Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.20888

78 (2017) 155–165
June

Removal of iron and manganese from water using Filtralite Mono-Multi

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Received 17 May 2016; Accepted 15 May 2017

ABSTRACT

In over 38% of the groundwater drinking water sources in Slovakia, iron and manganese concentrations exceed the recommended levels set by Regulation of the Government of the Slovak Republic No. 496/2010 on Drinking Water. Iron and manganese are not considered health hazards, although micro-environments may be supported in wells and distribution systems which harbor microorganisms. The main concern with these metals is the color imparted by the oxidized forms that rarely goes unnoticed by the consumer. In addition, clothes and plumbing fixtures are easily stained. The aim of this study was to verify the efficient removal of iron and manganese from water using the two-layer material Filtralite Mono-Multi and monitor the surface properties and chemical composition of each layer of Filtralite Mono-Multi (HC 0.8–1.6 and NC 1.5–2.5 (N = normal density, H = high density, C = crushed)) before and after the experiment. The results of the pilot-scale experiments at the water treatment plant in Kúty have shown that the gradual preparation of the Filtralite material using $KMnO_4$ and the creation of an MnO_2 contact layer on the surface of the Filtralite increased the efficient removal of manganese from the water. After the experiment, the surface properties of the Filtralite were improved.

Keywords: Treatment of water; Removal of iron and manganese; Filtration; Filtralite Mono-Multi; Surface properties; Chemical composition

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1. Introduction

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

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 Fe and Mn are evaluated every year within the groundwater monitoring done by the Slovak Hydrometeorological Institute (SHMI) for the whole territory of Slovakia.

According to the 2012 Reports on the Environment in Slovakia, 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 the 698 groundwater samples (they represent 211 objects of the operational monitoring) [1]. The above limit values are defined under the Regulation of the Government of the Slovak Republic No. 496/2010 on Drinking Water.

Iron and manganese occur in dissolved forms as single ions (Fe^{2+}, Mn^{2+}) or in undissolved higher forms, mainly as $Fe(OH)_3$ or $MnO_2.xH_2O$, respectively. They can also be present in colloidal form (bound to humic substances). The form of their occurrence depends on the oxygen concentration, the solubility of Fe and Mn compounds in water, the pH value, the redox potential, hydrolysis, the presence of complex-forming inorganic and organic substances, and the water temperature and composition (e.g., CO_2 content) [2,3].

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The process of the oxidation of Fe^{2+} can be represented by the schematic equation:

$$4\,Fe^{2+} + O_2 + 10\,H_2O \rightarrow 4\,Fe(OH)_3 + 8\,H^+ \quad (1)$$

In water containing bicarbonate this reaction can also take place:

$$4\,Fe^{2+} + 8\,HCO_3^- + 2\,H_2O + O_2 \rightarrow 4\,Fe(OH)_3 + 8\,CO_2 \quad (2)$$

The rate of oxidation depends on the pH, the concentration of the iron, the dissolved oxygen concentration, and the redox potential. Since the reaction produces hydrogen ions, the oxidation is accelerated in an alkaline medium [4–6].

The dependence of the oxidation on the pH is very strong. At a pH range of 5–8.2, the oxidation rate is about one hundred times higher when the pH level rises by one. Furthermore, it is affected by the temperature and light. The positive or negative impact of different anions or organics depends on the stability of their Fe^{2+} or Fe^{3+} complexes. If they form stable complexes with Fe^{3+}, the rate of oxidation increases and vice versa.

The stability of iron ions depends not only on the pH but also on the activity of electrons, which are represented by the redox potential E (V) (Fig. 1). The high positive value of E (or pE) indicates oxidizing conditions where iron is insoluble and the low values of E (or pE) indicates reducing conditions where iron is soluble.

The occurrence and behavior of manganese is not similar to iron. Manganese in the oxidation state of Mn^{2+} in waters containing dissolved oxygen under certain conditions is unstable. In alkaline conditions, manganese is rapidly oxidized and hydrolyzed to form the less soluble oxides of manganese in the higher oxidation state Mn^{4+}:

$$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^- \quad (3)$$

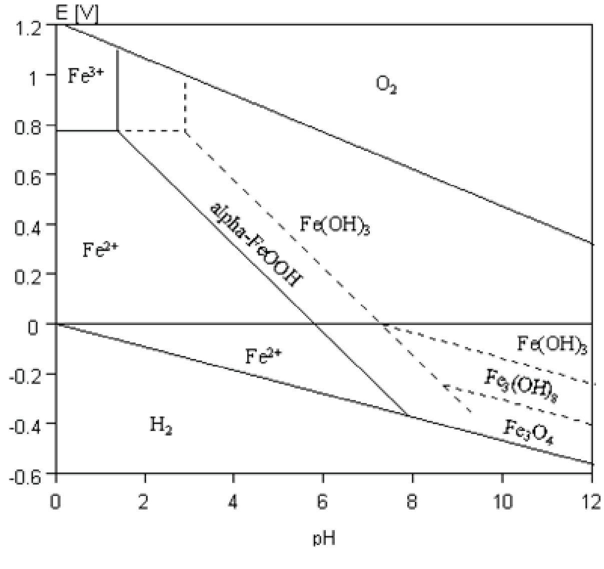

Fig. 1. E–pH stability diagram of iron [5].

The mechanism of the oxidation of Mn^{2+} in an actual rock environment is complicated. This is a set of the interconnected processes of oxidation, catalysis, sorption, ion exchange, and biological oxidation. The composition of the final products of oxidation, which are partially secreted in a colloidal form, depends on factors such as the pH, temperature, oxidation–reduction potential, reaction time, and rocks. The general scheme of Mn^{2+} oxidation by oxygen dissolved in water can be represented as follows:

$$Mn^{2+} \rightarrow Mn(OH)_2(s) \rightarrow Mn_2O_3.xH_2O \rightarrow MnO(OH) \rightarrow MnO_2.xH_2O \quad (4)$$

The relationship between iron and manganese under an increasing pH and redox potential (pE) suggests that ferrous iron (Fe^{2+}) normally occurs in an area with lower redox potential (<200 mV) and within a pH range of 5.5–8.2. This also means that Fe^{2+} is more easily and rapidly oxidized than Mn^{2+}. The latter often occurs with Fe^{3+} under pH values larger than 8 and higher redox conditions (>420 mV). The stable form of MnO_2 is found above this redox potential [4,7–10].

