NEW MATERIALS BASED ON NATURAL ZEOLITES USED IN THE FILTRATION OF UNDERGROUND WATER

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INTRODUCTION

In Romania most of the undergroud waters contain about 3 mg Fe/dm^3 and 1 mg Mn^{2+}/dm^3. Their utilisation for preparing drinking waters presumes the elimination of iron and manganese to levels below 0.05 mg/dm^3.

The experimental research carried out with waters with a variable content of calcium, magnesium, iron and manganese have showed that the natural zeolites chemically activated either as the acid form (Z-H) or the sodium one (Z-Na) achieve in a fair extent the elimination of the metal ions from water by an ion-exchange process[1-2].

For the undergroud waters the most important problem is not the elimination of the hardness, but that of the retention of the iron and manganese ions.

From the literature there are partially known the results of the experimental work of Tarasevich et al.[3-4], Polyak et al.[5], which used manganesed clinoptilolite, in order to retain iron and manganese from waters.

Consequently, the experimental research of the present paper aimed at the utilisation of Romanian natural zeolite as support for a manganese combination, as well as at the efficiency of the obtained material in the processes of elimination of iron and manganese.

EXPERIMENTAL

1. The mineralogical and chemical characterization of the natural zeolite.

This research used natural zeolite ore originated from Bârsana (Maramureş county).

Its mineralogical composition has been determined by X-ray diffraction using a Dron 3 instrument, with the radiation Cu K_α.

2. Obtaining and characterization of the manganesed zeolite.

The natural zeolite, with the grain size in the range 315-500 μm, has been subjected in the first stage to a chemical activation in order to increase the ion exchange capacity. The zeolite has been subsequently treated with a 2M solution of $MnCl_2$, at a ratio solid:liquid of 1:4, for 3 hours. After decantation and filtration, the material has been treated with a $KMnO_4$ solution of 5g/L concentration for 3 hours. The obtained product was washed in order to remove the excess of $KMnO_4$ and dried at 105°C for 6 hours.

The samples of manganese zeolite have been subjected to chemical analysis determining the content of manganese before and after the oxidation with $KMnO_4$.

3. Research concerning the utilization of the manganesed zeolite in the process of elimination of iron and manganese from waters.

These studies were carried out in dynamic regime, in closed laboratory columns of 10 mm diameter and 200 mm height, each equipped with 4 grams of zeolite material. There have been used manganesed zeolite (Z-MnO_2) and clinoptilolitic zeolite activated as the sodium state (Z-Na), of 315-500 µm grain size.

For the determinations have been used synthetic waters with different contents of Fe^{2+} and Mn^{2+}. It has been used a specific loading of $20 m^3/m^2h$, maintaining during the operating cycle a constant level above the zeolite layer of 30 mm. Effluent samples of 0.4 L were collected and analyzed. The concentration of the iron and manganese ions has been determined by atomic absorption spectrophotometry.

RESULTS AND DISCUSSION

1. Mineralogical and chemical characterization of the natural zeolite.

There are evidenced some diffraction signals, at angles, respectively interplane distances that are characteristic for clinoptilolite, according to data from the ASTM cards 25 – 13,49. Other minerals are also evidenced, such as albite and α-quartz[6].

By measuring the intensity of the spectral lines from the diffraction spectrum and comparing it with those of pure clinoptilolite, it has been determined an average clinoptilolite content in the zeolite ore of about 68%.

The average chemical composition of the zeolite ore (% weight) was : SiO_2 62.11, Al_2O_3 13.2,Fe_2O_3 2.20, CaO 3.56, MgO 1.11, K_2O 2.55, Na_2O 1.28, TiO_2 0.30, P_2O_5 0.05, MnO 0.06, calcination losses 8.66. From these data have been determined for the studied zeolite ore a SiO_2/Al_2O_3 ratio of 5.12, respectively a Si/Al ratio of 4.49, values that are characteristic for clinoptilolite.

