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MODIFIED CLINOPTILOLITE IN THE REMOVAL OF IRON AND MANGANESE FROM WATER

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ABSTRACT

It is necessary to treat water intended for drinking purposes in many cases to meet the requirements of the Regulation of the Government of the Slovak Republic No. 496/2010 on Drinking Water. There is a tendency to look for technology with new, more efficient and cost-effective materials and technologies. The goal of this study is to compare activated natural zeolite known as clinoptilolite (rich deposits of clinoptilolite were found in the region of East Slovakia Region in the 1980s) with the imported Greensand and Cullsorb materials in the removal of iron and manganese from water. The results obtained from experiments carried out at WTP Kúty prove that Klinopur-Mn is suitable for the removal of iron and manganese from water and is comparable with the imported materials.

KEY WORDS

- *Treatment of water*,
- *Removal of iron and manganese*,
- *Natural materials (Klinopur Mn, Greensand, Cullsorb M)*,
- *Modified Clinoptilolite*,
- *Water analysis.*

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. This issue has been dealt with by a team of experts at the Water Research Institute Bratislava. They developed the criteria for water quality as well as other technical and economic aspects of using a water resource for supplying the population with drinking water, since there are several regions with many municipalities without any connection to a public water supply located away from large distribution systems [1].

In the case of groundwater used for drinking purposes, water treatment is mostly needed for the removal of iron and/or manganese. Concentrations of dissolved iron and manganese are evaluated every year within the groundwater monitoring done by the Slovak Hydrometeorological Institute (SHMU) for the whole territory of Slovakia.

In 2009, there were approximately 5500 registered groundwater resources, which used on average 11045 L/s (including 8475.4 L/s for drinking water purposes). Of this amount 2632 l/s had to be treated, due to their higher concentration of iron and manganese.

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 represent 175 basic monitoring objects). 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 represent 211 operational monitoring objects). The limit values are defined under the Regulation of the Government of the Slovak Republic No. 496/2010 on Drinking Water [2].

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.

One of the new methods is the removal of dissolved manganese by using an oxidized film on the grains of a filtration medium.

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A film is formed on the surface of the filtration medium by adding potassium permanganate (not only $KMnO_4$, but also other strong oxidizing agents). This film serves as a catalyst of oxidation – the grains of the filtration medium are covered by metal oxides. In such a case, this special filtration is the so-called "contact filtration" – filtration by manganese filters. The oxidation state of the film of the MnO_x(s) medium has an important role in the removal of dissolved manganese. The efficiency of manganese removal is a direct function of the MnO_x(s) concentration and its oxidized state. Films with different abilities to remove dissolved manganese from water are formed on different filtration media [3, 4, 5, 6, 7].

2. STUDY OBJECTIVE

Based on the present knowledge concerning this natural material and works dealing with the removal of dissolved manganese from water through oxidizing films on various filtration materials, we have performed experiments with zeolite from Nižný Hrabovec, where a rich deposit of this material is located. The objective of the technological trials in the locality of Kúty (a water treatment plant) was to verify the efficiency of manganese and iron removal in water treatment using a filtration medium based on a chemically modified natural zeolite (Klinopur-Mn). At the same time the efficiency of manganese and iron removal was compared with the imported Greensand and Cullsorb M (USA) materials, which are often used abroad for dissolved manganese and iron removal from water in small-scale water treatment plants (small water resources).

3. EXPERIMENTAL PART

The water treatment plant in Kúty is a part of the Senica group of water supply systems (Fig. 1). The water from two wells with a yield of 80 L/s does not meet the requirements of Regulation No. 496/2010 on Drinking Water for iron, manganese, ammonium ions, and aggressive carbon dioxide. The technological water treatment process consists of aeration, a dosage of calcium hydrate, slow mixing, filtration and disinfection.

The technological scheme of the WTP Kúty is shown in Fig. 2. The figure also indicates the location of the filter columns (sampling points) used in our experiments.

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 Fe^{2+} and Mn^{2+} ions is carried out directly in the filtration column beds (the media). The following were used as filtration materials:

- Greensand
- Cullsorb M
- natural activated zeolite with MnO_2 (Klinopur-Mn)

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 cycles).