A diagram of the existence of the dominant areas Mn–CO_2–H_2O–O_2 is in Fig. 2.

The alkalinity and pH have a marked effect on the solubility of Mn(II). This solubility is governed by the formation of manganese carbonate. Manganese hydroxide has a much higher solubility. At pH values of 8 or higher, the calculated solubility of Mn(II) is very limited (1–2 mg/L or lower), even at a low alkalinity (1.2 mmol/L) [11].

The adverse effects of higher Fe and Mn concentrations in drinking water can be summarized as follows:

- iron(II) and manganese(II) ions are oxidized into higher forms in water distribution systems, and this results in

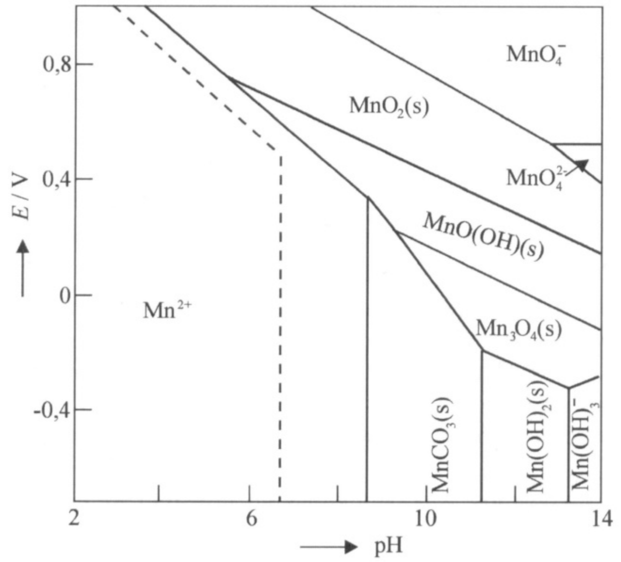

Fig. 2. E–pH diagram of the existence of the dominant areas Mn–CO_2–H_2O–O_2 [2]. The total concentration of 2 mmol/L CO_2 and the total concentration of manganese 0.055 mg/L. The dashed lines mark areas with a total concentration of manganese 5.5 mg/L.

the formation of hydroxide suspensions, which cause undesirable turbidity and change the color of the water;
- the presence of iron and manganese bacteria in a water supply system can cause changes in water quality (its smell) and bacterial growth in pipes; and
- in the event of the occurrence of iron(II) and manganese(II) ions when water reaches the consumer, iron and manganese are oxidized and precipitated under suitable conditions (e.g., in washing machines, boilers).

Due to the abovementioned facts, higher concentrations of iron and manganese in water can cause technological problems, failures in the operation of water supply systems, and deterioration in the water quality. In water with slightly higher concentrations of oxygen, iron, and manganese form undesirable incrustations, resulting in the reduction of the flow in a pipe's cross section.

The principle of most of the methods used for the removal of iron and manganese is that the originally dissolved iron and manganese are transformed into undissolved compounds that can be removed through a single-stage or two-stage separation. The oxidation and hydrolysis of these compounds are done under strict conditions with respect to the water properties and type of equipment for the iron and manganese removal.

The single-stage water treatment (filtration) is designed for iron and manganese concentrations up to 5 mg/L, and the two-stage treatment (settling tanks or clarifiers and filters) is used for water with iron concentrations higher than 5 mg/L. In case the water contains higher concentrations of CO_2, aeration is performed before settling or filtration.

The removal of Fe and Mn from groundwater and surface water can be done by several methods: oxidation by aeration, oxidation by oxidizing agents (O_2, Cl_2, O_3, $KMnO_4$), alkalization (by adding lime), contact filtration, ion exchange filtration, biological filtration, membrane processes, and the in situ method.

Removal by using a MnO_x coating on the grains of the filter medium is one of the methods for the elimination of dissolved iron and manganese. The MnO_x coating serves as a catalyst for the oxidation process. The grains of the filter medium are covered by the higher oxides of the metals. In such a case, the filter medium is related to a special filtration, the so-called "contact filtration", which is filtration that uses manganese filters. The oxidation state of the coating of the MnO_x(s) filter medium is very important in the removal of dissolved manganese. The effectiveness of Mn removal is a direct function of the MnO_x(s) concentration and its oxidation state. The oxidation coatings, which have various abilities to remove dissolved manganese from water, are formed on the surface of the various filter media [12–31].

For this type of treatment, natural materials or materials with a manufactured layer of MnO_x are used. As a natural material pyrolusite, which is the mineral form of MnO_2(s), is used. It is a mined ore consisting of 40%–85% manganese dioxide by weight. Aqua-mandix is the other natural, crushed manganese dioxide (it contains 78% of MnO_2) filter media for manganese removal from water.

Most drinking water production plants use rapid sand filters for the removal of manganese from groundwater. The start-up of manganese removal on newly installed sand media is slow, that is, it takes several weeks to several months. Reducing this period in order to prevent the loss of water during this phase has become an issue of concern. The materials (pyrolusite, Aqua-mandix) can be potential substitutes for sand in situations involving slow start-ups of manganese removal [32].

Except for natural media, which contain MnO_2, a layer of MnO_2 can be formed on the surface using suitable materials (sand, zeolite, coal, etc.) by dry or wet coating techniques. For dry coating, powdered manganese oxide ore was fixed on the media surface. Wet coating was achieved by depositing synthetic manganese oxides onto the bed surface. The addition of strong oxidants (sodium hypochlorite, ClO_2, etc.) and a solution with Mn^{2+} (0.05–0.2 mol/L) can form a layer of MnO_2 on the surface media too [33,34].

