1

Iron and Manganese Removal Effects Using Zeolites

Anna Maria Anielak
Technical University in Koszalin
Mirosława Arendacz
Technical University in Gdańsk

1. Introduction

Ground water has been a perfect source of drinking water from the earliest ages. Its basic asset is the highest quality, however iron and manganese elimination has always been a problem of the highest priority.

Natural source of these elements in the ground water are elution processes washing them out from rocks and ground. One of the man – induced source of iron in that type of water is a metallurgy industry, whilst manganese comes from wastewater from the main industry, steelworks, ceramics and chemical fertilizers. Groundwater that has anaerobic conditions contains dissolved iron compounds as ions {II} of concentrations from traces to few mg/dm^3.

Manganese compounds usually go along with iron compounds, which in anaerobic conditions appear as dissolved compounds as well {II}. Their values are much lower and usually do not exceed 10 mg/dm^3 [1,2].

Removal of iron and manganese compounds is particularly important for the septic reasons. They cause unpleasant taste of water, in aerobic conditions they form sediments: dark brown (manganese) or brown-red (iron). Those compounds precipitate also in water-pipe network. Their removal is being done by oxidation to ions 3^+, which are water – insoluble, whereas manganese compounds are oxidated to water – insoluble 4^+ ions. Oxidation is run on suitable beds, where filtration and adsorption take place simultaneously. The most often used bed are sand beds, which are often enriched in other materials. The works over searching for more effective materials as bed media for iron and manganese removal are still in progress. One of such materials are zeolites, which are the object of this paper [1.3].

Current regulations over permissible iron concentration in drinking water in Poland are more restrictive than from other European Union countries (3 mg/dm^3). That is due to oversize water-pipe network which was designed for to high unitary water intake per inhabitant. That situation causes slower water flow in water-pipe network, which may result in iron bacteria growth. According to Health Minister Regulation from 19th of November 2002 about demands for drinking water quality, permissible iron concentration is 0.2 mg/dm^3 and manganese concentration is 0.05 mg/dm$^{3.}$

The aim of this paper was analysis of usefulness of natural and modified zeolites as adsorption material for iron and manganese removal purposes.

2. Methods

Analyses were carried out at The Technical University of Koszalin, in the Department of Water and Sewage Technology[10].

An analyzed material was water solution prepared on distilled water, in which different chemical composition was formed by adding salts: $FeSO_4 \cdot 7H_2O$ and $MnSO_4 \cdot H_2O$. Analyzed adsorbents were: natural zeolite, containing 55% of klinoptylolite, 26% of volcanic ash, 6% of quartz and 13% of montmoryllonite. Granulation was from 0,5 to 1,00 mm.

Another analyzed adsorbent was modified zeolite, which composition was based on natural zeolite modified for higher selectiveness for removed ions.

The solution of known Fe or Mn concentration was poured to the vessel of 100 dm^3 then the measurement of pH and redox as well as the content of Mn and Fe was carried out. The next step was adding 10 mg/dm^3 of either natural or modified zeolite. After that the samples were shaken for 2 hours with the speed of 200 spin/minute. After 5 minutes sedimentations the water over the sediment was poured out and examined.

2.2 Range of experiment

2.2.1. Preliminary experiment

As a preliminary experiment, measurement according to Yates method, type “2^{3}“ were carried. Three factors, which values were on two levels, were measured. Factor A was pH of 4.5 and 9.5; factor B was manganese concentration of 0 and 1 mg/dm^3 and factor C - total iron concentration of 0 and 1 mg/dm^3. Matrix of experiment planning is shown on the table 1.

Consequential factors were: manganese concentration, total iron concentration, pH in solution and redox potential.

Results obtained as well as statistical analysis were a basis to carry out experiment in details in a wider range of independent parameters changes.

Table 1. Matrix type 2^3 for experiment planning
Tabela 1. Matryca planowania doświadczeń typu 2^3

Nr	Combinations	Analyzed factors			Factors values		
		A	B	C	A	B	C
1.	I	-	-	-	without correction	0	0
2.	a	+	-	-	9.5	0	0
3.	b		+	-	without correction	1	0
4.	ab	+	+	-	9.5	1	0
5.	c	-	-	+	without correction	0	1
6.	ac	-	-	+	9.5	0	1
7.	bc	-	+	+	without correction	1	1
8.	abc	+	+	+	9.5	1	1

A – pH
B – Mn concentration [mg/dm^3]
C – Fe_{total} concentration [mg/dm^3]

2.2.2. Main experiment

On the basis of statistical characteristics the most important effects for combinations of A, B and C factors were found. The next step was an experiment in a wider range of examined factors: manganese concentration from 0.00 to 3.00 mg/dm^3; total iron concentration from 0.00 to 3.00 mg/dm^3 and pH in solution from about 2 to 11.

