

# MODIFIED ZEOLITES IN GROUND WATER TREATMENT

## MODIFIKOVANÉ ZEOLITY V ÚPRAVE PODZEMNÝCH VÔD

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### Abstract

There are presented results of technological experiments carried out in Water Treatment Plant Kúty. The goal of this study was to compare modified zeolite known as clinoptilolite (rich deposits of clinoptilolite were found in the region of East Slovakia in the 1980s) with the imported modified zeolite from deposit situated in Hungary. Klinopur-Mn and Klinomangan were used for removal of iron and manganese from ground water to meet the requirements of the Regulation of the Government of the Slovak Republic No. 496/2010 on Drinking Water. The materials observed exhibit different efficiencies of manganese removal from water, since the quality of the treated water play a major role (oxygen content and pH value). In the case of the removal of the iron from the water, the quality of the raw water is not a limiting factor; both materials removed Fe from the water to below the limit value (0.20 mg.l<sup>-1</sup>).

### Abstrakt

Článok prezentuje výsledky technologických skúšok vykonaných v UV Kúty. Cieľom tejto práce bolo porovnať modifikované (povrchovo upravené) zeolity známe ako klinoptilolit (veľké nálezisko klinoptilolitu bolo objavené na Východnom Slovensku v 1980-tych rokoch) s dovážaným povrchovo upraveným zeolitom z náleziska v Maďarsku. Klinopur-Mn a Klinomangan boli použité pre odstraňovanie železa a mangánu z podzemnej vody na dosiahnutie limitných hodnôt pre pitnú vodu podľa Nariadenia vlády č. 496/2010 Z.z. Sledované materiály vykazovali rôznu účinnosť odstraňovania mangánu z vody, na účinnosť odstraňovania mala významný vplyv kvalita upravovanej vody (obsah kyslíka, hodnota pH). V prípade odstraňovania železa z vody kvalita surovej vody nie je limitujúcim faktorom, obidva materiály odstraňovali železo z vody pod limitnú hodnotu (0,2 mg.l<sup>-1</sup>).

**Keywords:** treatment of groundwater, removal of iron and manganese, filtration, modified clinoptilolite, Klinopur- Mn, Klinomangan, drinking water

## 1 INTRODUCTION

In Slovakia there are a number of groundwater resources. Larger resources are unevenly distributed throughout the territory; therefore, the water intended for drinking purposes is supplied from smaller ones. In an evaluation of the quality of water in small resources, more than 300 resources with higher concentrations of iron, manganese, nitrates, ammonium ions, arsenic and antimony have been identified.

According to the 2010 Reports on the Environment in Slovakia, the concentration of iron exceeded the 0.2 mg/L limit in more than 18.9 % of the samples, and the concentration of manganese exceeded the 0.05 mg/L limit in more than 19.4 % of 396 groundwater samples (which represents 175 objects of basic monitoring). The concentration of iron exceeded the 0.2 mg/L limit in more than 37.2 % of the samples, and the concentration of manganese exceeded the 0.05 mg/L limit in more than 40.1% of 698 groundwater samples (which represents 211 objects of operational monitoring). The limit values are defined under the Regulation of the Government of the Slovak Republic No. 496/2010 on Drinking Water [1].

In searching for suitable water treatment technology, an emphasis is placed on new, more efficient and cost-effective methods and materials compared to the technology currently used.

The natural Zeolites are known for more than 200 years. There were Zeolites as mineral substances discovered by the Swedish mineralogist Cronstedt in 1756. In the course of this period were more than 35 types of Zeolites discovered and described, but its practical importance has remained unused for a long time. Only the modern identification methods have contributed to the fact that in the last 30 years have been more than thousands important occurrences of more than 50 types of Zeolites recorded in more than 40 countries.

In the eighties the deposit of natural Zeolite, with high content of Zeolitic mineral – Clinoptilolite in Nižný Hrabovec in the area of the East – Slovakian neovolcanites, was discovered. Besides this deposit, the Zeolite accumulations were discovered in the complex of the Central Slovakian neovolcanites, in the South – Western border of Kremnické vrchy and in Zemplínske pohorie on the territory of the Slovak Republic.