The filter media covered with MnO_2 directly onto their surfaces include Greensand, Birm, MTM, Everzit Mn, Cullsorb M, Klinomangan, Klinopur Mn, etc. These manufactured media require regeneration with potassium permanganate ($KMnO_4$) or other strong oxidizing agents to retain their MnO_2 properties.

The aim of this study was to verify the effectiveness of the removal of iron and manganese from the water at the Kúty Water Treatment Plant (Slovakia) through the use of pilot-scale experiments with the two-layer material Filtralite Mono-Multi and to monitor the surface properties and chemical composition of each layer of Filtralite Mono-Multi before and after the experiment.

The Filtralite material is often used abroad as a single or multilayer filtration media for the removal of turbidity, color, and bacterial pollution from water (surface water resources); it can be used as a biological fixed film for the removal of nitrogen compounds, natural organic matter, iron, and manganese, or as a filter media for the pretreatment of seawater before reverse osmosis desalination. This material does not have a layer of MnO_2 on its surface; therefore, the purpose of the experiments was to modify the surface properties of the Filtralite added to $KMnO_4$, and thereby increase the effectiveness of the removal of Fe and Mn from the water.

2. Materials and methods

2.1. The Kúty water resource

The water treatment plant (WTP) in Kúty is a part of the Senica group of water supply systems. The water from two wells with a yield of 288 m^3/h 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. 3. The figure also indicates the location of the filter columns (sampling points) used in our experiments.

The water was supplied to the 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 by contact filtration (increased oxygen content and a pH of more than 8)

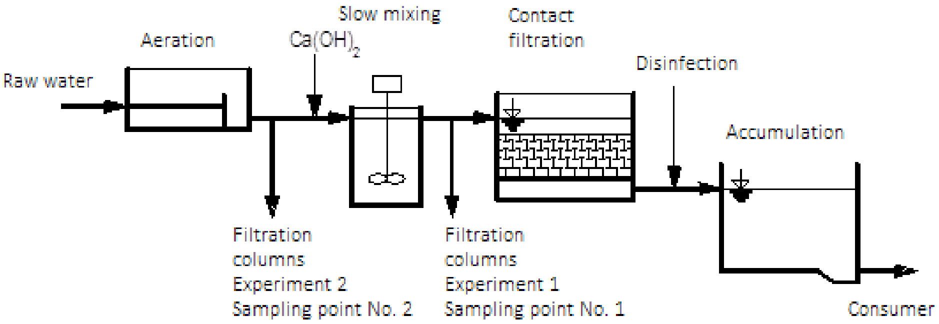

Fig. 3. Scheme of the technology of WTP Kúty and the location of the filter columns.

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 was increased.

During the model tests, the concentration ranges of the iron and manganese in the raw water were 0.21–1.154 mg/L for the manganese and 1.96–5.92 mg/L for the iron in Experiment 1, and 0.97–1.412 mg/L for the manganese and 1.14–5.96 mg/L for the iron in Experiment 2. The quality of the raw water in sampling points 1 and 2 was determined (Table 1). The filtration rate was 5.61 m/h in Experiment 1 and 5.37 m/h in Experiment 2. The filtration conditions are shown in Table 2.

Table 1
Water quality during the experiments

Parameter	Sampling point No. 1	Sampling point No. 2
pH	8.47	7.04
Conductivity, mS/m	61.6	62.7
Alkalinity (ANC$_{4.5}$), mmol/L	1.94	1.87
Acidity (BNC$_{8.3}$), mmol/L	0.0	0.36
Chemical oxygen demand, (COD)$_{Mn}$, mg/L	0.97	0.91
Total dissolved solids (TDS), mg/L	510	530
Cl, mg/L	58.9	60.4
NO_3^-, mg/L	2.9	2.9
SO_4^{2-}, mg/L	176.9	176.9
HCO_3^-, mg/L	118.3	114.1
CO_2, mg/L	0.0	15.8
NH_4^+, mg/L	0.12	0.07
Ca, mg/L	83.6	80.3
Mg, mg/L	20.9	20.9
Ca + Mg, mmol/L	2.94	2.86

Table 2
Filtration conditions

Parameter	Experiment 1	Experiment 2
Grain size, mm	0.8 – 1.6 + 1.5 – 2.5	0.8 – 1.6 + 1.5 – 2.5
Medium height, cm	130	130
Average flow through column, mL/min	183.7	175.7
Average filtration rate, m/h	5.61	5.37
Filtration total time, h	2,290	1,411
Average residence time in column, min	13.89	14.52

2.2. Water treatment model

To verify the effectiveness of the removal of the iron and manganese from the water resources in the locality of WTP Kúty, filtration columns containing Filtralite were used. The filtration columns were made of glass. The parameters of the filtration columns are as follows: a diameter of 5.0 cm, a height of 2 m, an internal area of 19.625 cm^2, a 130 cm height of the filtration medium, and the volume of the filtration medium of 2,551 cm^3. A simple device that allows for the splitting of the incoming water either for washing or filtration through a valve system was used.

The raw water was passed through the filtration equipment, and the removal of the Fe^{2+} and Mn^{2+} ions was carried out directly in the filtration column beds (the media). The quality of the raw water (Fe and Mn content) and treated water at the outlet from the separate filtration column was monitored two times a day during the experiments. At the same time, the amount of water (the filtration rate) at the outlet from the column was measured.