The quality of the raw water (Fe and Mn content) and treated water at the outlet from the separate filtration columns was monitored

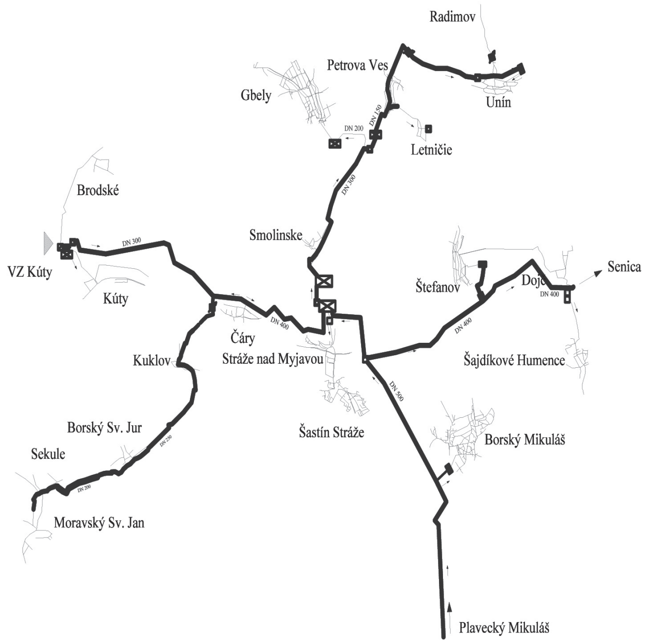

Fig. 1 *Scheme of part of the Senica group water supply system.*

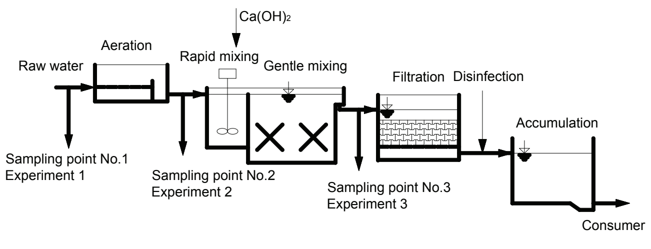

Fig. 2 *Scheme of the technology of WTP Kúty and the location of the filter columns.*

during the experiments. At the same time the amount of water (filtration rate) at the outlet from the columns was measured.

3.1 Filtration Materials

Klinopur-Mn, which is produced in Slovakia, is activated zeolite – clinoptilolite (Tables 1 and 2). On the surface of the grains there is a factory-made film consisting of manganese oxides, which enables this material to be used in contact filtration. This filtration material is much cheaper compared to imported materials from the USA. Based on experiments (pilot tests) performed by experts from the Department of Sanitary and Environmental Engineering at the Faculty of Civil Engineering of the Slovak University of Technology in Bratislava [8, 9, 10], it can be stated that the surface of clinoptilolite activated by manganese oxides is comparable with the imported Birm material, and it is possible to use it for the removal of Fe and Mn from water.

Clinoptilolite $[(NaK)_6(Al_6Si_{30}O_{72})\cdot 20H_2O]$ is one of the most frequently used natural zeolites. At present it is also applied in the water treatment process. Its sufficient mechanical resistance, chemical stability and abrasion values (even if they are categorized among soft materials) enable clinoptilolite to be used as a filtration material. The basic properties of clinoptilolite are shown in Table 3.

Greensand (imported from the USA) is a glauconitic mineral with a zeolite-type structure. It is produced from glauconitic sand, which is activated by potassium permanganate ($KMnO_4$). The resulting product is a granulated material covered by a MnO_2 film on its surface and other higher oxides of manganese. It is used for the removal of iron, manganese and hydrogen sulphide from water. Dissolved iron and manganese are oxidized and precipitated in contact with the higher oxides of manganese on the surface of Greensand. Undissolved iron and manganese are trapped in the "greensand medium" and removed by backwash. After the exhaustion of its oxidizing capacity, the bed is regenerated using a $KMnO_4$ solution. The regeneration frequency depends on the amount of iron, manganese and oxygen in the water as well as the filter size. We recognize two regeneration processes, i.e., with discontinuous or continuous regeneration.

The pH value of water is an important factor influencing the efficiency of filters. If the pH is lower than 6.8, the efficiency of greensand is reduced. The operating conditions for Greensand are listed in Table 4.

Greensand has been used for more than 20 years for the removal of Fe and Mn from water. The advantage is that water with a low oxygen content does not have to be pre-oxidized. Greensand can be used in cases with a higher content of iron (over 10 mg/L) and manganese. It can also be used in industry. A content of organic substances, oils and hydrogen sulphides has an adverse effect on its efficiency.