A primary structure unit of Zeolite is an octahedron – the even octahedron formed by atoms of silicium and aluminium with tetrahedrite-coordinated atoms of oxygen. The representation of the silicium and aluminium to the oxygen is usually 1:2. In this way, relatively big cavities mutually interconnected by small channels, the effective diameters of which differ from 0.2 to 0.7 nm and the total volume of vacant places forms from 20 % up to 50 % of mineral volume, are formed in the crystalline structure. There are the mobile mono-valent and bivalent cations of alkaline metals and alkaline earth metals (Ca, K, Na) encircled by molecules of water, which can be substituted by other ones from the surrounding solution, placed in these cavities.

In the last decades the Zeolitic mineral – Clinoptilolite has started to be also used in drinking water treatment. Zeolites are not to be found in the grained condition in the natural deposits, and before their use, Zeolites require crushing and sorting at the required fractions in the waterworks engineering. Sufficient mechanical strength, chemical stability and abrasion values, by which, though, they are classified among the soft filtration materials, and these properties made the natural Zeolites use as a filtration material.

One of the methods for elimination of dissolved iron and manganese is the elimination by means of the oxidized coat on the grains of filter medium. By addition of potassium permanganate (not only  $\text{KMnO}_4$ , but also other strong oxidizing agents) there is the coat form on the surface of filter medium, and this coat serves as a catalyst of oxidation, and the grain of filter medium are covered by higher metal oxides. In this case it can be said about the special filtration, so-called contact filtration, filtration on the manganese filters. These two ways of treatment are very closely connected and they can be hardly separated unambiguously. The oxidation condition of the medium coat  $\text{MnO}_x(\text{s})$  plays the obvious role in elimination of dissolved manganese, and the efficiency of manganese elimination is the immediate function of  $\text{MnO}_x(\text{s})$  concentration and oxidative condition. There is the formation of coats with different abilities to eliminate dissolved manganese from water on the various filter medium [1-11]. At present in addition to the traditional modified filtration sand is using a wide variety of materials with oxidation film on the surface of the grains of filter media (Klinopur-Mn, Greensand, Birm, Cullorb M, Everzit Mn, MTM and Pyrolox).

The objective of the technological experiments in the locality of Kúty (a water treatment plant) was to compare the efficiency of manganese and iron removal in water treatment using a filtration medium based on a chemically modified natural zeolites (Klinopur-Mn, Klinomangan) and monitoring the influence of water quality (pH, concentration of oxygen, iron and manganese) on efficiency removal iron and manganese from water.

## 2 MATERIALS AND METHODS

**Klinopur-Mn** - activated zeolite – clinoptilolite  $(\text{Na,K})^{6+}(\text{Al}_6\text{Si}_{30}\text{O}_{72})\cdot 20\text{H}_2\text{O}$  is produced in Slovakia. On clinoptilolite grains are industrially created a thin layer of manganese oxide, which allows the material used for contact filtration. Based on previous experiments (pilot tests) conducted by the Department of Sanitary and Environmental Engineering at the Faculty of Civil Engineering STU in Bratislava can be concluded that the surface of activated clinoptilolite is comparable with foreign materials and can be used for removing Fe and Mn in water [12,13].

**Klinomangan** - activated zeolite – clinoptilolite  $(\text{K,Na,Mn})^{6+}[(\text{AlO}_2)_6(\text{SiO}_2)_{30}]\cdot 24\text{H}_2\text{O}$  from the bearing Rátka in Hungary. Superficial layers of manganese oxide as in the case of Mn-Klinopuru allows to use this material in contact filtration for removal of iron and manganese from water. Depending on the quality of the treated water is required after a certain time, the filter cartridge to regenerate the solution of potassium or sodium permanganate [14].

**Table 1** shows the content of essential minerals forming clinoptilolite deposit, Nižný Hrabovec and clinoptilolite from the deposit Rátka in Hungary. **Table 2** is the chemical composition of clinoptilolite bearing Nižný Hrabovec and clinoptilolite from the deposit Rátka before activation and **Table 3** shows the chemical composition zeolites after activation with  $\text{KMnO}_4$  and the content of  $\text{MnO}_2$  on the surface of filter media. The selected parameters of the filtration materials used in the experiments are compared in **Table 4**.