2.3. Water analysis

For determining the concentrations of iron and manganese, a DR 2800 (Hach-Lange) spectrophotometer and the 8149 method (the PAN method, a wavelength of 560 nm, and a concentration range of 0.006–0.7 mg/L Mn) for determining the manganese was used. The 8008 method (FerroVer reagent, a wavelength of 510 nm, and a concentration range of 0.02–3.0 mg/L Fe) for determining the iron was used. All samples were collected into 100 mL plastic bottles and immediately acidified with 0.1 mL of highly pure nitric acid

(Merck, KGaA, Darmstadt, Germany). The oxygen and pH of the raw water were monitored with the Hach-Lange HQ40d multiparameter probe.

2.4. Properties of used materials

The Filtralite (imported from Norway) is a filter medium based on lightweight expanded aluminium silicate clay aggregates with a high degree of porosity. Filtralite is made by burning clay at about 1,200°C, which is followed by crushing and sieving. The material has a porous structure which, when crushed, exposes a large surface area. The dry particle densities were in a range of 500–1,600 kg/m^3 with a corresponding dry bulk density of 300–900 kg/m^3 and aggregate sizes in a range of 0–20 mm (Table 3).

The aggregates did not release any harmful substances, and the solubility of the acid was minimal. Despite its low density and high porosity, Filtralite has a high resistance to abrasion.

Filtralite has ideal properties to work with as a good filter media in both single and dual media filters for the filtration of coagulated water. In dual media filters, Filtralite has proved to be as good as, or better than, comparable media. By replacing the most traditional top-layer filter material, that is, anthracite, with Filtralite, the time between backwashes can be increased by about 25%. This means fewer stops for backwashes and the reduced use of backwash water, which results in a more stable quality of the water and lower operational costs.

An even better filter performance can be obtained by replacing the sand in the bottom layer with Filtralite. The so-called Filtralite Mono-Multi filter, which consists of a bottom layer of Filtralite HC 0.8–1.6 mm and a top layer of Filtralite NC 1.5–2.5 mm, results in extremely low head loss and good water quality. Due to the low density of both layers, the water velocity needed for backwash is much lower than that for filters using sand as a bottom layer.

Filters with Filtralite can be operated within a large range of filtration rates. The filtration rate will always be dependent on the configuration of the filter and the treatment process. Existing Filtralite filters operate from about 2 m/h up to around 20 m/h [37–39].

Before starting filtration, the HC 0.8–1.6 and NC 1.5–2.5 (at a ratio of 1:1) filter materials were added to the glass columns with tap water and dipped for 2 weeks. Then, the filter media were rinsed with tap water in the opposite direction from the filtration, that is, from the bottom to the top, when the water was discharged from the washing into the sewerage system. During the washing, the column flow rate was chosen so as to avoid the leaching of the filter media, which became suspended. A time of 5 min was used for all backwashing.

Table 3
Different size of filter media and their physical properties [35,36]

Properties	HC 0.8–1.6	NC 1.5–2.5
Grain size, mm	0.8–1.6	1.5–2.5
Particle density, kg/m^3	1,700	1,050
Bulk density, kg/m^3	850	500
Appearance	Crushed particles, porous surface structure	
Floating particles, %	2	2
Particle porosity, %	41	73
Voids, %	62	67

A 2.5% solution of $KMnO_4$ was used for the regeneration of the Filtralite. At the beginning of our experiments, we filtered 12 L of this solution through the Filtralite at the same filtration rate as in the experiments. Later, we left the filter material immersed in a solution of $KMnO_4$ for 1 week. Before starting the experiment, we washed the filter medium with water that did not contain Fe and Mn.

Before and after the experiments, the Filtralite HC 0.8–1.6 and NC 1.5–2.5 filtration materials were analyzed with a Jeol JXA-840A X-ray microanalyzer by the EDS system. The samples were evaporated with a thin carbon layer to ensure their electrical conductivity. The quantitative analysis of every sample was determined in three different areas, and the mean value was then calculated. The microstructure was observed by scanning electron microscopy (TESLA BS 300).

The surface properties of the sorption materials were studied through the physical adsorption of nitrogen at the temperature of liquid nitrogen (–197°C) by the volumetric method using an ASAP 2400 (Micromeritics). Before the measurements, the samples were activated for 15 h at a temperature of 350°C and a vacuum of less than 2 Pa. The adsorption data were processed using a standard Brunauer -Emmett -Teller (BET)-isotherm with a linearization in the range $0.05 \leq p/p_0 \leq 0.3$ (specific surface area, S_{BET}). The desorption branches of the isotherms were used for calculating the pore size distribution by the standard BJH method (the maximum on the pore size distribution curve r_k). The total pore volume was estimated from the nitrogen-adsorbed quantity at a relative pressure of $p/p_0 = 0.99$.

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) and
- raw water after aeration (sampling point No. 2)

The results of the removal of the manganese from the raw water after aeration and the addition of lime (sampling point No. 1) are documented by Fig. 4, in which the concentration of manganese in the raw water and the values measured after passing it through the monitored filter materials are shown. The figure also shows the manganese limit value (0.05 mg/L) in the drinking water as defined under Government Regulation No. 496/2010 on Drinking Water. The arrow presents the time of the regeneration of the filter media.

Fig. 4 (top) shows that in optimal conditions for contact filtration (pH 8.4–8.6; an oxygen content of 56%–57% saturation), the Filtralite material was reached after multiple regeneration with $KMnO_4$ to increase its efficiency and modify the surface with a layer of MnO_2. After seven regenerations with $KMnO_4$, the effectiveness of the removal of Mn from the water was better, which is illustrated in Fig. 4 (bottom); with