Tab. 1 *Mineralogical analysis of the zeolite from the deposit at Nižný Hrabovec [11].*

Mineral	Content %	Mineral	Content %
Clinoptilolite	84	Illite	4
Cristobalite	8	Quartz	traces
Feldspar	3-4	Carbonate minerals	traces (<0.5)

Tab. 2 *Chemical analysis of the clinoptilolite from the deposit at Nižný Hrabovec [11].*

Compound	Content %	Compound	Content %
SiO_2	66.4	MgO	0.56
Al_2O_3	12.2	Na_2O	0.29
K_2O	3.33	MnO	0.02
CaO	3.04	TiO_2	0.15
Fe_2O_3	1.45	P_2O_5	0.02

Tab. 4 *Conditions of Greensand use.*

Parameter	Operating range	Parameter	Operating range
pH	6.8 to 9.0	Organic matters	< 5 mg/L
Dissolved oxygen	> 15% of Fe content	Oils	≈ 0 mg/L
Fe^{2+}/Mn^{2+}	< 15 mg/L	Temperature	5 – 30 °C
Alkalinity	> 2x ($SO_4 2^-$ Cl^-)	H_2S	< 5 mg/L

Tab. 3 *Basic properties of clinoptilolite.*

Clinoptilolite			
Colour	grey-green	Effective diameter of pores	0.4 nm
Compressive strength	33 MPa	Absorbability	34 – 36 %
Specific gravity	2200 – 2440 $kg.m^{-3}$	Thermal stability	do 450 °C
Apparent density	800 – 900 $kg.m^{-3}$	Stability against acids	79.50 %

Tab. 5 *Basic properties of Cullsorb M.*

Cullsorb M	
Colour	from dark brown to black
Aspect	granular, spheric or angular
Water content at 105 °C < 2%	Manganese (as Mn) > 53%
Iron (as Fe) < 3.5%	Manganese dioxide (as MnO_2) > 80%

Cullsorb M (imported from the USA) is a natural, highly selected mineral (green sand), lacking in additives and impurities. It is based on manganese dioxide, which has an extremely high capacity for catalytic oxidation. It is specifically used in filtering plants for the removal of iron, manganese and hydrogen sulfide by oxidation in water. The filter cartridge requires periodic or continuous regeneration of the oxidized reagent, either potassium permanganate or air.
The selected parameters of the filtration materials used in the experiments are listed in Table 6.

3.2 Water Treatment Model

To verify the efficiency of iron and manganese removal from the water resources in the locality of WTP Kúty, three filtration columns containing Greensand, Cullsorb M and Klinopur-Mn were used. The adsorption columns were made of glass. The parameters of each adsorption column are as follows: diameter = 5.0 cm; height = 2 m; surface = 19.635 cm^2; filtration medium height 110 cm; and volume of filtration medium 2160 [cm^3]. The filtration equipment is shown in Fig. 3. The figure shows a simple device that allows splitting the incoming water either for washing or filtration through a valve system.
The water was supplied to filtration columns from three different sites for the technological water treatment process. The water for Experiment 1 (sampling point No. 1) was taken from the inlet of the raw water to the water treatment plant. 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. The water for Experiment 3 (sampling point No. 3) 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. Table 7 shows the values of the basic parameters during the experiments.

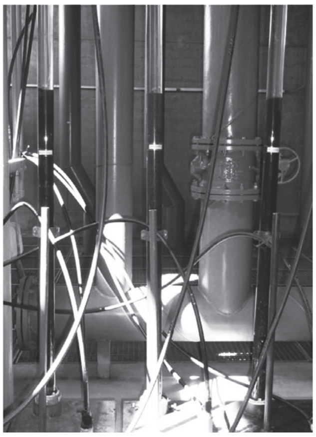

Fig. 3 *Filtration equipment – filtration columns.*

Tab. 7 *The basic parameters during the pilot test.*

Parameter	Sampling point		
	No.1	No.2	No.3
Fe (mg/L)	2.28 – 5.16	0.90 – 3.87	1.96 – 4.22
Mn (mg/L)	0.82 – 1.12	0.816 – 1.092	0.198 – 0.524
pH	6.64 – 6.98	6.81 – 7.14	8.40 – 8.62
Oxygen (% saturation)	6 – 7	59 – 60	56 – 57

4. RESULTS AND DISCUSSION

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

- for raw water from wells,
- for raw water after aeration,
- for raw water after aeration and the addition of lime.