3. Results

3.1. Preliminary experiment

In the adsorption process on a modified zeolite fallowing results were obtained: for a dependence Fe = f (Mn, Fe, pH) the main effect was iron concentration; for a dependence Mn = f (Mn, Fe, pH) the main effect was manganese concentration and finally for a dependence pH = f (Mn, Fe, pH) the main effect was pH in solution. All main effects were positive which indicate proportional dependence.

In the adsorption process on a natural zeolite the main effects were the same for manganese and iron dependence – both effects were positive whereas for pH dependence an obtained effect was negative which means an inversely proportional dependence.

Figure 1 and 2 show percentage of ions removal on both analyzed zeolites under different conditions: solutions with or without pH correction (to 9.5 value); in the presence of another ion (concentration about 1 mg/dm^3) or not.

In the case of manganese ions solutions pH has a significant importance on the effectiveness of removal process. In the solutions without pH correction (1 and 2 on the figure 1) better results were reached using modified zeolite. The average percentage of manganese ions removal was 85.8% for solutions without another ion presence and 90.2% for solutions containing iron ions. The average percentage of manganese removal using natural zeolite in the solutions without pH correction, with and without the presence of iron was similar, as fallow: 65.2% and 67.4%.

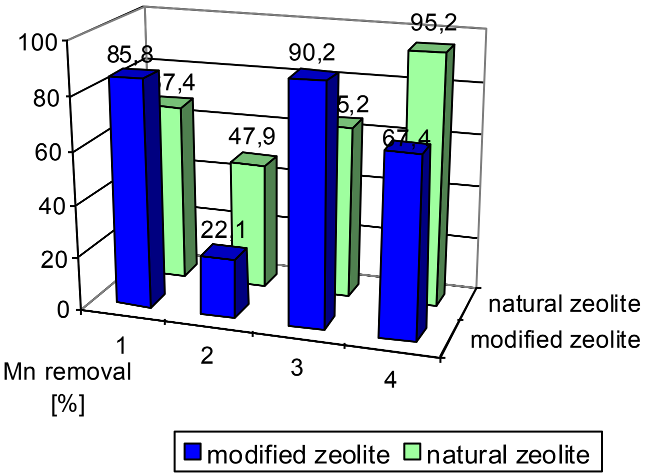

Fig. 1. Manganese removal on natural and modified zeolites in percentages

1. solutions without pH correction, no accompanying ions
2. solutions with pH correction, no accompanying ions
3. solutions without pH correction, accompanying Mn ions mg/dm^3
4. solutions with pH correction, accompanying Mn ions mg/dm^3

Rys. 1. Usuwanie manganu na zeolitach naturalnych i modyfikowanych w procentach

1. roztwory bez korekty pH, bez dodatkowych jonów
2. roztwory z korektą pH, bez dodatkowych jonów
3. roztwory bez korekty pH, z dodatkiem jonów Mn mg/dm^3
4. roztwory z korektą pH, z dodatkiem jonów Mn mg/dm^3

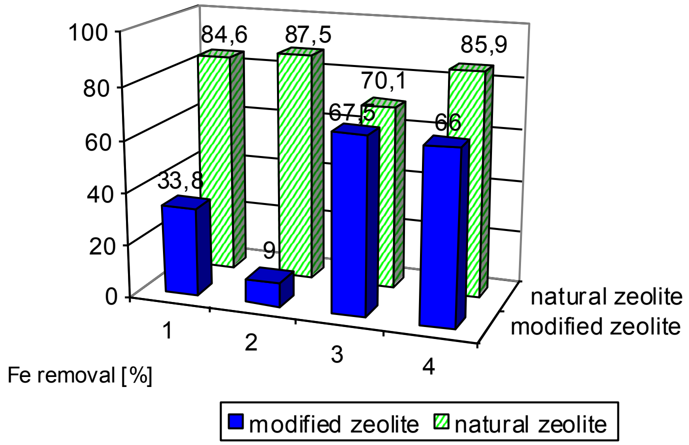

Fig. 2. Iron removal on natural and modified zolites in percentages
1. solutions without pH correction, no accompanying ions
2. solutions with pH correction, no accompanying ions
3. solutions without pH correction, accompanying Mn ions mg/dm^3
4. solutions with pH correction, accompanying Mn ions mg/dm^3

