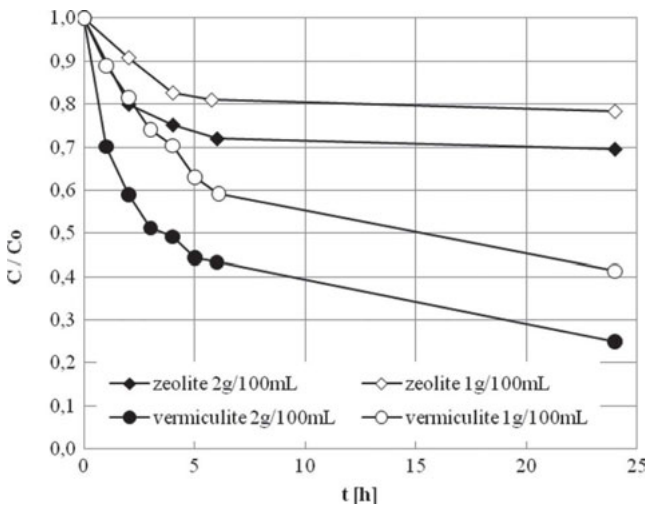


Fig. 5. Mn depletion using fixed beds in closed loop operation to treat natural groundwater.

<0.05 mg/l either using 2 or 1 g of vermiculite per 100 ml of liquid. With linear interpolation, it can be found that with either 2 or 1 g of vermiculite/100 ml of liquid the Fe content reached the desirable level of 0.20 mg/l (corresponding to $c/c_0 \approx 0.05$) after 15 h. Zeolite, on the other hand, was not as efficient: After 24 h, Fe removal reached only 82% using 2 g of zeolite per 100 ml of liquid and 64% with a solid-to-liquid ratio = 1 g/100 ml, the final Fe concentrations being still too high for human consumption. At any rate, the Fe concentrations of the zeolite bed experiments (Fig. 4) show an asymptotic trend with a tendency to converge to values quite higher than the desirable 0.05 (0.20 mg/l in absolute numbers).

As far as Mn removal is concerned, the zeolite beds performance was very poor. With a solid-to-liquid ratio of 1 g/100 ml, the Mn removal after 24 h reached 22% while operation with 2 g of zeolite per 100 ml of groundwater resulted in a 30% removal of the Mn content. Vermiculite achieved higher uptake, resulting in 75% and 59% (with 2 and 1 g/100 ml respectively) Mn removal. For batch mode operation in absence of agitation, Inglezakis has shown that after 24 h of treatment and solid-to-liquid ratio = 2 g/100 ml, Fe and Mn removal levels are almost 91% and 77% for vermiculite and 52% and 68% for clinoptilolite, respectively [8]. It should be noted that Inglezakis used a different groundwater water sample, with lower Fe and Mn concentration, 1.5 and 0.5 ppm, respectively which manifests an advantage for the batch system in comparison to CLFB system [8]. However, comparing the results for Fe, CLFB system exhibits better results for vermiculite (90%–100%) and clinoptilolite (52%–82%). For Mn, the results are similar for vermiculite (77%–75%) while the achieved removal in the batch system by clinoptilolite is higher (68%–30%). Due to the lower Mn concentration in the batch system is clear that the CLFB system performs better as in the case of clinoptilolite it removed 0.405 mg/l of water in comparison to 0.34 mg/l in the batch system. Concluding, it can be stated that for CLFB system is more promising for groundwater treatment. Similar were the results in a study for ammonium removal from a wastewater by using clinoptilolite, where the CLFB system, under the same experimental conditions (solid-to-liquid ratio and treatment duration), achieved better results than batch system [11].