Tab. 6 *Filtration materials and some selected parameters.*

Material	Clinoptilolite	Cullsorb M	Greensand	Silica sand
Grain size [mm]	0.3 – 2.5	> 0.4	0.25 – 0.8	0.7 – 2.0
Specific gravity [g/cm^3]	2.39	3.5 – 4.0	2.4 – 2.9	2.66
Apparent density [g/cm^3]	0.84	1.75 – 1.85	1.36	1.55
Porosity [%]	64.8	–	–	41.7
Abrasion [%]	8.2	–	–	0.57

Experiment 1

Raw water passed through the filtration columns in a downward direction. The average filtration rate was 6.23 m/h for the Greensand, 5.98 m/h for the Klinopur-Mn and 5.83 m/h for the Cullsorb M. The filtration conditions are shown in Table 8.
The results of removing the iron and manganese from the raw water are documented in Figs. 4 and 5. They show the concentration of manganese and iron in the raw water and the values measured after they passed through the monitored filter materials. The figures also show the manganese limit value (0.05 mg/L) and respectively the iron limit value (0.2 mg/L) for drinking water in the Regulation of the Government of the Slovak Republic No. 496/2010 on Drinking Water. The arrow represents the regeneration time of the filter media.
Fig. 4 shows that the quality of the raw water (low pH – 6.6 to 6.9, low oxygen content – 6 to 7%) has an influence on the efficiency of the removal of the manganese and that the efficiency for the monitored materials was different. The best results were achieved with Cullsorb M, which even after 260 hours of operation did not exceed the limit value for manganese (0.05 mg/L). It is a fact that Cullsorb M is the material with the highest MnO_2 content on its surface. The Greensand exceeded the limit of 0.05 mg/L after 20 hours and the Klinopur-Mn after 42 hours of operation. Those materials had to be regenerated (2.5% solution of $KMnO_4$). After the regeneration, the columns were operating again, but for this type of water, their efficiency was too low.
The Greensand and Klinopur released the manganese from their surfaces into the water because of the pure quality of the treated water, the low oxygen content and the low pH value.
Fig. 5 shows that all the materials are effective for removing iron from the water during the operation of the filtration columns and did not exceed the limit value of 0.20 mg/L.

Experiment 2

Figs. 6 and 7 show the results of removing 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,

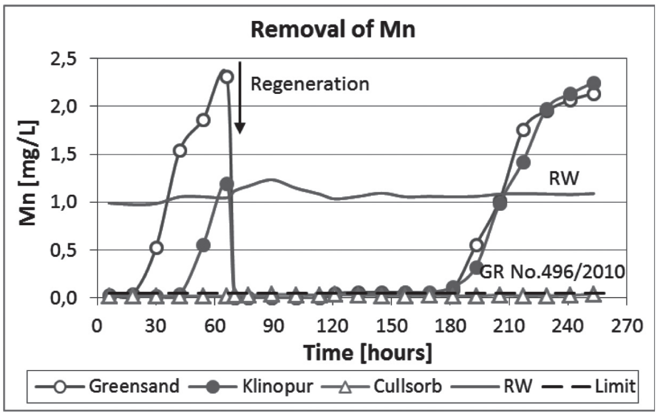

Fig. 4 *Course of removing the manganese from the water.*

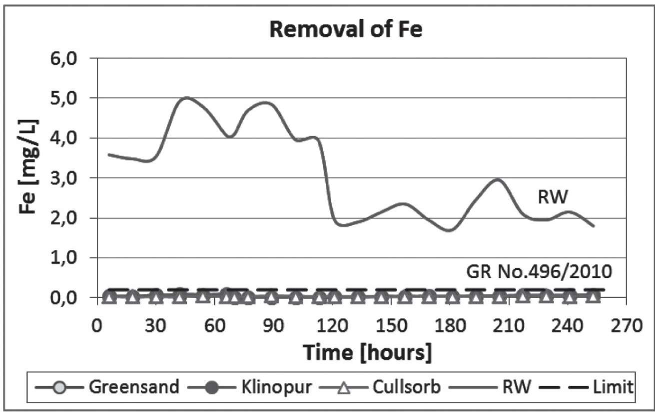

Fig. 5 *Course of removing the iron from the water.*

Tab. 8 *Filtration conditions for the first sampling point.*

Parameter	Greensand	Klinopur	Cullsorb
Grain size [mm]	0.25 – 0.8	0.6 – 1.6	0.4 – 0.6
Height of filtration medium [cm]	110	110	110
Average discharge through column [mL/min]	204	195.75	190.83
Average filtration rate [m/h]	6.23	5.98	5.83
Filtration total time [h]	260	260	260
Total volume of water flown through [m^3]	3.182	3.054	2.977
Average residence time in column [min]	10.587	11.034	11.318

