

# Efficiency of Removal of Iron, Manganese, Ammonium and Organic Matter from Groundwater

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**Abstract.** The acceptable concentrations in groundwater are usually in excess of iron, ammonium and manganese. These compounds are inefficiently removed by means of ordinary technologies of ammonium ions, iron and manganese compounds removal from groundwater (water aeration and filtration through granular filter fillings) where groundwater contains high concentrations of organic compounds. Increased concentrations of organic compounds in groundwater occur in well fields where exploited aquifers have contact with surface water wells and are supplemented with water from open water bodies. Such well field is located in the town of Nida (Lithuania). The norms permitted by Council directive 98/83/EC on the quality of water intended for human consumption are exceeded by iron, ammonium, manganese and organic compounds in this well field. The present study examines the efficiency of drinking water treatment technology of three-stage filtration with aeration and insertion of coagulant (polyaluminum chloride) where ammonium ions, iron, manganese and organic compounds are removed from groundwater in an integral manner. Three fillings were used for filtration: quartz sand, zeolite and quartz sand with oxidizing bacteria. The drinking water treatment technology examined removes ammonium ions, iron, manganese and organic compounds from groundwater in an integral manner until the requirements of the norms of directive 98/83/EC are achieved.

**Keywords:** groundwater, iron, manganese, ammonium, organic matter, filtration, coagulation.

**Conference topic:** Water engineering.

## Introduction

The acceptable norms of 98/83/EC are usually exceeded by iron concentrations in groundwater. Upon high concentrations of iron compounds in groundwater, the concentrations of ammonium ions and manganese compounds also exceed the acceptable norms of 98/83/EC (0.5 mg/L and 50 µg/L). These compounds are inefficiently removed by means of ordinary technologies of ammonium ions, iron and manganese compounds removal from groundwater (water aeration and filtration through granular filter fillings) (Hanbay *et al.* 2009; Bruins *et al.* 2015) where groundwater contains high concentrations of organic compounds. Upon high concentrations of organic compounds in groundwater, a hydrophobic membrane is formed on the surface of filter filling grains which is difficult to remove by simple cleaning (Valentukevičienė, Rimeika 2004). Due to the formation of this membrane the removal of ammonium ions, iron and manganese compounds from water is disturbed. Organic compounds uptake oxygen first which is necessary for the further oxidation of iron compounds, ammonium ions and manganese compounds. Metals may form complex organic compounds (Munter *et al.* 2008). The removal of iron complex organic compounds becomes complicated and they are not removed by merely aeration and filtration through granular fillings. Organic compounds condition the taste and smell of water that are not acceptable for consumption (Shao *et al.* 2013). During the disinfection process dissolved organic compounds constitute secondary disinfection compounds such as haloacetic acid and trihalomethanes (Qu *et al.* 2012; Zhou *et al.* 2014; Bongiovani *et al.* 2016). Most of them are active pharmacologically and have qualities harmful to the human body (Pavagadhi, Balasubramanian 2013). When groundwater contains organic compounds, ammonium ions, iron and manganese compounds are efficiently removed by means of chemical water treatment methods (Rahman *et al.* 2010). In employing chemical water treatment methods various chemical reagents (coagulants, oxidants, acids and alkalis) are used in the technology (Potgieter *et al.* 2005). The application of chemical reagents makes the process of water treatment more complex as it requires larger investments and operating costs (chemical reagents, tankages for reagents, reagent dosing equipment). As groundwater is used for drinking water treatment, it is important to use water treatment methods which require as few additional chemical reagents as possible.

The manner in which drinkable water is treated has been investigated: by removing organic compounds from surface water (Odegaard *et al.* 2010; Matilainen *et al.* 2010; Tang *et al.* 2016), by removing iron, manganese and ammonium ions from groundwater (Tekerlekopoulou, Vayenas 2008) and iron complex organic compounds (Munter *et al.* 2008). However, studies on drinkable water treatment technologies by which all the said compounds are removed

from groundwater in an integral manner are lacking. Therefore, the present study describes and provides the structure for a particular sequence of three-stage filtration with aeration and the insertion of coagulant (polyaluminum chloride) (Tang *et al.* 2015; Tang *et al.* 2016; Sperczyńska *et al.* 2016) where ammonium ions, iron, manganese and organic compounds are removed from groundwater in an integral manner with the minimum number of reagents used. Also, the efficiency of this technology was examined over time.