Rys. 2. Usuwanie żelaza na zeolitach naturalnych i modyfikowanych w procentach
1. roztwory bez korekty pH, bez dodatkowych jonów
2. roztwory z korektą pH, bez dodatkowych jonów
3. roztwory bez korekty pH, z dodatkiem jonów Mn mg/dm^3
4. roztwory z korektą pH, z dodatkiem jonów Mn mg/dm^3

In the case of manganese removal in solutions with pH correction to the value 9.5, better results were obtained on a natural zeolite. The average adsorption percentage of manganese ions on a natural zeolite was 47.9 for solutions without accompanying ions and 95.2 for solutions in the irons presence.

Comparing the results of an experiment for the iron adsorption on a modified and natural zeolite, higher removal effectiveness was observed on a natural zeolite for all analyzed cases. Distinct differences in iron removal using both zeolites were obtained for solutions without manganese. The least effective combination for iron removal was the one with modified zeolite not containing manganese ions; for solutions without pH correction the percentage of irons removal was 33.8 whereas for solutions with pH correction that was only 9.0%.

3.2. Main experiment

Fig. 3 and 4 show the comparison of manganese and iron ions adsorption on investigated materials: modified and natural zeolite in a wider range of initial concentration of analyzed ions (from 0.00 to 3.00 mg/dm^3).

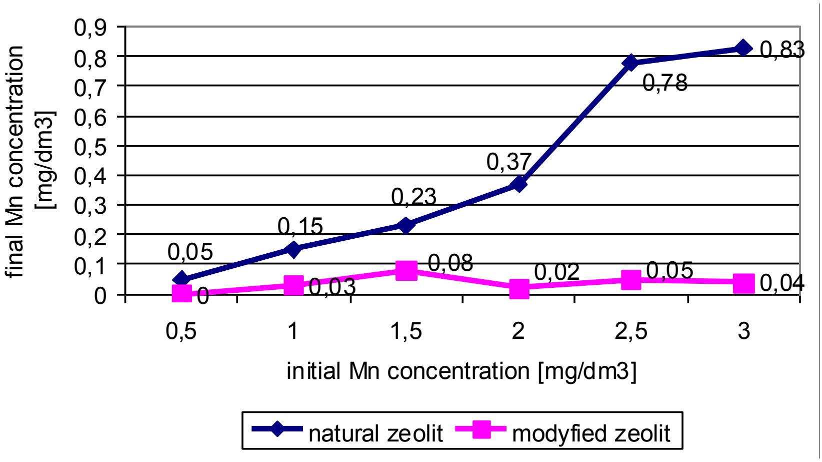

Fig. 3. Results of manganese adsorption on natural and modified zeolites
Rys. 3. Wyniki adsorpcji manganu na zeolitach naturalnych i modyfikowanych

Analyses of effectiveness of manganese ions adsorption on both investigated zeolites with different initial concentration of these ions in solutions (in the range from 0.00 to 3.00 mg/dm^3) confirm significantly better results of manganese removal using a modified zeolite. The difference in effectivness is particularly noticeable in the case of higher initial manganese concentration in solution, for instance: for initial Mn concentration of 3.00 mg/dm^3 the removal percentage of this ion using a natural zeolite was 72.3 whereas using modified zeolite 98.7%. However, applying modified zeolite caused the rise of pH values in solution to the range from 9.11 to 9.52. Natural zeolite implementation resulted in a slight decline of pH value in solution.

Comparing adsorption process of iron ions on the natural and modified zeolite (Fig. 4) it can be noticed that there were significant differences in the results. Much better results were obtained using a natural zeolite. Higher effectiveness of an adsorption process was gained for the lowest initial concentration of iron ions in solution, for example for the initial Fe concentration of 0.5 mg/dm^3 the percentage of Fe removal was 92. Along with the growth of initial concentration of iron, the effectiveness of its removal decreases.

Assessing a usefulness of a modified zeolite as an adsorption material for iron removal, it can be said that the adsorption was very low and the percentage of iron removal ranged from 14.7 to 30. Alike to the manganese adsorption on both analyzed zeolites, they caused an increase of pH in the solution. Using natural zeolite the pH increase was slight whereas using modified zeolite solution pH reached the values from 9.14 to 9.36.