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Tab. 9 *Filtration conditions for the second sampling point.*

Parameter	Greensand	Klinopur	Cullsorb
Grain size [mm]	0.25 – 0.8	0.6 – 1.6	0.4 – 0.6
Height of filtration medium [cm]	110	110	115
Average discharge through column [mL/min]	191.1	167.5	185.2
Average filtration rate [m/h]	9.734	8.532	9.434
Filtration total time [h]	5.84	5.12	5.66
Total volume of water flown through [m^3]	910	910	910
Average residence time in column [min]	10.435	9.148	10.113

contrasted with the manganese limit value (0.05 mg/L), and respectively the iron limit value (0.2 mg/L) in the drinking water defined under Regulation of the Government of the Slovak Republic No. 496/2010 on Drinking Water and the regeneration time for the filter media, are illustrated.

Fig. 6 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 materials improved significantly. All three materials obtained a high level of efficiency of the manganese removal from the water. In the case of the Cullsorb M and Greensand materials during the 910 hours of the operation of the filtration process, the limit value for manganese (0.05 mg/L) was not exceeded. It is necessary to modify Klinopur Mn by a gradual backwashing and regeneration with a solution of $KMnO_4$. In the first filtration step it exceeded the limit value of 0.05 mg/L after 162 hours of operation; in the second filter cycle the limit value was exceeded after 258 hours, and the limit value was exceeded in the third filter cycle after 277 hours. The filtration time without regeneration was gradually extended. This means that the industrially activated clinoptilolite (Klinopur-Mn) should be modified directly on-site in the 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 2 to 3 days) (given the amount of precipitated ferric hydroxide collected). Over time, as shown in Fig. 6, the concentration of manganese in the treated water after passing through Klinopur-Mn exceeded the value of 0.05 mg/L; then the filter materials were regenerated with a solution of $KMnO_4$ (2.5% solution).

Fig. 7 shows the course of removing the iron from the water for sampling point No. 2 (after the water aeration). 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 Fe $(OH)_3$, which gradually clogged the system. In general, all three materials removed the iron effectively and, during the operation of the filtration columns did not exceed the limit value of 0.20 mg/L as defined under Regulation No. 496/2010 on Drinking Water.

The filtration rates during the second experiment were lower compared to the first experiment, which was caused by precipitations of iron after the oxidation and ferric hydroxide clogged the columns.

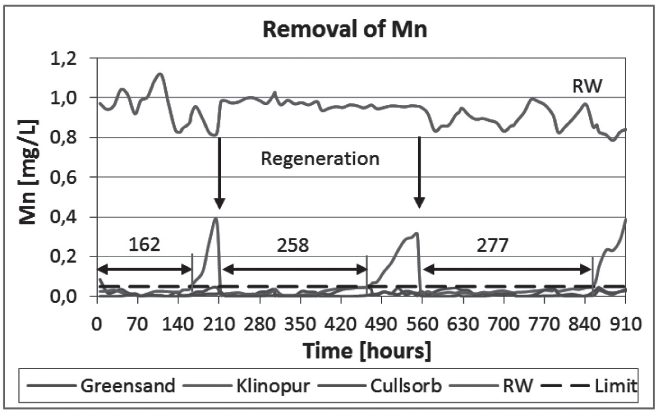

Fig. 6 *Course of removing the manganese from water.*

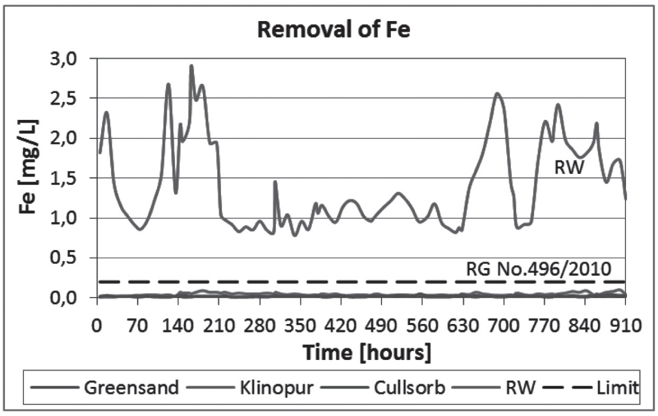

Fig. 7 *Course of removing the iron from water.*

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Tab. 10 *Filtration conditions for sampling point No.3.*