## Materials and methods

### Water well and characterisation

The drinkable water treatment plant stand is constructed at Neringos Vandenyys, Ltd in Nida well field in Lithuania. Nida well field (55°33'N21°04'E) is situated in the Curonian Spit, which is washed by the Baltic Sea from the one side and the Curonian Lagoon is on the other side. Nida well field belongs to the groundwater open well field group. It is a well field which exploits open surface groundwater layers (lagoon water). The source well of the groundwater of this well field is the groundwater flow flowing through the aquifer which is constantly refilled up to the groundwater level by the sediment that comes through the aeration zone. Nida well field is located 3 km to the North from the city centre. Its eastern side meets the lagoon. The groundwater level of Nida well field settles in the depth of 2–5 m and in the lagoon coast it practically coincides with the lagoon level. The aquifer is constituted by medium and small marine-eolian sand the thickness of which is 14–20 m. The average yearly capacity of Nida well field is equal to 533 m<sup>3</sup>/h (lowest in December and highest in August). In this well field the concentrations of iron, manganese, ammonium and organic compounds are in excess According to Klimas (2006), this well field has no source of pollution and these compounds in water are sourced from groundwater accumulated in marine sediment. Water quality indicators of the composite of wells of Nida well field are presented in Table 1.

Table 1. Groundwater quality data average for the Nida well field (Courtesy of Neringos Vandenyys, Ltd.) and measured for the well no. 2

Water quality indicator, units	Average	For well no. 2
pH	7.45	7.39 ± 0.07
Permanganate index, mgO <sub>2</sub> /L	6.27	6.02 ± 0.32
Total iron, µg/L	4280	5650 ± 220
Ammonium, mg/L	3.17	1.66 ± 0.08
Manganese, µg/L	250	252 ± 10
Colour, mgPt/L	53	± 2

### Water treatment facility

The setup of the test plant for drinking water treatment is sketched in Fig. 1. The water from the well was pumped into an open aerator. The water debit was 100 L/h. The aerator is an open container for 200 L of water, which is sprayed by a specially designed sprayer and reaches the container flowing down via three percolated steps to improve the saturation of water with air oxygen and enhance the oxidation of hydrogen sulphide and iron. The next pump delivers the water to the first filter acting at the filtering rate of 2.5–3.0 m<sup>3</sup>/m<sup>2</sup>/h. Before the filter, polyaluminum chloride, acting as coagulant, is introduced using coagulant dosing pump to maintain the coagulant concentration in the water entering the filter at 5 mgAl/L. The coagulant concentration is fixed to optimize formation of flakes of organic compounds and coagulant. The flakes are removed by filtration through sand filter. The water with coagulant flows through a plastic pipe, 50 m long and 25 mm in diameter, acting as a reaction chamber, which ensures the reaction time sufficient for flake formation. The water passes the reactor in 22 min. and enters the first pressure filter, which is 1200 mm high and 250 mm in diameter. The filter is filled in with quartz sand, grain size fraction 1–2 mm. The filter decreases the concentrations of iron and organic compounds. After passing the filter, the water flows to a closed aerator, 1100 mm high and 200 mm in diameter, which is fed with oxygen by using a compressor. The aerator enriches the water with oxygen, which is necessary for further oxidation of ammonium ions and manganese compounds. Then, the water enters the second pressure filter, 1200 mm high and 250 mm in diameter, which contains zeolite (size fraction 0.3–0.6 mm). The third pressure filter, 1200 mm high and 250 mm in diameter, is filled in with quartz sand (size fraction 1–2 mm) containing oxidizing bacteria. The output of the third filter delivers clean water.

The water flow meter is installed after the pump delivering the water into the filters. The manometers installed before and after each filter measure the pressure drop on the filter. The pressure difference is used as an indicator to start filter washing. The filters are washed when either the pressure drop on the filter reaches 0.6 bar or the water quality indicators decrease below the standard limits. Backwashing was used for the down-flow filters employed in the facility. Filtered water collected into 1 m<sup>3</sup>-volume containers was used for washing at a rate of 20 m<sup>3</sup>/m<sup>2</sup>/h for 15 min.

