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Removal of iron and manganese from underground water by use of natural minerals in batch mode treatment

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ABSTRACT

In the present study 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. 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. Pretreatment as well as the use of smaller particle size increased the removal of both metals. The experimental results showed that the maximum permissible concentrations according to the legislation can be achieved.

Keywords: Drinking water; Manganese; Iron; Clinoptilolite; Vermiculite

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 the most widespread use of both metals; 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 $Fe(OH)_3$ and MnO_2, the first has a reddish-brown color and the second has a brownish-black appearance [1].

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Iron and manganese in potable water cause aesthetic and operational problems such as odor and brown color, stain and deposition in the water distribution systems leading to high turbidity. Iron released from iron pipes is the most common reason for colored water formation. Iron release refers to the transport of iron from corrosion scale or the metal surface to the bulk water, either in soluble or particulate form. Colored water is formed when iron enters the bulk water as ferric particles, or as Fe(II) that oxidizes and then forms ferric particles. 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 [1,2]. 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%) [3].

Concerning Mn, concentrations 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 μg/L [4]. 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 [5]. 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 [4].

Physicochemical treatment methods have been used to remove soluble ferrous iron (Fe^{2+}) and dissolved Mn^{2+} for a long time. The biological removal of iron and manganese by Fe–Mn oxidizing bacteria is gradually replacing the conventional physicochemical treatments [1,5]. 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 alumino silicate minerals. They belong to the class of minerals known as "tectosilicates." The structure of zeolites consists of the three-dimensional frameworks of SiO_4 and AlO_4 tetrahedra. The aluminum ion is small enough to occupy the position in the centre of the tetrahedron of four oxygen atoms, while the isomorphous replacement of Si^{4+} by Al^{3+} produces a negative charge in the lattice. The net negative charge is balanced by the exchangeable cations (Na, K, or Ca). These cations are exchangeable with certain cations in solutions, such as lead, cadmium, zinc, and manganese [6]. Vermiculite is typical clay and consists of tetrahedral–octahedral–tetrahedral sheets. The two tetrahedral silicate layers are bonded together by one octahedral magnesium hydroxide-like layer and the structure is often referred to as 2:1 phyllo silicate. When tetravalent silicon is substituted by trivalent aluminum in the tetrahedral layer of the vermi culite sheet, a negative charge is generated on the layer and, thus, hydrated magnesium is adsorbed on the tetrahedral layer between the sheets to maintain electro neutrality. These magnesium ions can be easily cation-exchanged with other cationic species such as copper, which partly contribute to the high cation-exchange capacity of vermiculite [6]. Clinoptilolite (natural zeolite), 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, Na-montmorillonite 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 [5].

There was not found in the literature any studies dealing with the simultaneous removal of iron and manganese from natural water samples, using natural zeolites and clays as a means of environmental pollution control. An exception is the work of García–Mendieta et al. of 2009, who study the case of zeolite clinoptilolite but they use synthetic aqueous solutions [1]. In the present study natural clinoptilolite and vermiculite as well as their Na-forms are used for simultaneous removal of Fe and Mn from natural water samples.

2. Experimental section

Two different minerals were used in order to examine the removal of Fe and Mn from aqueous solutions. Natural zeolite (clinoptilolite) and vermiculite (clay) were supplied from Institute of Geology & Mineral Exploration (IGME). The samples were washed for the removal of surface dust and then ground and sieved to different fractions of which 0.5–0.85 and 0.85–1 mm were used in this study. The chemical composition of the materials was determined by XRF method (Table 1). The samples were washed and air dried at 80°C and then kept in desiccators. Pretreated samples prepared according to standard methods, in columns by use of 25 BV (bed volumes) of NaCl 1.1 M and 15 BV/h flow rate (upflow mode) [7].

Water samples are coming from a natural underground deposit in Attica region. The specific deposit exhibits relatively high Fe and Mn concentrations and in order to be used for households it should be effectively

Table 1
Chemical analysis of clinoptilolite and vermiculite.

Oxide (%w/w)	SiO_2 (%)	Al_2O_3 (%)	TiO_2 (%)	Fe_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	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.

Table 2
Experiments and conditions.