**Tab. 1 Mineralogical composition of the zeolite deposits from Nižný Hrabovec and Rátka**

| Mineral         | Nižný Hrabovec (Slovakia) | Rátka (Hungary) |
|-----------------|---------------------------|-----------------|
|                 | Content [%]               |                 |
| Clinoptilolite  | 84                        | 55              |
| Cristobalite    | 8                         | 15              |
| Feldspar        | 3-4                       | 10              |
| Illite          | 4                         | -               |
| Montmorillonite | -                         | 10              |

**Tab. 2 Chemical composition of the nature zeolites from Nižný Hrabovec and Rátka**

| Zeolite         | Content [%]      |                                |                  |      |                                |      |                   |                  |
|-----------------|------------------|--------------------------------|------------------|------|--------------------------------|------|-------------------|------------------|
|                 | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | CaO  | Fe <sub>2</sub> O <sub>3</sub> | MgO  | Na <sub>2</sub> O | TiO <sub>2</sub> |
| Nižný Hrabovec  | 66.40            | 12.20                          | 3.33             | 3.04 | 1.45                           | 0.56 | 0.29              | 0.15             |
| Rátka (Hungary) | 72.15            | 12.86                          | 3.72             | 1.84 | 1.22                           | 0.53 | 0.26              | 0.10             |

**Tab. 3 Chemical composition of the Klinopur-Mn and Klinomangan**

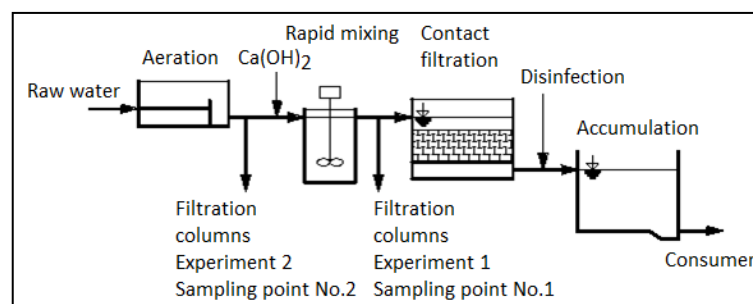
| Material    | Content [%]      |                                |                  |      |                                |                               |      |                   |                  |                  |
|-------------|------------------|--------------------------------|------------------|------|--------------------------------|-------------------------------|------|-------------------|------------------|------------------|
|             | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | K <sub>2</sub> O | CaO  | Fe <sub>2</sub> O <sub>3</sub> | P <sub>2</sub> O <sub>3</sub> | MgO  | Na <sub>2</sub> O | TiO <sub>2</sub> | MnO <sub>2</sub> |
| Klinopur-Mn | 69.56            | 8.19                           | 5.58             | 3.79 | 3.32                           | 1.08                          | 0.81 | -                 | 0.74             | <b>6.92</b>      |
| Klinomangan | 61.68            | 8.29                           | 4.77             | 3.51 | 2.87                           | 0.81                          | 0.27 | 2.56              | -                | <b>15.16</b>     |

**Tab. 4 Grain size and bulk density (in a dry state) of the selected filtration materials**

| Material                           | Klinopur-Mn | Klinomangan | Silica sand | Greensand |
|------------------------------------|-------------|-------------|-------------|-----------|
| Grain size [mm]                    | 0.6 – 1.6   | 0.5 – 1.2   | 0.5-1.0     | 0.25-0.8  |
| Bulk density [g.cm <sup>-3</sup> ] | 0.84        | 1.04        | 1.55        | 1.36      |

## 2.1 Water treatment plant Kúty

The water treatment plant in Kúty is a part of the Senica group of water supply systems. The water from two wells with a yield of 80 l.s<sup>-1</sup> does not meet the requirements of Regulation No. 496/2010 on Drinking Water for iron, manganese, sulfate ions and aggressive carbon dioxide. The technological water treatment process consists of aeration, a dosage of calcium hydrate, rapid mixing, contact filtration and disinfection. The technological scheme of the WTP Kúty is shown in **Fig. 1**. The figure also indicates the location of the filter columns (sampling points) used in experiments.