The water treatment facility was started to use in April 2012 and was tested for 8 months. The water samples, 1 L in volume, were being extracted directly from the well and from 6 locations in the facility: after the open aerator, the

reaction chamber, the first filter, the closed aerator, and the second and third filters. The samples were stored in cooled containers at temperature fixed at 5 °C. The samples were being delivered to the testing laboratory within 24 hours. The measurements of iron, ammonium, manganese, and organic matter concentrations, colour, pH, and amounts of dissolved oxygen and rest aluminium have been carried out using the methods specified by the international ISO standards. The measured values presented below are the averages of 5 measurement results with deviations below 5%.

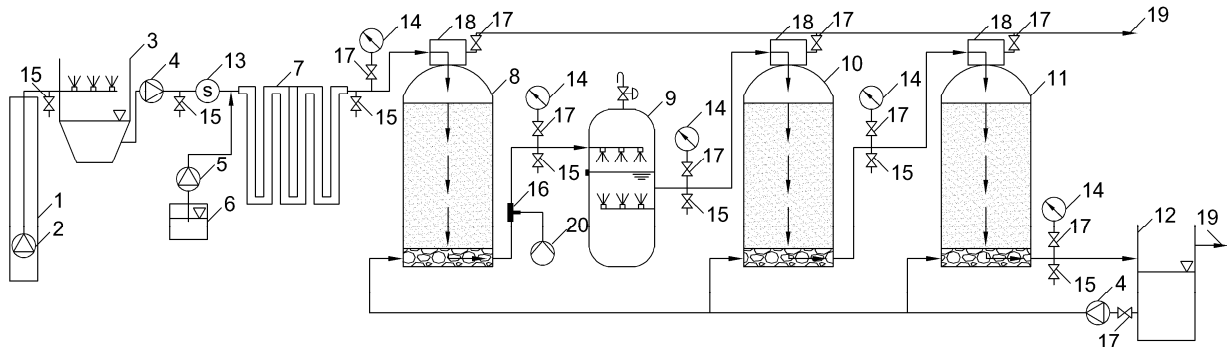


Fig. 1. Setup of the test plant for drinking water treatment:

well (1); pump (2,4); open aerator (3); coagulant dosing pump (5); coagulant tank (6); reaction chamber (7); filter (8, 10, 11); closed aerator (9); clean water tank (12); water meter (13); manometer (14); sample taking place (15); injector (16); valve (17); filter control valve (18); discharge into wastewater network (19); compressor (20)

## Results and discussion

Upon the start of operation, the water treatment facility was efficiently removing organic compounds, iron compounds, ammonium ions and manganese compounds. However, it is important to identify the period of time during which these compounds are removed efficiently by the filters. Also, the number of working days and the amount of water to flow for the filters to be cleaned and/or regenerated need to be determined. Water samples were collected after a particular amount of water has flown 1, 2 and 3 days after filter cleaning. The changes of iron compound concentration upon filtration through three filters over time are presented in Figure 2.