Sample	Particle size (mm)	m/V (g/100 ml)	Duration (h)
Clinoptilolite	0.85–1	1–2–4	2–4–24–48
Clinoltilolite	0.5–0.85	2	24
Na-Clinoptilolite	0.85–1	2	24
Vermiculite	0.85–1	1–2–4	2–4–24–48
Vermiculite	0.5–0.85	2	24
Na-Vermiculite	0.85–1	2	24

treated. The initial Fe and Mn concentration in water samples was 1.5 and 0.5 ppm, respectively and the pH of was 7.1 ± 0.2. The limits set by the European Union by the Directive 98/83/EC are 0.2 and 0.05 ppm, respectively. Thus, the target removal levels are 87% for Fe and 90% for Mn. These removal targets are indicated in all figures by bold lines for easy evaluation of the achieved results.

All experiments executed in batch mode at ambient conditions (25°C). A measured quantity of mineral was added to a vessel containing measured volume of water sample. Different parameters were tested (Table 2) and the solutions were analyzed after a specified time interval. The experiments were repeated for each different period of time in order to avoid sampling during experiment (one experiment for each time interval). Following the separation of the two phases by vacuum filtration, the concentration of metal ions in the solution was measured by atomic absorption spectroscopy (AAS), using a Perkin Elmer Model 2380 spectrophotometer.

3. Results and discussion

3.1. Removal of Fe and Mn by use of vermiculite

Approximately 90% of Fe is removed after 2 h of treatment (Fig. 1). Following 2 h, no significant change in removal is observed (0–5%). At this level of removal, the m/V ratio does not have any significant influence on the removal of Fe. The most significant change is after 48 h of treatment, where the difference between 1 and 4 g/100 ml is about 3.3%.

The removal of Mn is lower by at least 10% in comparison to Fe and reaches its maximum level of 80% only for 4 g/100 ml and 48 h of treatment. However, the final water concentrations are above the maximum allowable level of the EU legislation. Furthermore, is evident that in contrast to Fe case, the Mn removal is far from complete after 2 h of treatment. The higher removal of Fe in comparison to Mn is expected, as Mn is a metal which is not easily removed by ion exchange/adsorption, partly due to its high hydrated ion radius [8]. Finally, the ratio m/V has a significant effect on the removal, in contrast to the case of Fe.

Although the removal of Fe by vermiculite is about 90% for 24 h treatment, the use of smaller particle size, as well as the pretreatment, leads to even higher

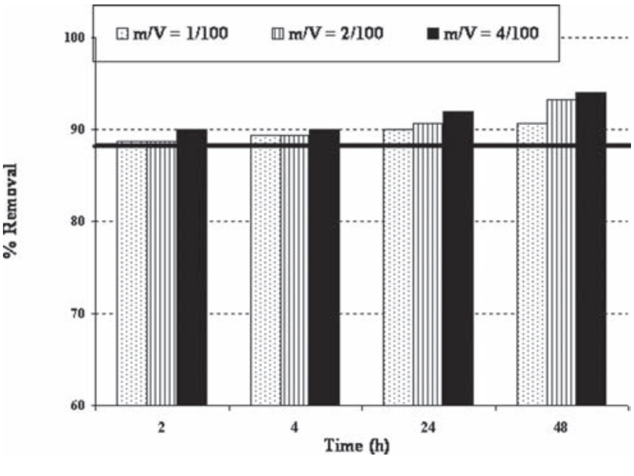

Fig. 1. Fe removal by use of vermiculite (particle size 0.85–1 mm and m/V = 1, 2 and 4 g/100 ml).

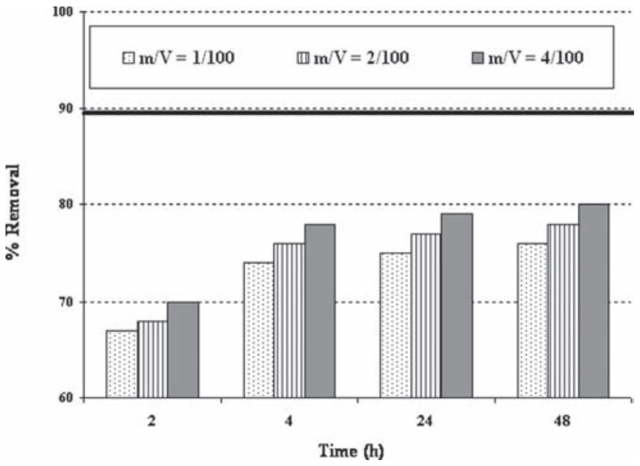

Fig. 2. Mn removal by use of vermiculite (particle size 0.85–1 mm and m/V = 1, 2 and 4 g/100 ml).