At any rate, the Mn concentration never reached the desirable value of 0.05 mg/l. However, from a literature review, it is easy to conclude that vermiculite should be expected to show better efficiency in taking up Mn^{2+} ions from the aqueous phase than clinoptilolite, both in terms of kinetics and selectivity [24–26,30–33]. This, in contrast with the open flow experiments, where the emergence of $\text{Fe}(\text{OH})_3$ residue within the fixed beds limits blurred the operating conditions, is verified by the results from

the closed loop experiments conducted with zeolite and vermiculite fixed beds. With the problem of $\text{Fe}(\text{OH})_3$ precipitation extinguished by the process itself, ion-exchange is, essentially, the sole mechanism for the Mn and Fe uptake and the differences in behavior of the two natural minerals come to light. Thus, it seems natural that the zeolite beds showed better efficiency in removing Fe than Mn. Finally, it is clear in Table 5 that the c/c_0 values of the zeolite beds at 24 h are higher than the respective ones of the vermiculite beds at ~3.7 h (same number of recycle loops). So, higher Fe and Mn uptake achieved by the vermiculite beds must be attributed to better kinetics and higher total ion-exchange capacity.

Surprisingly, vermiculite showed higher selectivity for Fe^{3+} than for Mn^{2+} . With a solid-to-liquid ratio of 2 g/100 ml, the maximum Mn charge on vermiculite was found to be equal to 2.0 $\mu\text{mol/g}$, with the respective solution concentration diminished at 0.35 mg/l. This is about 10^3 times lower than experimental equilibrium data found in literature for a vermiculite/Mn ion-exchange at $\text{pH} = 7$ [42]. The critical difference is that Fonseca et al. conducted their experiments with synthetic solutions. It can be easily concluded that the complexity inherent in a natural groundwater sample can raise difficulties in the removal of Mn^{2+} ions through ion-exchange. Competitiveness from other cations, especially Ca^{2+} , is a priori an unfavorable factor, together with the already high Mg^{2+} concentration of the aqueous phase. Moreover, the presence of ions naturally occurring in groundwater, such as NO_3^- and Cl^- , can lead to the formation of Mn^{2+} -complexes with a negative charge that are stable in the aqueous phase and will not be substituted by the vermiculite Mg^{2+} or any other exchangeable cation potentially available for ion-exchange [43].

Specific electric conductivity in the feed tank was also measured periodically and the results are presented in Fig. 6. With vermiculite, SEC alterations were insignificant throughout the whole process, verifying that ion-exchange is the mechanism responsible for the uptake of Mn and Fe ions, like in the open flow experiments. But with the zeolite beds, an unexpected rise in the order of 60–70 $\mu\text{s/cm}$ in SEC values is evidenced for the first

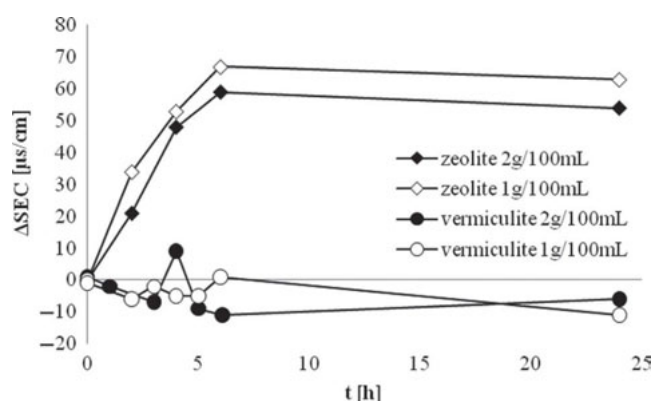


Fig. 6. Specific electric conductivity changes in the feed tank of closed loop experiments with natural groundwater (ΔSEC in the y -coordinate is the difference between the SEC measured at time intervals and the starting value of 805 $\mu\text{s/cm}$).