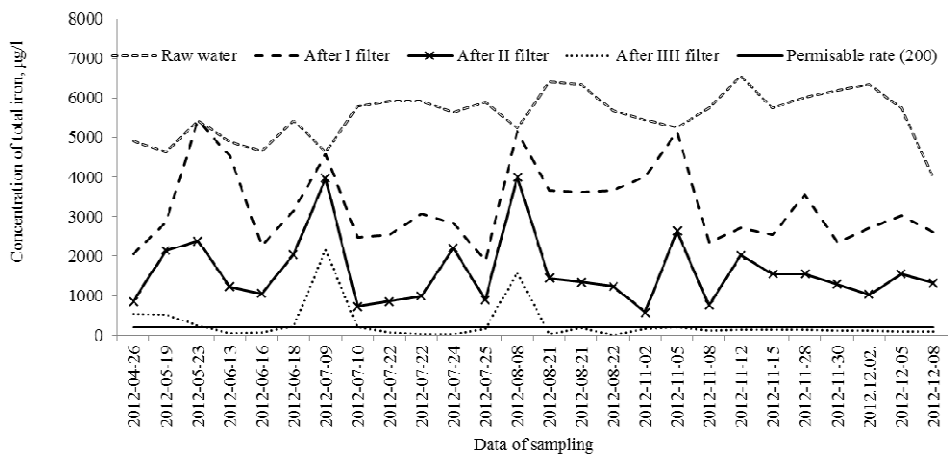


Fig. 2. Changes of total iron concentration throughout plants

The efficiency of reduced total iron concentration depends on the iron concentration in the untreated water, the concentration of dissolved oxygen in the water and filter operation time. It is seen from Figure 2 that the total iron concentration in untreated water changes from 4000 to 7000 µg/L. The higher iron concentration, the faster fouling and the more frequent cleaning of filters. The oxygen concentration in the water varies between 6.16 and 6.93 mgO<sub>2</sub>/L before it enters the first filter. This means that the oxygen concentration is sufficient for the oxidation of iron compounds. Although the iron concentration is reduced to 05.23 after the first filter, its concentration exceeds the permissible hygiene rate. It is related with insufficient oxygen saturation. After the compressor is connected to the closed aerator and the concentration of dissolved oxygen is increased in the water, the total iron concentration no longer exceeds the permissible hygiene rate. The increased total iron concentration after the first filter is visible at four points

(05.23, 07.09, 08.08 and 11.05). These increases of iron concentrations are related with the fact that the first filter was working without being cleaned for two (05.23 and 11.05) or three (07.09 and 08.08) days. Therefore, it can be concluded that the first filter needs to be cleaned every day in order to ensure effective operation of the first filter by reducing the total iron concentration. The increased total iron concentration is observed without cleaning the second and the third filters for three days (07.09 and 08.08). Therefore, it is recommended that the second and the third filters are cleaned at least every second day.

The changes of ammonium ions concentration as the water is filtered through three filters over time are presented in Figure 3.

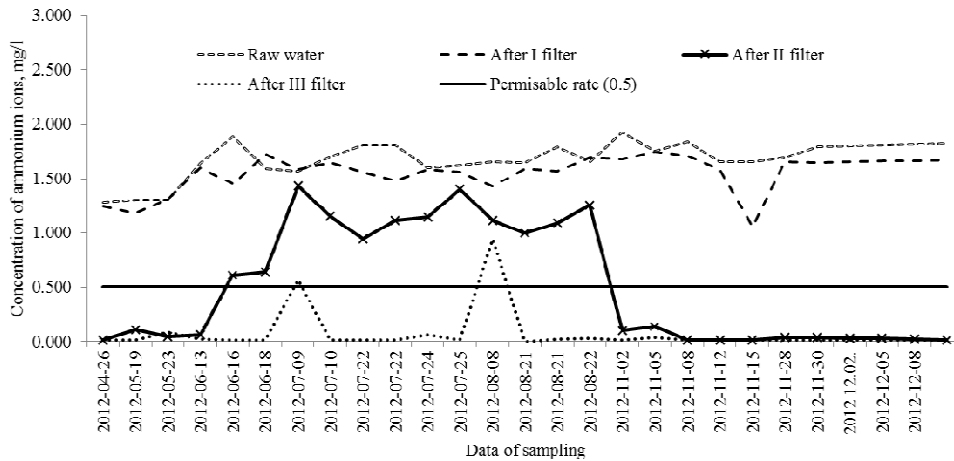


Fig. 3. Changes of ammonium ions concentration throughout plants

The figure above illustrates that the concentration of ammonium ions is reduced after the first filter, although very slightly. Such results can be explained by the fact that iron compounds are not fully removed; therefore, the amount of oxygen is not sufficient for an ammonium ion to oxidize. As all oxygen supplied from the open aerator is used for the oxidation of sulphur dioxide and iron compounds, the concentration of ammonium ions is not reduced after the first filter. Zeolite constitutes the filling of the second filter. As can be seen from the figure above, zeolite efficiently reduces the concentration of ammonium ions in the water from the beginning of water treatment facility operation. The ammonium concentration is reduced from 1.24 to 0.01 mg/L. As the water is further filtered through the zeolite filling, the concentration of ammonium ions is low and it does not exceed the permissible hygiene rate. However, after 42 m<sup>3</sup> of water have passed (06.13), the concentration of ammonium ions after the second filter remains the same as it was after the first filter. The concentration of ammonium ions exceeds the permissible hygiene rate. This might be the consequence of poor filter cleaning. After further cleaning of the filters, the ammonium concentration is reduced by 58%; however, it exceeds the permissible hygiene rate (0,61 mg/L). After 73 m<sup>3</sup> of water have passed, the efficiency of cleaning slightly increased to 62%. However, the concentration of ammonium ions exceeds the permissible hygiene rate. As the water is further filtered, the concentration of ammonium ions is increased after the second filter, the efficiency of ammonium ions removal is decreased and the concentration of ammonium ions is not reduced to less than 1 mg/L. This means that zeolite became contaminated and it needs to be regenerated. Previous studies have shown that the concentration of ammonium ions in water may also be efficiently reduced by means of quartz sand with oxidizing bacteria. Therefore, after 125 m<sup>3</sup> of water have passed (08.25), zeolite was replaced by quartz sand with oxidizing bacteria. It is seen from the figure that the concentration of ammonium ions is efficiently reduced and it no longer exceeds the permissible hygiene rate.