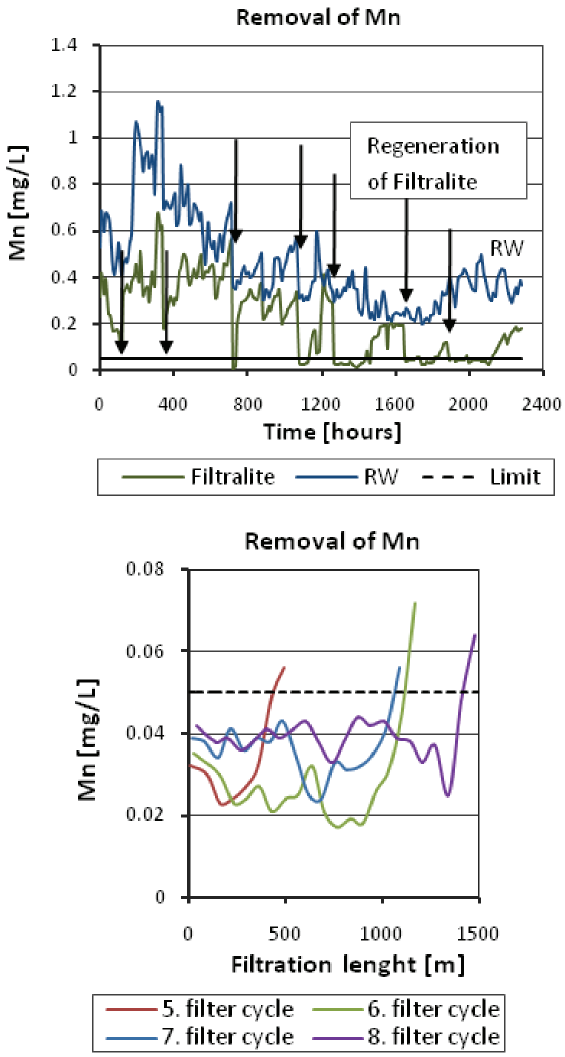

Fig. 4. Course of the removal of the manganese from the water depending on the operation time (top) and the length of the filtration for the last four filtration cycles (bottom).

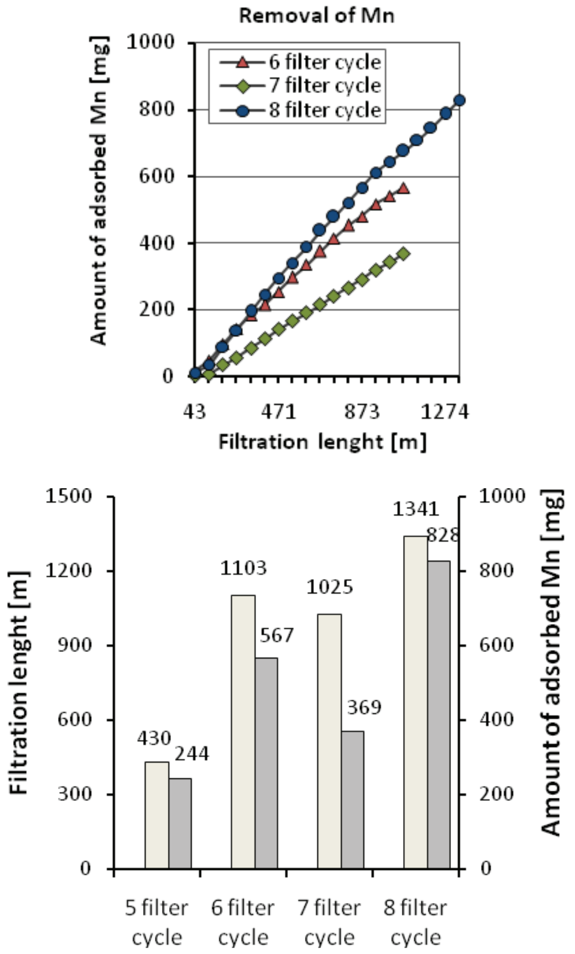

Fig. 5. Course of the amount of adsorbed manganese in the filtration media, depending on the length of the filtration (top) and the values of the amount of adsorbed manganese in the filtration media, and the length of the filtration when reaching the limit concentration 0.05 mg/L of Mn at the outlet of the media for the last four filtration cycles (bottom).

each filtration cycle the filter's length increased (except for cycle 7). The filter material was backwashed approximately every 3–4 d.

According to the material balance of the manganese in this experiment, Fig. 5 shows the amount of adsorbed manganese depended on the length of the filtration, as well as on the amount of adsorbed manganese in the adsorption media and the length of the filtration when reaching the limit concentration Mn (0.05 mg/L) at the outlets of the Filtralite Mono-Multi media.

Fig. 6 shows the progress made in removing the iron from the water for sampling point No. 1 (after the water's aeration and the addition of lime). The concentration of iron in the raw water changed considerably, depending on the production of the precipitated $Fe(OH)_3$, which gradually clogged the system. As seen in Fig. 6 on the bottom, after the creation of the layer of MnO_2 on the surface of the Filtralite grains, its efficiency gradually increased, and the filtration cycles were extended when the concentration of the Fe was lower than the limit value of 0.20 mg/L for drinking water.

The effectiveness of the removal of the Fe was also influenced by the water treatment process (aeration, alkalization, and filtration), the pH of the water, the filtration rate, sludge capacity, and the materials used.

According to the material balance of the iron present during this experiment, Fig. 7 shows the amount of adsorbed iron, depending on the length of the filtration, as well as the amount of adsorbed iron in the adsorption media and the length of filtration when reaching the limit concentration of Fe (0.20 mg/L) at the outlets of the Filtralite Mono-Multi media.