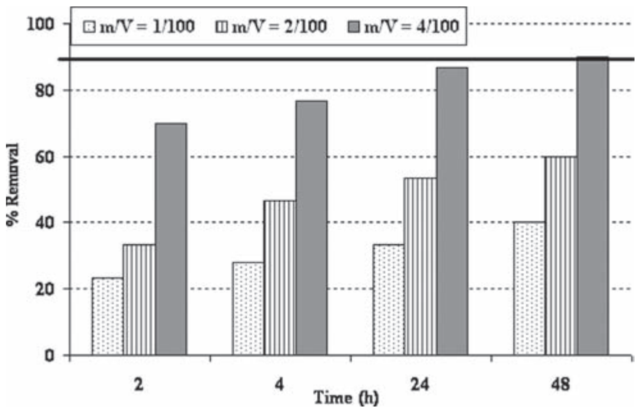

Fig. 4. Fe removal by use of clinoptilolite (particle size 0.85–1 mm and m/V = 1, 2 and 4 g/100 ml).

removals, by almost 3%. On the other hand, the effects on the removal of Mn are much more significant, where an increase of about 23% occurred (Fig. 2).

From Fig. 3 is clear that the decrease of particle size as well as the pretreatment of the natural sample they both lead to Mn removal by more than 98%, leading thus in final concentrations well below the maximum limits set in EU legislation of drinking water.

The positive effect of pretreatment and smaller particle size is well documented for a number of natural minerals [7,9,10].

3.2. Removal of Fe and Mn by use of clinoptilolite

In contrast to vermiculite, the removal of Fe by clinoptilolite is lower and after 2 h of treatment the removal reaches the levels of only 23% at 1 g/100 ml, 33% at 2 g/100 ml and almost 70% for 4 g/100 ml. The removal reaches considerable percentages only after 48 h, where the respective removal rates are 40%, 60% and 90%, respectively (Fig. 4).

Is important to note that only the ratio 4 g/100 ml, after 48 h of treatment reaches the required solution concentration of Fe, according to EU legislation. In the case of Mn, the achieved removal is higher in vermiculite in comparison to clinoptilolite. Again, the final concentration of Mn is higher that the maximum permissible limit for drinking water (Fig. 5).

As is evident, the removal of Mn is higher that Fe, with the exception of the higher m/V ratio. From Figs. 4 and 5 it can been seen that Mn is removed with very high rate the first 2 h and it seems it approaches equilibrium, while Fe removal is slower but evolves continuously, indicating that is far from equilibrium.

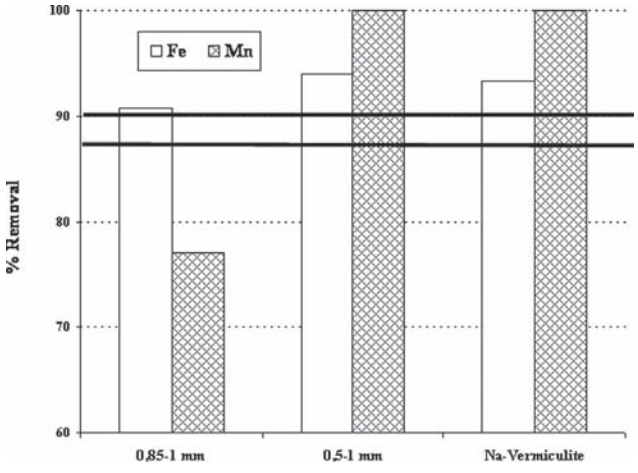

Fig. 3. Effect of particle size and pretreatment on Mn and Fe removal by use of vermiculite (Na – vermiculite particle size of 0.85–1 and m/V = 2 g/100 ml).

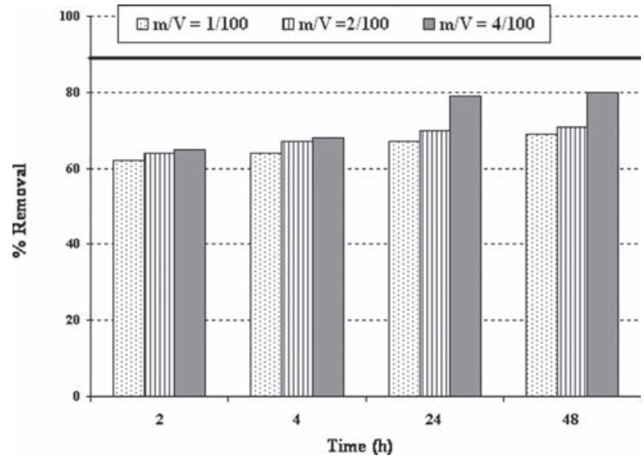

Fig. 5. Mn removal by use of clinoptilolite (particle size 0.85–1 mm and m/V = 1, 2 and 4 g/100 ml).