The third filter filled with quartz sand with oxidizing bacteria removes ammonium ions efficiently. The concentration of ammonium ions no longer exceeds the permissible hygiene rate after the third filter, except for several cases (07.09 and 08.08) where the filters remained uncleaned for three days. These data show that the zeolite filter which loses its efficiency quickly is not needed for the removal of ammonium ions and quartz sand with oxidizing bacteria and a continuous supply of oxygen are enough. However, such filter filling is only efficient where the ammonium concentration is lower than 2 mg/L.

The third filter is intended for the removal of manganese compounds. This filter is filled with quartz sand which contains oxidizing bacteria. The changes of manganese compounds concentration as the water is filtered through three filters over time are presented in Figure 4.

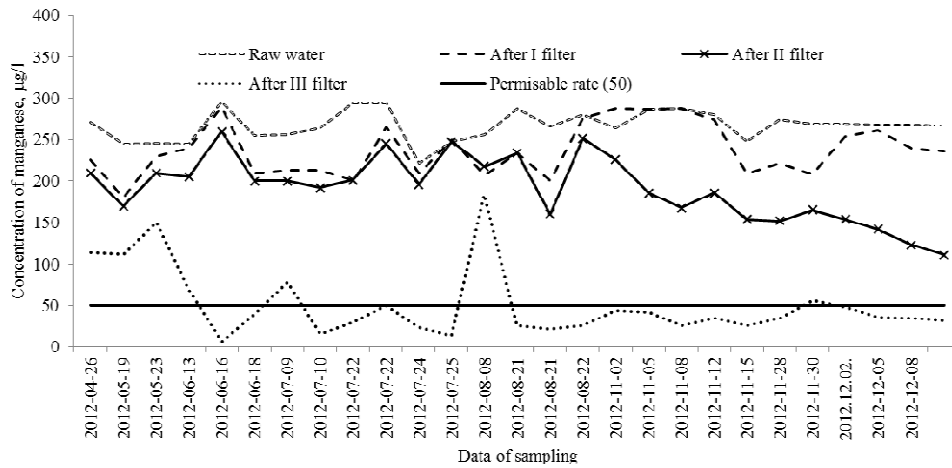


Fig. 4. Changes of manganese concentration throughout plants

In order to remove manganese compounds without employing chemical material catalyzers, sufficient and consistent amount of oxygen and the respective value of pH index are necessary and organic compounds, iron compounds and ammonium ions need to be removed before. Although iron compounds are removed in the first filter, iron compounds are not removed until concentrations are low; also, ammonium ions are not removed after this filter and, therefore, as seen from the figure, during the whole period of operation of water treatment facilities manganese compounds are not removed after the first filter. Although the oxygen concentration (6 mgO<sub>2</sub>/l) is sufficient for the oxidation of manganese compounds, this filling contains no microorganisms that catalyze the oxidation of manganese. The second filter filled with zeolite does not remove manganese compounds. The manganese concentration remains stable after the second filter over time. However, if quartz sand with oxidizing bacteria is placed into the second filter instead of zeolite, the concentration of manganese compounds starts to decrease after the second filter. The efficiency of manganese compounds removal in the second filter filled with quartz sand with oxidizing bacteria reaches 48%. However, the concentration of manganese compounds did not reach the permissible hygiene rate. Such results were determined by the fact that the water does not contain a sufficient amount of oxygen necessary for the oxidation of manganese compounds. After the third filter intended for the removal of manganese compounds the concentration of manganese compounds is reduced to the acceptable norms after 42 m<sup>3</sup> of water have passed (05.23). In the beginning the concentration of manganese compounds exceeded the permissible hygiene rate after the third filter because the oxygen supply was insufficient. Upon increased oxygen concentration in the water, the concentration of manganese compounds after the third filter no longer exceeds the permissible hygiene rate. The increase in the manganese concentration (07.09 and 08.08) is related with filter cleaning performed every third day.