Fig. 8 shows the results of the removal of the iron and manganese from the raw water after aeration (sampling point No. 2). The concentrations of iron (Fig. 8, bottom) and manganese (Fig. 8, top) in the raw water and the concentration measured after they passed through the monitored filter materials and the manganese or iron limit values in the drinking water as defined under the Regulation of the

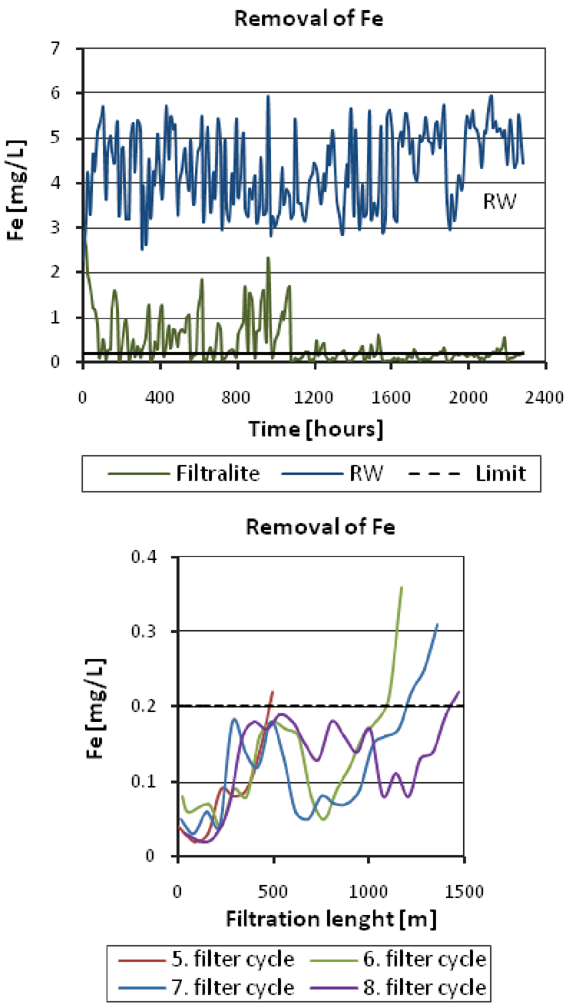

Fig. 6. Course of the removal of the iron from the water, depending on the operation time (top) and the length of the filtration for the last four filtration cycles (bottom).

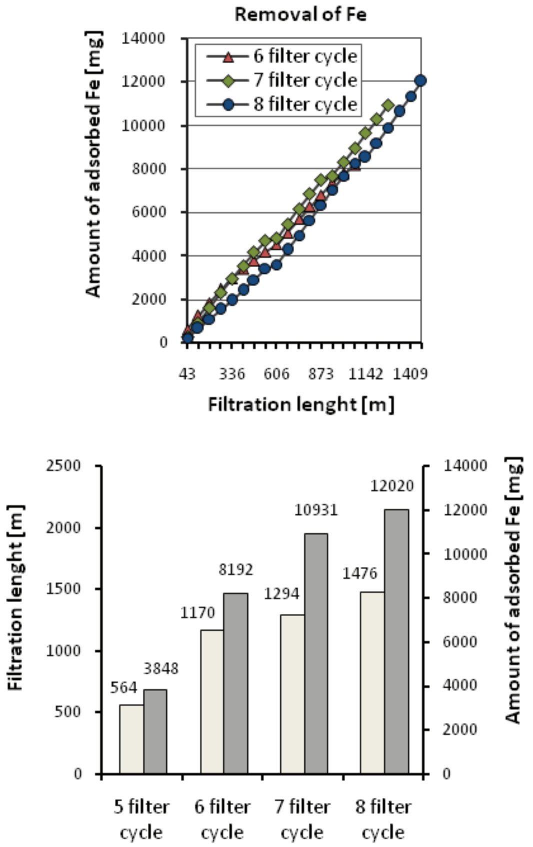

Fig. 7. Course of the amount of adsorbed iron in the filtration media, depending on the length of the filtration (top) and the values of the amount of adsorbed iron in the filtration media, and the length of the filtration when reaching the limit concentration 0.20 mg/L of Fe at the outlet of the media for the last four filtration cycles (bottom).

Government of the Slovak Republic are shown. The arrow presents the regeneration of the filter media.

Fig. 8 (top) shows that the effect of the changes in the quality of the raw water (pH 6.8–7.2, oxygen content from 59% to 60% saturation) on the efficiency of the manganese removal from the water through the filtration media improved significantly. For this type of water, Filtralite is not effective, even though this experiment was conducted after the first experiment, when a layer with MnO_2 was created on its surface. The concentrations of the manganese after the filtration through Filtralite were approximately the same as the values in the raw water and, in some cases, even higher (this was due to the release of the manganese from the filtration bed). The filter media were backwashed approximately every 3–4 d; for the backwashing, water without Fe and Mn was used.

Fig. 8 (bottom) shows the course of the removal of the iron from the water for sampling point No. 2. The concentration of the iron in the raw water changed significantly, depending on which well was used for the pumping or production of the precipitated $Fe(OH)_3$, which gradually clogged the system. In general, the Filtralite material 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 Government Regulation No. 496/2010 on Drinking Water.

As to the efficiency of the removal of the Fe from the water, it was influenced by the treatment process used (oxidation, alkalization, and filtration), the pH value, the filtration rate, the sludge capacity of the Filtralite, and backwashing. The removal of Fe at a pH range of 6.8–7.2 did not occur as contact filtration but mainly as adsorption.

Within the frame of the experiments, the chemical composition and surface properties of the filter materials used were studied. The chemical composition was determined by X-ray microanalysis methods; the values are listed in Table 4.

Figs. 9 and 10 illustrate the differences in the character of the Filtralite NC 1.5–2.5 and Filtralite HC 0.8–1.8 surface filtration materials.

Changes in the Filtralite surface textures before and after the experiments are illustrated in Figs. 11 and 12. The surface properties of these materials are summarized in Table 5.

The adsorption isotherms of the Filtralite HC and NC samples (Fig. 10) of type IV show H2-type hysteresis loops, which are typical of mesoporous materials. The specific surface areas (S_{BET}) are 2.39 and 0.29 m^2/g for the Filtralite HC and Filtralite NC samples, respectively. Their total pore volumes V_a are 0.0034 and 0.0009 cm^3/g. At the end of all the experiments, the specific surface areas increased to 6.44 and 5.0 m^2/g for the Filtralite HC and Filtralite NC samples. The total pore volumes after the experiments were 0.0117 and 0.0094 cm^3/g. Table 5 shows that Filtralite HC 0.8–1.6 and Filtralite NC 1.5–2.5 are materials with predominant mesopores and macropores (S_t = value of the surface area with mesopores + macropores and external area), with a minimum of micropores (V_{Micro} – volume of micropores).