2. Characterization of the manganesed zeolite.

The process of manganese doping may be expressed by the chemical equation :

$(7 - 2x)Mn^{2+} + (2x - 2)MnO_4^- + (8 - 3x)H_2O \longrightarrow 5MnO_x + (16 - 6x)H^+$ (1)

where x is the average oxidation index of manganese. This is defined according to the relation :

$$\frac{7-2x}{5} = \frac{Mn_i^{2+} - Mn_f^{2+}}{Mn_t - Mn_f^{2+}} \qquad (1)$$

where : Mn_i^{2+} - the initial content of Mn^{2+} in the zeolite after treatment with the 2M solution of $MnCl_2$ (7.50 mg/g) ;

Mn_f^{2+} - the final content of Mn^{2+} in zeolite found after the oxidation with $KMnO_4$ (2.10 mg/g) ;

Mn_t - the overall content of Mn^{2+} and Mn^{4+} in the zeolite (9.8 mg/g).

It follows that it has been obtained manganese zeolite of about 10 mg Mn/g and an average oxidation index of 1.75.

3. Research concerning the utilization of the manganesed zeolite in the process of elimination of iron and manganese from waters.

The results obtained concerning the retention of iron on sodium state zeolite (Z-Na) , at concentrations of 1, 3, and 5 mg/dm^3, respectively of manganese zeolite, are presented in Figure 1 and Figure 2.

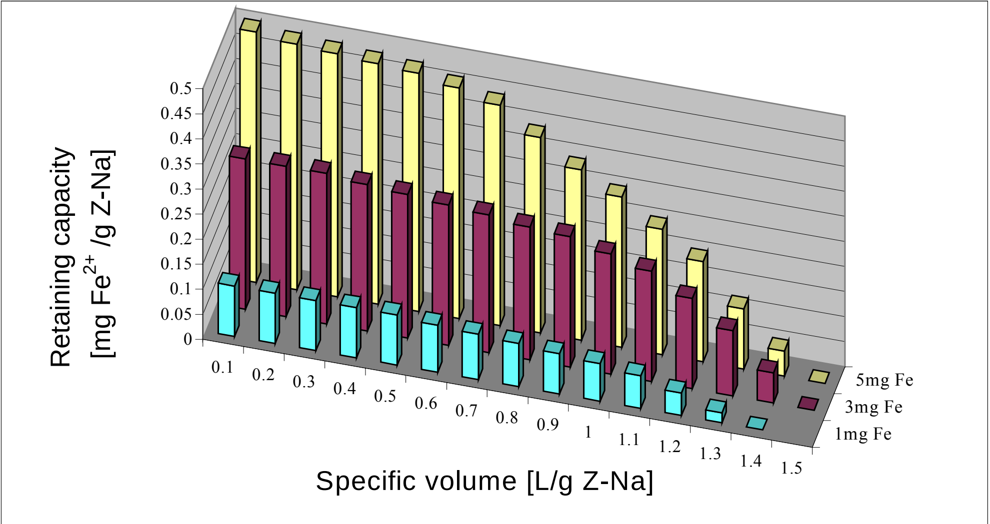

Figure 1. Iron retention on Z-Na versus the specific volume of influent.

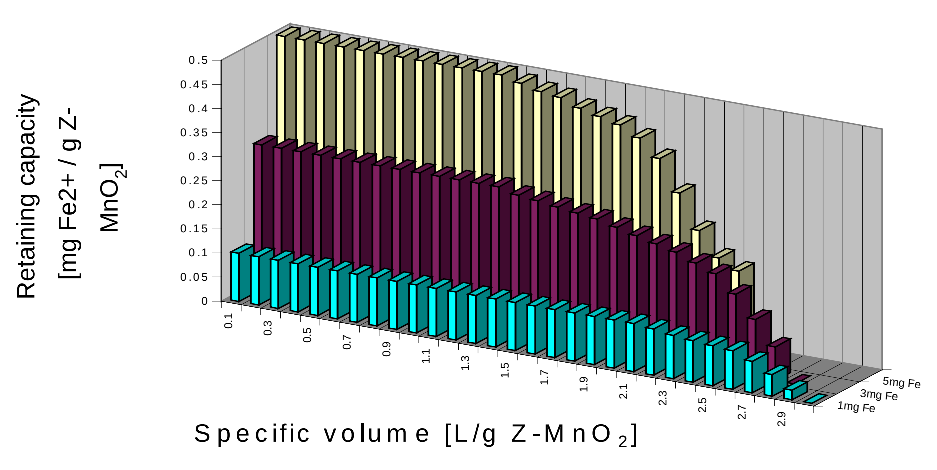

Figure 2. Iron retention on Z-MnO$_2$ versus the specific volume of influent.