5–6 h, and then the SEC values seem to settle down. This must be a side effect from the presence of $\text{Fe}(\text{OH})_3$ residue within the zeolite fixed beds for the same time period. Probably, some $\text{Fe}(\text{OH})_3$ was adsorbed on the zeolite surface taking the place of pre-adsorbed ions, thus increasing the concentration of electric charge carriers in the solution. Alternatively, the alterations in ion concentrations as the ion-exchange progresses might derange pre-set equilibria in a way that leads to higher oxidation state of other compounds already present in the groundwater, or even dissolution of suspended solids (including Fe^{3+} -species). The latter, is also supported by total solids and dissolved oxygen measurements in the final products of the experiments. Total solids concentration was lower in groundwater treated with zeolite than with vermiculite (average values were 0.40 and 0.85 mg/l, respectively). Likewise, after treatment with the zeolite beds, the dissolved oxygen in the solution deteriorated to 63% whereas, with the vermiculite beds, it was 82%, practically equal to the original 80% (Table 1). With vermiculite, it is safe to consider simpler ion-exchange courses taking place, since the only cation available for exchange from the solid phase side is Mg^{2+} . Thus, the equilibrium

Table 5

Experiments with natural groundwater: Comparison of Mn and Fe removal efficiency of the two minerals based on the same number of recycle loops (the c/c_0 values for vermiculite were calculated with linear interpolation through original data)

Mineral	SL (g/100 ml)	Time (h)	R (-)	Fe (c/c_0)	Mn (c/c_0)
Zeolite	1	24	2.6	0.36	0.78
	2	24	5.1	0.18	0.70
Vermiculite	1	3.7	2.6	0.18	0.72
	2	3.7	5.1	0.13	0.50

in the solution were not deranged as drastically and the SEC values were practically unaltered throughout the whole experiments duration. Yet, the probability of some $\text{Fe}(\text{OH})_3$ being adsorbed on the vermiculite surface cannot be neither excluded, nor verified.

Unlike specific electric conductivity, pH measurements showed a specific trend of the pH values to increase with higher uptake of Mn and Fe. This is in agreement with previous works, according to which the uptake of dissolved metals by natural minerals raises the solutions pH value, since metallic ions are substituted primarily by alkali and alkali earths [32,41]. In the present work, with starting pH values very close to 7, H_3O^+ -exchange should be expected to be of very little importance.

3.3. Closed loop experiments with pretreated groundwater

The operational conditions for these experiments are summarized in Table 6. In order to compare the minerals, the solid-to-liquid ratios were fixed at 1 or 2 g/100 ml and (Q_{rel}) was kept constant at 10 BV/h. It should be noted that the same relative flow rate is not equivalent to same residence time as the materials do not exhibit the same bed voidage. Also, given the big difference in bed density of the two minerals, and under the prospective of possible large-scale applications, additional experiments with the same steady solid/liquid volume ratio (1 ml solid/100 ml liquid) were conducted, so as to make a direct comparison between operational units of the same size treating the same water quantities. Furthermore, as the zeolite fixed beds exhibit a bed density of ≈ 0.96 g/ml, so it is acceptable to compare between the results obtained with 1 g zeolite/100 ml liquid and 1 ml zeolite/100 ml solution and as the later experiments are conducted under much higher volumetric flow speed, an investigation is possible on the effect of increased flow rate on the process.

Specific electric conductivity measurements carried out for these experiments showed insignificant alterations in SEC values during these experiments. The higher

variations measured were $\pm 12 \mu\text{s}/\text{cm}$. With the SEC values essentially unchangeable, it is safe to conclude that the main mechanism for the metal ions uptake was ion-exchange, throughout the whole process.

The groundwater pretreatment had no impact on the Mn uptake by either zeolite or vermiculite. After 24 h, the c/c_0 values in Fig. 7 are essentially the same with the corresponding ones in Fig. 5. Also, all trends of the c/c_0 values imply that no equilibrium has been attained. It seems that the uptake of Mn is governed by very slow kinetics. The zeolite fixed beds had a bed density of ≈ 0.96 g/ml, so it is acceptable to compare between the results obtained with 1 g zeolite/100 ml liquid and 1 ml zeolite/100 ml solution. From this comparison, it becomes apparent that the great increase in volumetric flow rate accelerates Fe removal while the result is less intense for Mn removal (Figs. 7 and 8).