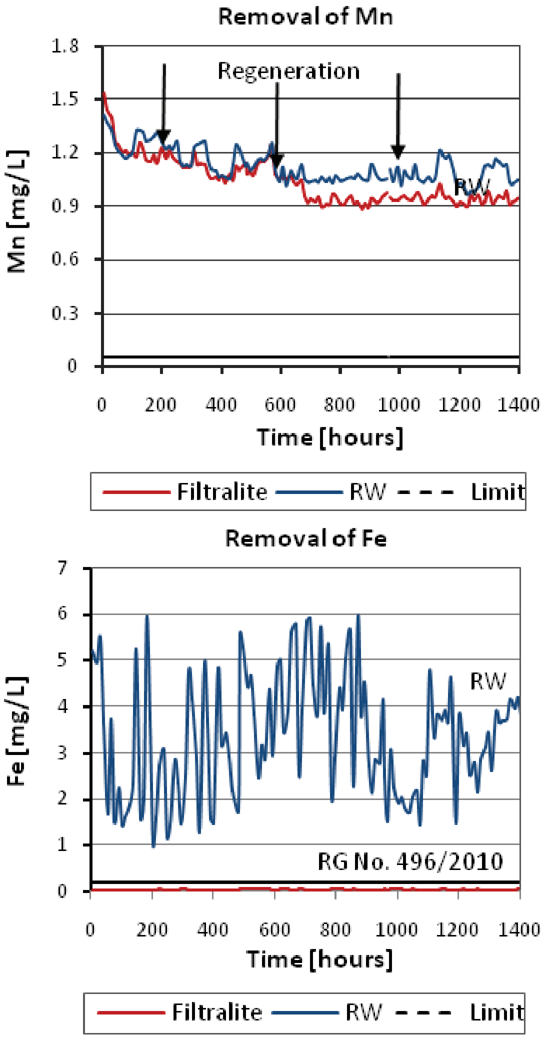

Fig. 8. Course of the removal of the manganese (top) and iron (bottom) from the water depending on the operation time.

4. Conclusion

The research conducted allowed us to draw the following conclusions:

- The pilot-scale experiments of iron and manganese removal from the groundwater at WTP Kúty (Slovakia) using the two-layer material Filtralite Mono-Multi and two different conditions of water quality (pH and O_2 content) were demonstrated.
- The highest efficiency of the manganese removal was achieved at optimal conditions for contact filtration (pH 8.4–8.6; oxygen content of 56%–57% saturation) after the creation of the MnO_2 contact layer on the surface of the Filtralite Mono-Multi. The operation time, the length of the filtration, the amount of adsorbed manganese, the effectiveness of the removal of the Mn below the limit value for Mn in drinking water (0.05 mg/L), and the time between regenerations is gradually lengthened.
- In the case of the removal of iron from the water under the same conditions, the Filtralite Mono-Multi was efficient in the removal of Fe from the water. The effectiveness of the removal of the Fe was influenced by the water treatment process (aeration, alkalization, and filtration), the pH of the water, the filtration rate, the adsorption, or the sludge capacity materials used. The effectiveness of the removal of the Fe below the limit value for Fe in the drinking water (0.2 mg/L) gradually improved.
- The Filtralite Mono-Multi was not efficient in the removal of Mn from water at pH 6.8–7.2; for the removal of

Table 4
Chemical composition of Filtralite before and after experiments

Compound in mass, %	Before experiments		After experiments	
	HC 0.8–1.6	NC 1.5–2.5	HC 0.8–1.6	NC 1.5–2.5
SiO_2	55.82	51.98	50.36	49.05
Al_2O_3	15.36	18.62	13.01	13.52
K_2O	5.59	6.17	8.19	8.20
CaO	3.78	2.48	3.98	3.76
MgO	2.35	2.76	2.05	2.30
Na_2O	1.35	1.95	1.45	1.37
TiO_2	1.12	1.22	1.12	1.04
MnO_2	0	0	6.27	5.11
Fe_2O_3	13.57	14.02	13.76	15.93

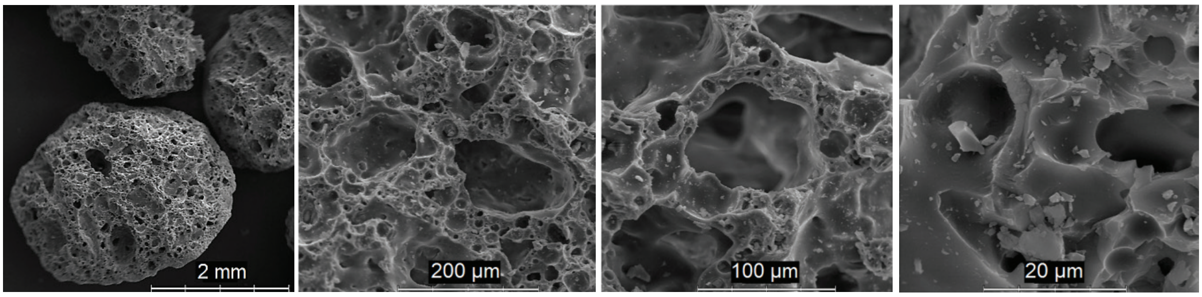

Fig. 9. The microstructure of the Filtralite NC 1.5–2.5 (40×, 250×, 1,000×, and 5,000× magnification).