Parameter	Greensand	Klinopur	Cullsorb
Grain size [mm]	0.25 – 0.8	0.6 – 1.6	0.4 – 0.6
Height of filtration medium [cm]	110	110	115
Average discharge through column [mL/min]	181.2	176.5	178.8
Average filtration rate [m/h]	5.54	5.39	5.46
Filtration total time [h]	802	802	802
Total volume of water flown through [m^3]	8.719	8.493	8.604
Average residence time in column [min]	11.920	12.237	12.080

Experiment 3

The results from removing the iron and manganese from the raw water after aeration and the addition of lime are best documented by Figs. 8 and 9, 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 figures also show the manganese limit value (0.05 mg/L), and respectively the iron limit value (0.2 mg/L) in the drinking water as defined under Regulation No. 496/2010 on Drinking Water. The arrow represents the regeneration time of the filter media.

Fig. 8 shows that the changes in the quality of the raw water (pH 8.4 to 8.6; an oxygen content of 59 to 60% saturation) has an efficiency in the removal of manganese from the water. The high removal efficiency of the manganese was achieved by all three materials – Cullsorb, Greensand and Klinopur-Mn. Even after 802 hours of operation of the filtration system, they did not exceed the value of the manganese in the treated water limit value of 0.05 mg/L. The filter materials were backwashed continuously (approximately every 2 to 3 days). There was no need to regenerate these materials.

Fig. 9 shows the progress made in removing the iron from the water for sampling point No.3 (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 $Fe(OH)_3$, which gradually clogged the system. In general, all three materials removed the iron effectively and, during the operation of the filtration columns, did not exceed the limit value of 0.20 mg/L as defined under Regulation No. 496/2010 on Drinking Water.

5. CONCLUSION

The results obtained proved the possibility of using Klinopur-Mn in removing iron and manganese from water (the so-called contact manganese removal) and is comparable with the Greensand and Cullsorb M materials imported from abroad.

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

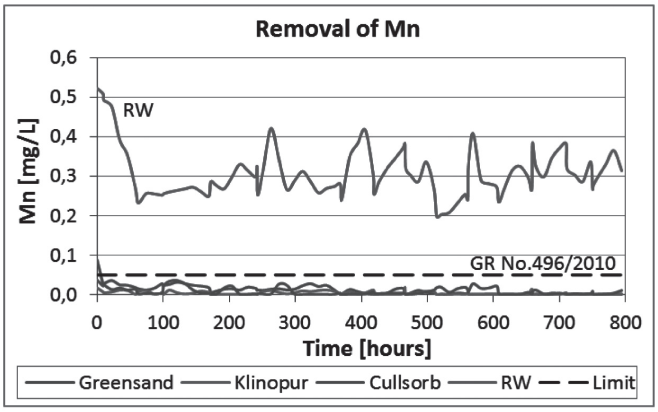

Fig. 8 *Course of removing the manganese from water.*

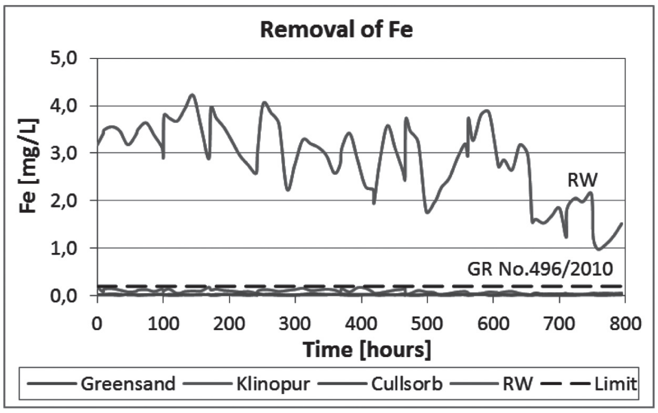

Fig. 9 *Course of removing the iron from water.*

a limiting factor; all the materials removed Fe from the water to below the limit value (0.20 mg/L).

The rate of filtration, backwashing time and intensity (self-carriage filter material during the washing) and the method of regeneration of the filter media with $KMnO_4$ (a 2.5% solution of $KMnO_4$) were also measured during the pilot plant experiments.

The insertion of aeration and the pH adjustment of the raw water before the filtration column to increase the efficiency of the filter media provide an effective treatment of the water as seen from the experimental results.

The technology of the removal of Fe and Mn with contact filtration is often used for small water resources (the water treatment is directly on the water resource). Based on our experiments, the most suitable material for the water quality and filtration conditions was Cullsorb M (contains over 80% of MnO_2 on its surface).

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