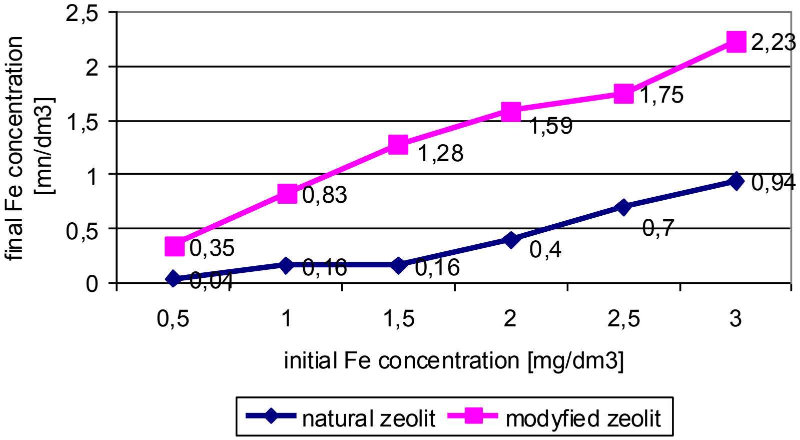

Fig. 4. Results of iron adsorption on natural and modified zeolites
Rys. 4. Wyniki adsorpcji żelaza na zeolitach naturalnych i modyfikowanych

An issue of iron and manganese removal has become of a great importance again, after introducing new restrict requirements about their content in the drinking water according to the Health Minister Regulation from 19th of November 2002 (permissible iron concentration dropped from 0.5 to 0.2 mg/dm^3 and for manganese from 0.1 to 0.05 mg/dm^3). The introduction of such regulations significantly more restrictive than in other Europeans countries resulted in oversized water-pipe network, what caused slower wastewater flow increasing the risk of iron and manganese bacteria growth. The presence of such bacteria has a widely disadvantageous effect on physical and chemical properties such as: higher watercolor, turbidity and characteristic smell and taste of water. Moreover, the bacteria growth in water eases conditions for bacteria illnesses and causes corrosions of network [4]. Such situation forced the necessity of modernization of many water treatment plants as well as the necessity of searching for new, more effective technologies.

The most popular way of iron and manganese compounds removal is filtration and adsorption on sand filters. One of the most effective ways of manganese removal from water is applying filters with bacteria settled on the material. The experiment of manganese removal on the anthracite – sand filter naturally covered with manganese dioxide have shown an effective manganese removal to the values < 0.1 mg/dm^3 [5]. Chemical methods of manganese removal have been reasonable effective, however not in each case effective enough to fulfill the new requirements. The researches over the effectiveness of applying different chemical methods have shown that the best results were obtained using $KMnO_4$ as an oxidant as well as using two-step filtration on sand mixed with granulated activated carbon [6]. Another experiments applied on a practical scale showed very good results, especially for manganese removal, of filtration media activated with MnO_2 (mass G-1) [12]. Other works comparing three media: mature quartz sand, Metallex (composed mainly of MnO_2) an manganese sand (mass G-1) for manganese removal in 2-stage filtration from water containing high ammount of ammonia nitrogen, showed similar effects after the media had rippened. However, an important fact was that the mass G-1 reached satisfactory extend of manganese removal in the shortes time from all analysed media, whereas the longest times was for sand media [13].

On account of insufficient effectiveness of traditional methods, the works over new materials that can be used to iron and manganese removal to the permissible value, have started. The searches over applying chalcedonies sand as a filtration material to iron and manganese removal have shown that its high effectiveness especially for iron removal, which often reached almost 100 % [7]. All properties of that material have not been found so far. The most intensive works are being carried out over such materials as activated carbon and zeolites. The searches over using modified zeolite Crystal- Right showed high efficacy for groundwater conditioning, satisfactory results were obtained in the case of iron compounds and ammonia nitrogen elimination, worse results were obtained for manganese removal. A high rise of water hardness was observed; therefore it is suggested to be used mainly for industry rather than for drinking water purposes [8]. Similar works with natural materials: klinoptylolite and manganese zeolite (MZ-10) showed a high capacity for iron removal for both analysed media and far higher effectiveness of MZ-10 for manganese removal [9] Comparative works over manganese removal on two investigated media: quartz –sand and zeolite modified with manganese, showed that media with zeolite was removing analyzed ions with a high effectiveness over the whole investigated period (200 days). Sand media did not reach sufficient level of manganese ions removal. In the case of iron compounds removal both media showed sufficient removal effectiveness [11].