This indicates that Fe could under certain conditions (time, m/V rate etc) reach higher removal levels than Mn. Mixed results are observed in the related literature for clinoptilolite: while in single (Fe or Mn) system the sorption of iron is higher than manganese, in binary system (Fe/Mn) the opposite behavior was observed at pH 6, due to competition between them [1]. It should be noted that in the later study, the concentration of Fe was equal to Mn (10 mg/l) and considerably higher than the one used in the present study. Furthermore, another characteristic example is a study on the simultaneous removal of Fe (1–1.5 ppm), Mn (1–1.5 ppm) and NH_4^+ (1–1.5 ppm) from water by use of impregnated activated carbon [11]. In the batch experiments the series was Fe > Mn > NH_4^+, while mixed results were observed in the fixed bed experiments with Mn to be preferred against Fe. The authors concluded that the adsorption of manganese, iron and ammonia nitrogen on impregnated activated carbon is a complex process and it depends on the initial concentrations of these compounds as well as on the pH and filtration speed.

From the experimental results is clear that Fe as well as Mn removal is higher in vermiculite than in zeolite (Figs. 6 and 7). The same conclusion was drawn for Cu^{2+} removal elsewhere as well [6]. A possible explanation is that the movement of ions in the rigid zeolite structure is harder than in the layered and expanded (due to hydration) phylosilicate structure of vermiculite.

The increase in removal of Fe by pretreated clinoptilolite is low for the about 35% for 24 h treatment, while use of smaller particle size lead to an increase of the removal by only 8%. The pattern is opposite for Mn, as the higher increase of about 30% is found for the smaller particle size, while the removal increase is lower for the pretreated sample, about 12% (Fig. 8).

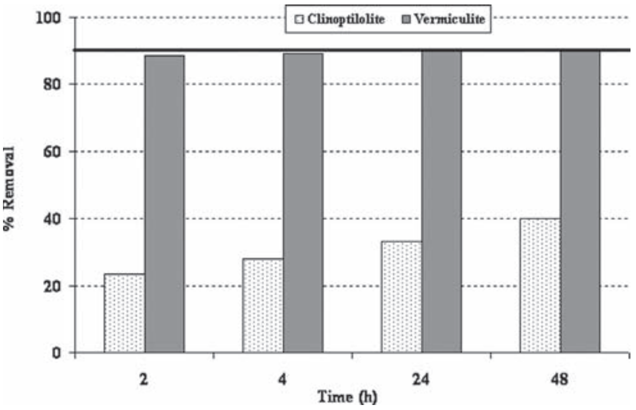

Fig. 6. Samples comparison for Fe removal (particle size 0.85–1 mm and m/V = 1/100).

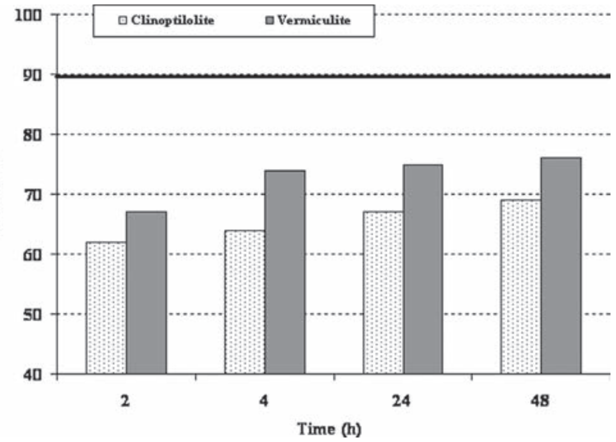

Fig. 7. Samples comparison for Mn Removal (particle size 0.85–1 mm and m/V = 1/100).