One may observe from both the above figures a diminishing in time of the retaining capacity, which can be explained by the exhaustion of the ion-exchange capacity for Z-Na, respectively the decrease of the oxidation capacity of the MnO$_2$ layer and the accumulation of insoluble iron oxides clogging the zeolite material.

The total amount of iron retained on the two types of zeolites is presented in Table 1.

Table 1. Retaining capacity for Fe^{2+} on Z-Na and Z-MnO_2 at different iron concentrations in the influent.

Crt. No.	Fe^{2+} concentration (mg/L)	Retaining capacity (mg/g zeolite)	
		Z-Na	Z-MnO_2
1	1	1.06	2.66
2	3	3.90	7.05
3	5	4.98	10.90

It may be observed the doubling of the iron amount retained on the manganesed zeolite.

The results obtained for the elimination of Mn^{2+} from waters with different initial concentrations are presented in Figure 3.

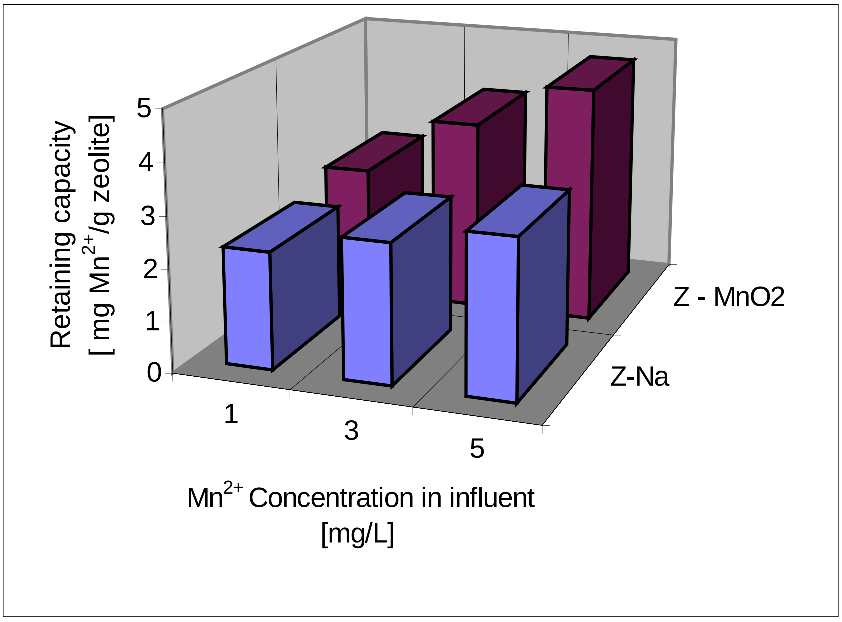

Figure 3.Retaining capacity for Mn^{2+} on Z-Na and Z-MnO_2 at different manganese concentrations in the influent.

Mn^{2+} is retained on Z-Na, like in the case of iron, by ion exchange. On Z-MnO_2 it takes place a complex process of ion exchange and oxidation of Mn^{2+} by MnO_2, with the formation of insoluble oxides. The total amount of Mn^{2+} retained on the two types of zeolites is presented in Table 2.

Table 2. Retaining capacity for Mn^{2+} on Z-Na and Z-MnO_2 at different manganese concentrations in the influent.

Crt. No.	Mn^{2+} concentration (mg/L)	Retaining capacity (mg/g zeolite)	
		Z-Na	Z-MnO_2
1	1	2.30	2.61
2	3	2.71	3.78
3	5	3.05	4.66

CONCLUSIONS

The X-ray studies, as well as those concerning the chemical composition, evidenced that the most important component of the Bârsana zeolite ore is clinoptilolite (about 68%).

From this raw-material there has been obtained a manganesed zeolite with a content of 10 mg/g and an average oxidation index of 1.75.

For the synthetic waters prepared it has been established that the manganesed zeolite exhibited a higher retaining capacity than that of the Z-Na state, for both iron and manganese. The process of retaining iron and manganese is a complex one, consisting of ion-exchange, oxidation and filtration of the two cations.

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