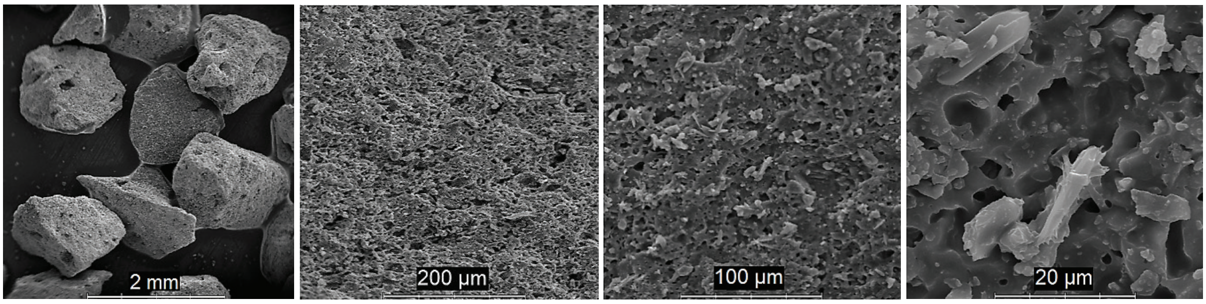

Fig. 10. The microstructure of the Filtralite HC 0.8–1.5 (40×, 500×, 1,000×, and 5,000× magnification).

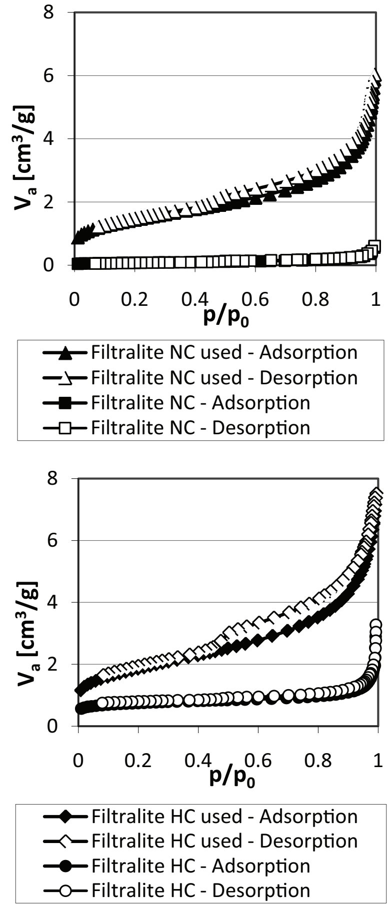

Fig. 11. Adsorption isotherms of Filtralite NC (top) or Filtralite HC (bottom) samples before and after the experiments.

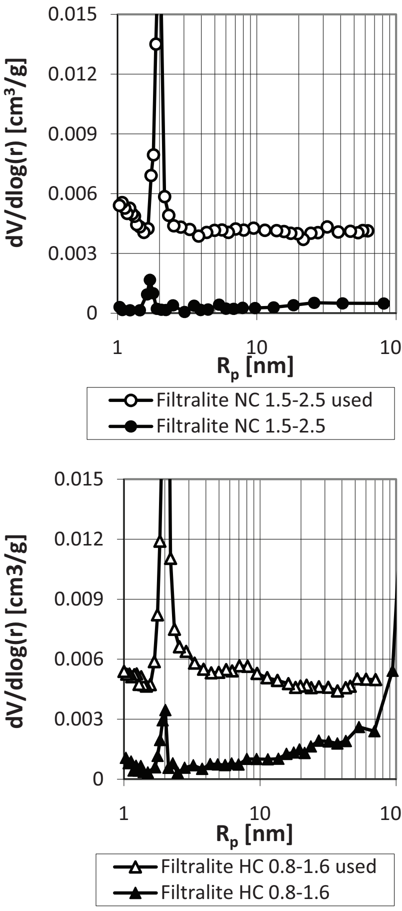

Fig. 12. Pore size distributions for Filtralite NC (top) and HC (bottom) before and after the experiments.

Table 5
Surface properties of materials Filtralite

Surface properties	Filtralite			
	Before experiments		After experiments	
	HC 0.8–1.6	NC 1.5–2.5	HC 0.8–1.6	NC 1.5–2.5
S_{BET}, m^2/g	2.39	0.29	6.44	5.0
S_t, m^2/g	1.12	0.28	5.61	4.4
V_a, cm^3/g	0.0034	0.0009	0.0117	0.0094
V_{Micro}, cm^3/g	0.0007	0.0000	0.0004	0.0003

manganese by contact filtration, a pH of water of more than 8 [10,18,19], oxidation conditions, and surface layer of MnO_2 is required. The removal efficiency of Mn influences the concentration of Mn and Fe in treated water.

- The groundwater at WTP Kúty has a lower alkalinity (1.7–1.9 mmol/L), but a higher concentration of sulfates and chlorides. The water was used in our experiments after the aeration. Since it has a higher redox potential (more than 400 mV), it follows that it would not result in the poorly soluble $MnCO_3$, but the solid MnO_2, as shown by the chemical composition of Filtralite and the values 5–6 mg/L of MnO_2 on their surface.
- The composition of the raw water and the leaching of the material caused a change in the chemical composition of the Filtralite, a reduction of SiO_2 and Al_2O_3, and an increase of MnO_2 on the material's surfaces compared to the original composition. At the end of all the experiments, the Filtralite HC 0.8–1.6 and Filtralite NC 1.5–2.5 material contained 6.27 wt% MnO_2 and 5.11 wt% MnO_2, respectively.
- At the same time, there was also a change in the surface (sorption) properties of the Filtralite Mono-Multi material; the specific surface areas increased to 6.44 and 5.0 m^2/g for the Filtralite HC and Filtralite NC samples.
- The Filtralite Mono-Multi filter material can be used to remove Fe and Mn; the advantage of Filtralite Mono-Multi is its greater adsorption and sludge capacity, higher flow rates for filtration, and a lower consumption of water for backwashing. This advantage can affect the economics of the water treatment.

Acknowledgments

Experimental measurements were carried out within the research projects VEGA 1/0400/15 from the Scientific Grant Agency of the Slovak Ministry of Education, Science, Research and Sport and grant number APVV-15-0379 from the Slovak Research and Development Agency.

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