**Fig. 1 Scheme of the technology of WTP Kúty and the location of the filter columns**

The methodology for the verification of suitable filtration materials for iron and manganese removal is based on their properties and possible technological applications in the water treatment process. The following technological water treatment method was proposed:

*raw water → filtration and oxidation (backwashing and regeneration)*

Raw water is passed through the filtration equipment, and the removal of the  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  ions is carried out directly in the filtration column beds. The following were used as filtration materials:

- activated zeolite from Nižný Hrabovec with  $\text{MnO}_2$  on the surface (Klinopur-Mn)
- activated zeolite from Rátka with  $\text{MnO}_2$  on the surface (Klinomangan)

The experiments were designed to optimize the filtration rate (contact time of the raw water with the filter media) and washing and regenerating the filter materials (filter length of cycles). The quality of the raw water (Fe and Mn content) and treated water at the outlet from the separate filtration columns was monitored during the experiments. At the same time the amount of water (filtration rate) at the outlet from the columns was measured.

## 2.2 Filtration Model

To verify the efficiency of iron and manganese removal from the water resources in the locality of WTP Kúty, two filtration columns containing Klinopur-Mn and Klinomangan were used. The parameters of each adsorption column are as follows: diameter = 5.0 cm; height = 2 m; surface =  $19.635 \text{ cm}^2$ ; filtration medium height 110 cm; and volume of filtration medium  $2160 \text{ cm}^3$ .

The water was supplied to filtration columns from two different sites for the technological water treatment process. The water for Experiment 1 (sampling point No. 1) was taken after aeration and lime dosing, where the optimal conditions for the removal of the iron and manganese (increased oxygen content and a pH of more than 8) were achieved. The water for Experiment 2 (sampling point No. 2) was taken after aeration of the water, where the content of the oxygen in the water had increased. **Table 5** shows the values of the basic parameters during the experiments.

**Tab. 5 The basic parameters during the pilot test**

| Parameter                 | Sampling point |               |
|---------------------------|----------------|---------------|
|                           | No.1           | No.2          |
| Fe [ $\text{mg.l}^{-1}$ ] | 2,28 – 5,92    | 1,18 – 5,96   |
| Mn [ $\text{mg.l}^{-1}$ ] | 0,210 – 1,154  | 0,969 – 1,412 |
| pH                        | 8,26 – 8,68    | 6,81 – 7,28   |
| $\text{O}_2$ [%]          | 56 – 58        | 62 – 65       |

## 3 RESULTS AND DISCUSSION

The model tests and the results of the experiments are divided into two parts:

- raw water after aeration and the addition of lime (sampling point No.1)
- raw water after aeration (sampling point No.2).

### 3.1 Experiment 1

During the model tests, an average concentration of iron and manganese in raw water were  $0.506 \text{ mg.l}^{-1}$  for manganese or  $3.92 \text{ mg.l}^{-1}$  for iron and the filtration rates were  $5.16 \text{ m.h}^{-1}$  for Klinopur-Mn or  $4.74 \text{ m.h}^{-1}$  for Klinomangan. Filtration conditions are shown in a **Table 6**.