From Fig. 8 is clear that the decrease of particle size leads to increased Mn removal to reach almost 100%, leading thus in final concentrations well below the maximum limits set in EU legislation of drinking water, while fails to meet the requirements for Fe. The opposite holds for the pretreated sample, which leads to Fe removal by more than 87%, leading thus in final concentrations below the maximum limits set in EU legislation of drinking water, while fails to meet the requirement for Mn.

The improvement in the removal efficiency is attri buted to the increase of easy removable Na+ ions in the zeolite structure, while smaller particle size leads to higher exchange rates as the distances within the particle are decreased [7,9,10]. An exception on this basic rule is found in the case of pore clogging by surface dust or in cases where the mechanical treatment causes structural damages to smaller particles. In these cases the result could be opposite, i.e. lower rates in the smaller particles [10]. Here it should be noted that in the case of adsorption, which frequently accompanies ion exchange processes, the decrease of particle size could

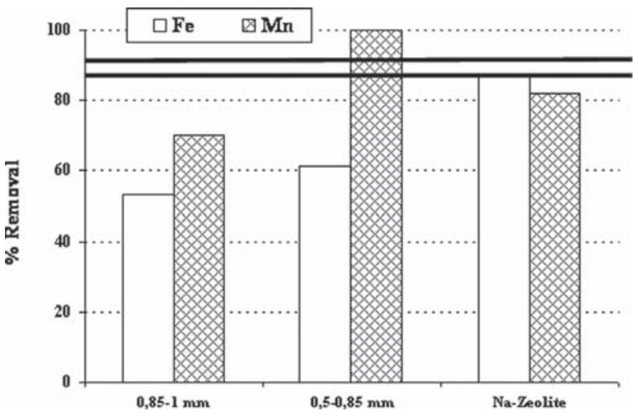

Fig. 8. Effect of particle size and pretreatment on the removal of Fe and Mn by clinoptilolite (Na – clinoptilolite particle size of 0.85–1 and m/V = 2 g/100 ml).

be linked to the increase of surface area but only in the cases where a considerable part of the total surface area is external; in highly porous solids the vast majority of this area is internal, characteristic and constant for each material, and thus the decrease of particle size has little effect on the increase of surface area.

In general, Fe removal is higher than Mn for vermiculite and the opposite holds for clinoptilolite. Overall, Fe and Mn removal levels are between 88–94% and 65–100% for vermiculite and 22–90% and 61–100% for clinoptilolite, respectively. These removal levels are comparable to the ones obtained by other techniques for simultaneous iron and manganese removal from water samples. For instance, in a treatment of iron and manganese in simulated groundwater via ozone technology, at ozone dose of 1.25 ppm and initial iron concentration of 2.6 ppm and manganese concentration of 1 ppm more than 90% of iron was removed, while just only 15% of manganese was eliminated at the same conditions. Increasing the ozone concentration to about 3 ppm improved removal of iron to more than 96% while about 83% of manganese was removed [12]. In another case, the biological removal or Fe (II) and Mn (II) from drilled well water in a biological treatment continuous flow unit in China, resulted in 99% removal of Fe and 35–75% for Mn, under initial concentration of 3–8 ppm for Fe and 2 ppm for Mn [13].

In general, in conventional ground water treatment plants, Fe is more easily removed than Mn . It is not possible to directly compare the results and the achieved removal levels as the concentrations are different as well as the techniques used. As an indicative case, a study on eight ground water treatment plants for the production of drinking water in Saudi Arabia, observed that, with the exception of one plant where the Fe removal was very low (8%), the removal levels of Fe were within the narrow range of 89 ± 6%, while in the case on Mn the removal level for six plants was found in a narrow range of 93 ± 3% and for two of them was 29 and 32% [14]. The influent Fe and Mn concentrations were in the range of 23–1864 μg/l and 10–299 μg/l, respectively. In these plants, the treatment processes include cooling, chemical softening, filtration, reverse osmosis and post treatment (pH adjustment and chlorination).

4. Conclusions

In the present study natural clinoptilolite and vermiculite as well as their Na-forms are used for simultaneous removal of Fe and Mn from natural water samples. 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. Pretreatment as well as the use of smaller particle size increased the removal of both metals. Taking into account all results, it could be stated that under the experimental conditions used, in order to achieve the requirements of the EU legislation for both Fe and Mn, 0.85–1 mm natural vermiculite or Na-vermiculite should be used while acceptable results could be achieved by using Na-clinoptilolite of smaller particle size (e.g. 0.5–0.85 mm).

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