As is well known, higher flow rate leads to lower residence time, which in turn lowers the contact time given to the system for reacting. Parallel to this, increased flow rate results in thinner boundary layers (less resistance to mass transfer) on the surface of the grains.

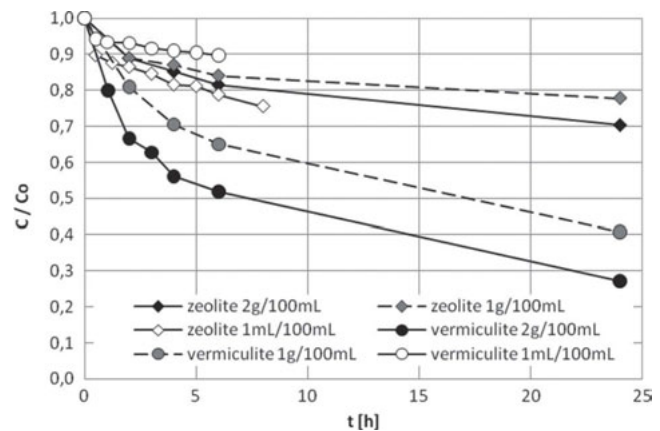


Fig. 7. Mn depletion of pretreated water using fixed beds in closed loop operation.

Table 6

Closed loop experiments with pretreated groundwater samples: Operational conditions

Material	Bed height (cm)	Q_{rel} (BV/h)	Q (ml/min)	SL (g/100 ml)	Duration (h)	Solid mass (g)	Water volume (l)	R (-)
Zeolite	33	10	19	1	24	105	10.45	2.6
	38	10	22	2	24	120	6.01	5.0
	31	200	355	1 ml/100 ml	8	98	10.22	16
Vermiculite	52	10	30	1	24	25.7	2.57	16
	57	10	33	2	24	28.2	1.41	32
	31	200	355	1 ml/100 ml	6	15.3	10.22	12

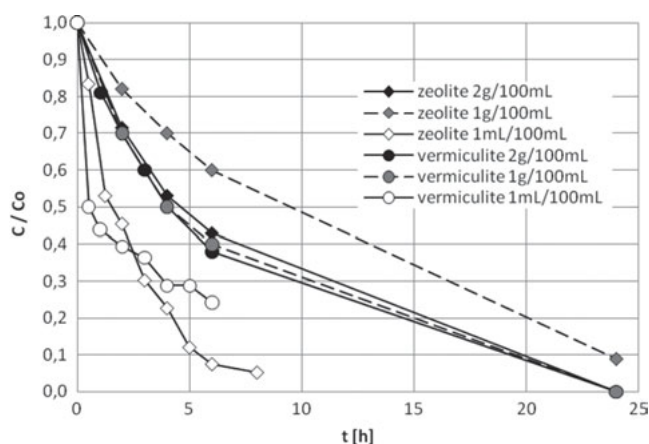


Fig. 8. Fe depletion of pretreated water using fixed beds in closed loop operation.

Ion diffusion will be easier in the bulk liquid flow, too, by means of convection [44]. Increased flow rate can also prevent the emergence of non-ideal flow phenomena and of poor wetting, making solid/liquid contact more prolific and effectual [20,45]. However, in an open flow fixed bed, with the exception of severe liquid maldistribution, the net result of higher flow rate is a decrease on the operation efficiency. In contrast, in a closed loop fixed bed contact time per pass is not important. Instead, as the liquid phase passes through the bed for several times (loops) higher flow rate leads to better solid–liquid contact and higher mass transfer rates and more loops. It is worthwhile to mention that, in a close loop operation the real “residence time” is the total duration of the process and, eventually, the number of total loops which is equivalent to the time and agitation speed in a batch system. This is the explanation of the increase of the operation performance.