**Tab. 6 Filtration conditions**

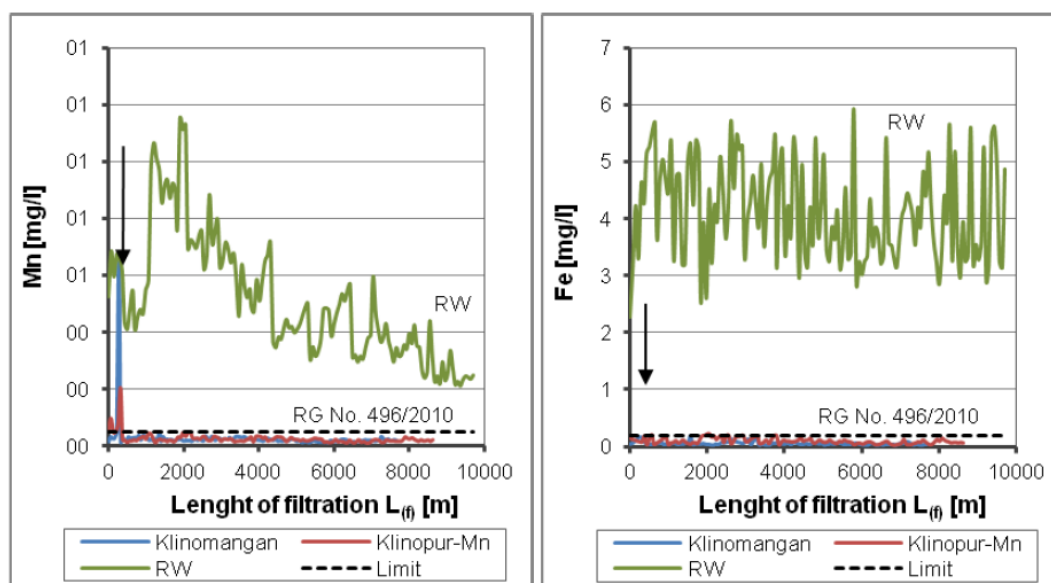
| Parameter  | Klinopur-Mn | Klinomangan |
|--|-------------|-------------|
| Grain size [mm]  | 0.6-1.6     | 0.5-1.2     |
| Medium height [cm]                                     | 110         | 110         |
| Average flow through column [ $\text{l.h}^{-1}$ ]      | 168.95      | 155.07      |
| Average filtration rate [ $\text{m.h}^{-1}$ ]          | 5.16        | 4.74        |
| Filtration total time [h]                              | 1644        | 1644        |
| Total volume of water flowing through [ $\text{m}^3$ ] | 16.665      | 15.296      |
| Average residence time in column [min]                 | 12.78       | 13.93       |

The results removal of the iron and manganese from *the raw water after aeration and the addition of lime* (sampling point No. 1) are documented by **Fig. 2**, in which the concentration of manganese and iron in the raw water and the values measured after passing through the monitored filter materials are shown. The figure also

shows the manganese limit value ( $0.05 \text{ mg.l}^{-1}$ ), and respectively the iron limit value ( $0.2 \text{ mg.l}^{-1}$ ) in the drinking water as defined under Regulation No. 496/2010 on Drinking Water. The arrow presents the regeneration of the filter media.

**Fig. 2 left** shows that in optimal conditions for contact filtration (pH 8.2 to 8.6; an oxygen content of 56 to 58% saturation) materials Klinopur-Mn and Klinomangan achieved a high efficiency for removing of manganese from the water. After regeneration materials at the beginning of the experiment (after 60.5 hours of operation model devices) they did not exceed the value of the manganese in the treated water limit value of  $0.05 \text{ mg.l}^{-1}$  even after 1600 hours of operation of the filter columns. The filter materials were backwashed continuously (approximately every 3 to 4 days). There was no need to regenerate these materials.

**Fig. 2 right** shows the progress made in removing of the iron from the water for sampling point No.1 (after the water aeration and the addition of lime). The value of the iron in the raw water is quite changed, depending on the production of precipitated  $\text{Fe(OH)}_3$ , which gradually clogged the system. In general both materials removed the iron effectively and, during the operation of the filtration columns, did not exceed the limit value of  $0.20 \text{ mg.l}^{-1}$  as defined under Regulation No. 496/2010 on Drinking Water.



**Fig. 2** Course of the removal of the manganese (left) and iron (right) from the water.

### 3.2 Experiment 2

During the model tests, an average concentration of iron and manganese in raw water were  $1.124 \text{ mg.l}^{-1}$  for manganese or  $3.28 \text{ mg.l}^{-1}$  for iron and the filtration rates were  $4.74 \text{ m.h}^{-1}$  for Klinopur-Mn or  $4.60 \text{ m.h}^{-1}$  for Klinomangan. Filtration conditions are shown in a **Table 7**.