Considering zeolite usefulness based on date from the literature and results obtained in this experiment it can be said that the effectiveness of zeolites as media for iron and manganese compounds removal was high, especially when both ions were present in the solution. The important thing is a proper material selection for different iron and manganese content. It would be advisable to carry out the works over material consisting of a mixture of sand and zeolite that could point out the best proportion for an effective groundwater conditioning.

4. Conclusions

- Water filtration using sand media is still the most popular method for iron and manganese compound removal. Depending on chemical composition of water individual processes go along with filtration. One of the alternative methods is using new media, for example: activated carbon or zeolites.

- The most important dependences obtained during adsorption process on modified zeolite was an initial concentration of iron and manganese ions resulting in its final concentration as well as the pH values resulting in the solution after the adsorption process. The greater influence on iron and manganese adsorption on natural zeolite had their initial concentration in solution.
- An implementation of modified zeolite enabled gaining very high extent of manganese removal (the average removal percentage was over 94), regardless of its initial concentration in solution. However, this method caused an increase of pH in solution to the value > 9.0.
- A natural zeolite showed better results for iron compounds adsorption, however the percentage of iron removal declined along with the rise of its initial concentration in solution. Natural zeolite did not cause an increase in pH values in solution, moreover a slight fall was observed.

Literature

1. **Kowal A., Świderska-Bróż M.:** *Oczyszczanie wody.* Wydawnictwo Naukowe PWN, Warszawa 1996.
2. **Magrel L.:** *Uzdatnianie wód i oczyszczanie ścieków. Urządzenia, procesy, metody*. Wydawnictwo Ekonomia i Środowisko. Białystok 2000.
3. **Anielak A.M.:** *Chemiczne i fizykochemiczne oczyszczanie ścieków*. Wydawnictwo Naukowe PWN, Warszawa 2000.
4. **Olańczuk-Neyman K.:** *Mikroorganizmy w kształtowaniu jakości i uzdatnianiu wód podziemnych.* Politechnika Gdańska. Gdańsk 2001.
5. **Szmechting-Gauden E., Dajewska B., Buczkowski R.:** *Biologiczne usuwanie mnganu z wód podziemnych ujęcia w Jedwabnie.* Ekologia i Technika 2001.
6. **Szmechting-Gauden E., Dajewska B., Buczkowski R.:** *Chemiczne metody usuwania manganu z wody podziemnej.* Ekologia i Technika 2001.
7. **Jeż-Walkowiak, Sozański M., Weber Ł.:** *Wykorzystanie piasku chalcedonitowego do uzdatniania wody podziemnej z ujęcia wrzesińskiego.* Gaz, Woda i Technika Sanitarna 7-8/2005.
8. **Kaleta J.:** *Oczyszczanie wód podziemnych z zastosowaniem modyfikowanego zeolitu naturalnego.* Gaz, Woda i Technika Sanitarna 4/2006.
9. **Kaleta J.:** *Zastosowanie modyfikowanego klinoptylolitu do oczyszczania wód podziemnych.* XIX Krajowa, VII Międzynarodowa Konferencja Naukowo-Techniczna „Zaopatrzenie w Wodę, Jakość i Ochrona Wód" Zakopane, 18-21.06.2006.
10. **Arendacz M.:** „*Oczyszczanie wody podziemnej na zeolitach* praca po kierunkiem prof. dr hab. inż. A. M. Anielak, Wydział Budownictwa i Inżynierii Środowiska Politechniki Koszalińskiej, Koszalin.
11. **Anielak A.M., Wojnicz M.:** *Wpływa składu wody na proces usuwania manganu na złożu zeolitowym i piaskowym.* Gaz, Woda i Technika Sanitarna 6/2004.
12. **Łasińska E., Marjanowski J.:** *Usuwanie związków żelaza i manganu z wód podziemnych.* Instal, 2004/5.

13. **Bray R., Olańczuk-Neyman K.:** *Oczyszczanie wody podziemnej o podwyższonym stężeniu manganu azotu amonowego z wykorzystaniem aktywnych złóż filtracyjnych.* V Międzynarodowa Konferencja Naukowo-Techniczna „Zaopatrzenie w Wodę, Jakość Wód”, Poznań-Gdańsk 26-28.06.2002.