Likewise, with 1 ml (≈ 0.15 g) vermiculite per 100 ml solution, better kinetics are not enough to cover for the solid mass decrease: after 6 h of contact time with vermiculite, the c/c_0 values are 0.90 and 0.65 for 1 ml/100 ml and 1 g/100 ml, respectively. Other factors that can possibly slow down the uptake of Mn are the formation of very large complexes whose diffusion in the mesopores of the grains is suppressed by their size and/or electric charge, alterations in selectivity due to parallel actions and competitiveness from other cations [22] and chemical binding by ions or complexes in the liquid phase [24]. At any rate, even with 2 g of vermiculite per 100 ml solution, 24 h were not enough to diminish the Mn concentration to values acceptable for human consumption.

As it can be seen in Fig. 8, the pretreatment of the water was beneficial for the uptake of Fe. After precipitation, 24 h of closed loop operation with $Q_{rel} = 10$ BV/h

are sufficient for the desired removal of the remaining in the groundwater Fe ions using 1 g of either material. Besides, the benefits of increased volumetric flow rate are soundly manifested in Fig. 8: With $Q_{rel} = 200$ BV/h, the target of reducing Fe concentration of 100 ml of pretreated groundwater below 0.20 mg/ml ($c/c_0 < 0.18$, correspondingly) is achieved within ~ 4.5 h using 0.96 g (1 ml) zeolite. From the trend of the c/c_0 values measured for 1 ml vermiculite/100 ml solution, it can be assumed that 0.15 g vermiculite would achieve the same Fe depletion in less than 10 h. With higher flow rate, the performance of vermiculite is superb at the very early stages: Indicatively, Fe c/c_0 is equal to 0.50 when the first loop is completed, that is after only 30 min of operation. This is indicative of the relatively uninhibited movement of the Fe ions in the vermiculite mesopores as long as mass transfer resistance in the grain boundary layer is largely worn down. The respective c/c_0 value for zeolite is 0.83, despite the fact that the solid mass to liquid volume is $>$ six times higher. Inevitably, as both systems start to approximate equilibrium, the big difference in solid mass to liquid volume ratios is manifested and the c/c_0 values of the zeolite bed settle at lower level. Finally, pH values in the feed tanks steadily increased as the uptake of Mn and Fe by the fixed beds led to enrichment of the aqueous phase in alkali and alkali earths [32,41].

4. Conclusions

In the present study natural clinoptilolite and vermiculite are utilized for simultaneous removal of Fe and Mn from underground water samples in open flow and closed loop fixed bed systems. Vermiculite exhibited higher removal levels than clinoptilolite for both Fe and Mn. For both materials Fe removal is higher than Mn. In the closed loop fixed bed system after 24 h of treatment, Fe and Mn removal levels are almost 100% and 59–75% for vermiculite and 64–82% and 22–30% for clinoptilolite, respectively. Pretreatment of groundwater by precipitation increases removal of Fe and the system could reach 100% removal for clinoptilolite as well. Combining the results of the present study with other studies it can be stated that under the same conditions, i.e. solid-to-liquid ratio and treatment duration, CLFB system is more efficient than the batch system. The main mechanism for the uptake of Fe and Mn from natural groundwater using vermiculite and zeolite fixed beds was found to be ion-exchange. Exfoliated vermiculite performed much better than natural clinoptilolite in taking up Fe and Mn from a natural groundwater sample using similar solid mass to liquid volumes. On the other hand, zeolite is much preferable from a practical point of view, since it will be more efficient than vermiculite in a given sized operation unit.

In order to design a well-operating unit for the treatment of Fe-contaminated water, zeolite fixed beds operating at closed loop mode seem very promising. Yet, it is essential to involve a preliminary Fe³⁺-precipitation step. The overall performance will be largely enhanced and operational problems due to Fe(OH)₃ residue will be prevented, as well.

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