**Tab. 7** Filtration conditions

| Parameter   | Klinopur-Mn | Klinomangan |
|---|-------------|-------------|
| Grain size [mm]                                     | 0.6-1.6     | 0.5-1.2     |
| Medium height [cm]                                  | 110         | 110         |
| Average flow through column [ $\text{l.h}^{-1}$ ]   | 155.94      | 150.64      |
| Average filtration rate [ $\text{m.h}^{-1}$ ]       | 4.74        | 4.60        |
| Filtration total time [h]                           | 1408        | 1408        |
| Total volume of water flow through [ $\text{m}^3$ ] | 13.174      | 12.726      |
| Average residence time in column [min]              | 13.85       | 14.34       |

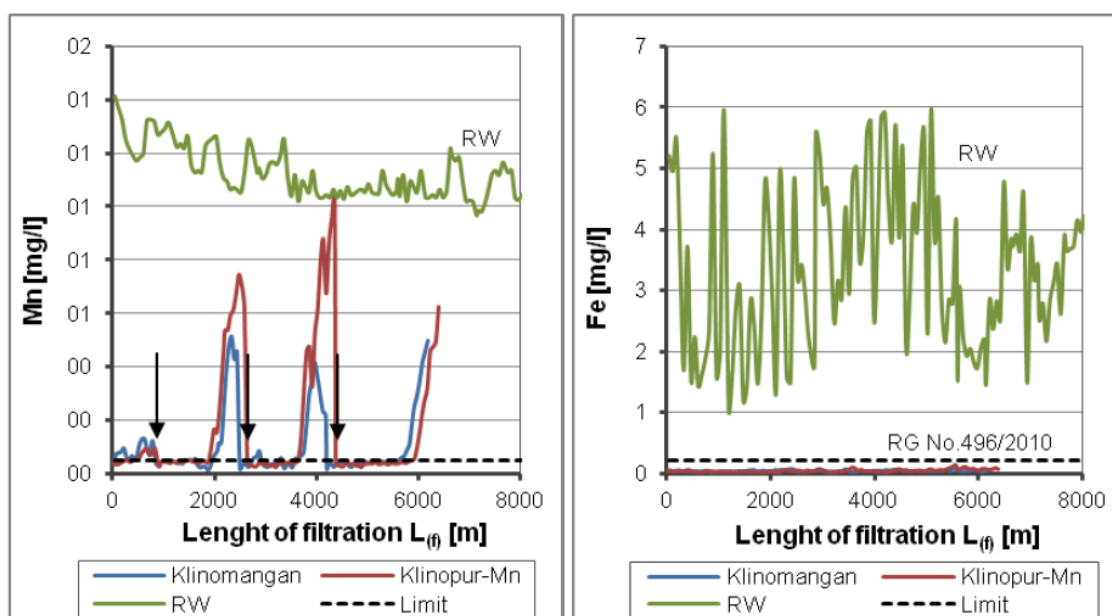
**Fig. 3** shows the results of removal of the iron and manganese from the raw water after aeration (sampling point No.2). The concentration of manganese and iron in the raw water and the values measured after they passed through the monitored filter materials, the manganese limit value ( $0.05 \text{ mg.l}^{-1}$ ), and respectively the iron limit value ( $0.2 \text{ mg.l}^{-1}$ ) in the drinking water defined under Regulation of the Government of the Slovak

Republic No. 496/2010 on Drinking Water and the regeneration for the filter media, are illustrated. The arrow presents the regeneration of the filter media.

**Fig. 3** left shows that the influence of changes in the quality of the raw water (pH 6.8 to 7.2, the oxygen content from 56 to 57% saturation) for the efficiency of the manganese removal from the water through the filtration media improved significantly. Klinopur-Mn and Klinomangan are necessary to be modified by the gradual backwashing and regeneration with 2,5% solution of  $\text{KMnO}_4$ . In the first filtration step it exceeded the limit value of  $0.05 \text{ mg.l}^{-1}$  after 194 hours of operation; in the second filter cycle after 216 hours for Klinopur-Mn or 268 hours for Klinomangan, in the third filter cycle after 232 hours for Klinopur-Mn and 280 hours for Klinomangan; in the fourth filter cycle the limit value was exceeded after 338 hours for both materials. The filtration time without regeneration was gradually extended. This means that the industrially activated clinoptilolite (Klinopur-Mn, Klinomangan) should be modified on-site directly in water treatment plant. The filter cycles will be extended, and after some time, regeneration will not be needed.

The filter media were backwashed continuously (approximately every 3 to 4 days) (given the amount of precipitated ferric hydroxide collected).

**Fig. 3** right shows the course of the iron removing from the water for sampling point No. 2. The value of the iron in the raw water was quite changed, depending on which well was used for pumping or the production of precipitated  $\text{Fe}(\text{OH})_3$ , which gradually clogged the system. In general both materials removed the iron effectively and, during the operation of the filtration columns did not exceed the limit value of  $0.20 \text{ mg.l}^{-1}$  as defined under Regulation No. 496/2010 on Drinking Water.



**Fig. 3** Course of the removal of the manganese (left) and iron (right) from the water.

#### 4 CONCLUSION

Obtained results prove the possibility to use Klinopur-Mn for removal of iron and manganese in water treatment process. Klinopur-Mn is comparable with imported filtration material Klinomangan. The results also show that the repeated use of Klinopur-Mn leads to extended filtration cycles and based on this fact it is comparable with prepared filtration sand. In comparison with filtration sand, the advantage of Klinopur-Mn is that it requires lower amount of water for backwashing which results in more cost-effective operation.

The content and form of occurrence of iron and manganese in water as well as water pH and dissolved oxygen concentration (min. 15 % of Fe + Mn content) are among the important criteria for Fe and Mn removal efficiency (lower efficiency in removal of iron bound to humic acids). The efficiency of Mn removal is influenced by the contact time between water and filter material (height of filtration layer, filtration time), properties of preparation active layer, i.e. layer thickness and its chemical composition, regeneration method,  $\text{KMnO}_4$  concentration as well as the time of backwashing and regeneration.

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## RESUMÉ

V článku sú uvedené výsledky práce, ktorej cieľom bolo porovnať povrchovo upravené zeolity známe ako klinoptilolit (veľké nálezisko klinoptilolitu bolo objavené na Východnom Slovensku v 80-tych rokoch 20. stor.) s dovážaným povrchovo upraveným zeolitom z náleziska v Maďarsku. Klinopur-Mn a Klinomangan boli použité pre odstraňovanie železa a mangánu z podzemnej vody.

Dosiahnuté výsledky pri odstraňovaní mangánu a železa z vody poskytujú podklad pre využitie filtračných materiálov (Klinopur-Mn, Klinomangan) v úprave vody.

Sledované materiály vykazovali rôznu účinnosť odstraňovania mangánu z vody, nakoľko veľkú úlohu zohráva kvalita surovej vody (obsah kyslíka a hodnota pH) a obsah oxidačnej vrstvy MnO<sub>2</sub> na povrchu filtračného materiálu.

Z Rtg analýzy materiálov vidieť, že Klinopur Mn obsahuje 6,92% MnO, v porovnaní s Klinomanganom (15,16% MnO), čo môže mať vplyv na ich účinnosti pri odstraňovaní rozpusteného mangánu z vody kontaktnou filtráciou, potrebu regenerácie náplne v priebehu prevádzky a „zapracovanie“ filtračných materiálov priamo na mieste úpravy.

V prípade odstraňovania železa z vody kvalita surovej vody nie je limitujúcim faktorom, všetky materiály odstraňovali Fe z vody na hodnotu nižšiu ako je limitná hodnota (0,20 mg.l<sup>-1</sup>).

Pri výbere vhodného materiálu je nutné zvážiť viacero faktorov, ktoré môžu ovplyvniť efektivnosť technologického procesu, napr. chemické vlastnosti a zloženie upravovanej vody, požiadavky na upravenú vodu, rovnako je dôležité posúdenie investičných a predpokladaných prevádzkových nákladov. Kontaktná filtrácia cez vhodný materiál predstavuje ekonomicky prijateľnú a nenáročnú technológiu na odstraňovanie železa a mangánu z vody, ktorá z hľadiska obsluhy je zároveň maximálne bezpečná.