These tests show that the concentration of manganese compounds remains stable over time when using zeolite and quartz sand filters. The filter filling of quartz sand with oxidizing bacteria is the most efficient means of removing manganese compounds and its efficiency mostly depends on the consistent and sufficient amount of oxygen supplied.

Organic compounds and the color of water are removed by means of coagulation. The resulting flakes are filtered by the first quartz sand filter. The changes of organic compounds concentration over time are presented in Figure 5.

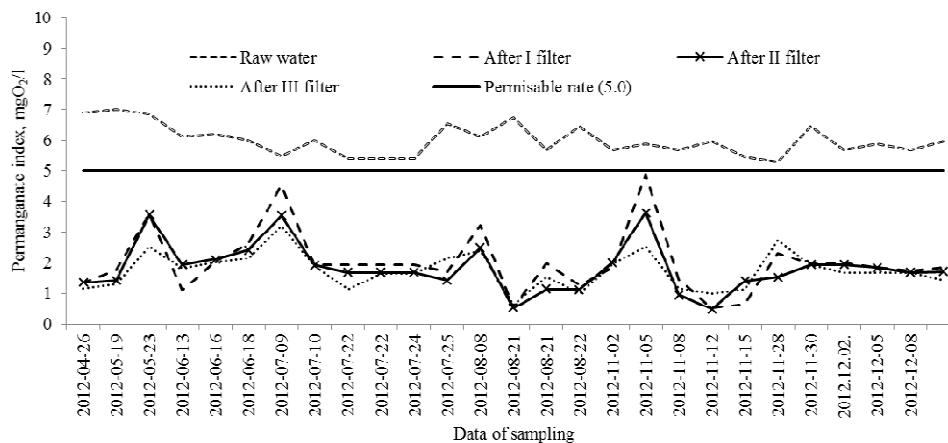


Fig. 5. Changes of permanganate index concentration throughout plants

In performing tests under laboratory conditions organic compounds are efficiently removed after the coagulation process as the water is filtered through the quartz sand filter. The permanganate index does not exceed the acceptable norms after the first filter. At some points (05.23, 07.09, 08.08 and 11.05) the increase in the concentration of organic compounds is observed. It is related with the fact that the quartz sand filter was operating for two or three days without being cleaned. The filter became contaminated with insoluble iron compounds and the products of coagulation process which resulted in the increased concentration of organic compounds in the water. It can also be noticed from the figures above that the efficiency of organic compounds removal remained stable over 8 months. A constant supply of coagulant and frequent cleaning of filters (every day) are important for this process. The second and the third filters do not reduce the concentration of organic material. However, its concentration no longer exceeds the acceptable norms. As the concentration of organic compounds is reduced to such concentrations ( $<2 \text{ mgO}_2/\text{L}$ ) and iron complex organic compounds are removed, iron, ammonium and manganese are further efficiently removed.

## Conclusions

Having performed the tests, it was determined that the concentration of iron, manganese, organic compounds and ammonium ions in groundwater is reduced to the acceptable norms by means of this technology.

The first filter needs to be cleaned every day in order to ensure efficient operation of the first filter in reducing the total iron concentration. The increase in the total iron concentration is observed if the second and the third filters are not cleaned for three days. Therefore, it is recommended that the second and the third filters are cleaned at least every second day.

In removing ammonium, once  $42 \text{ m}^3$  of water have passed, the concentration of ammonium ions after the second filter with zeolite remains the same as it was after the first filter and the concentration of ammonium ions exceeds the permissible hygiene rate. In order to remove ammonium no zeolite filter is needed which quickly loses its efficiency and a quartz filter with oxidizing bacteria as well as a constant supply of oxygen are sufficient. However, such filter filling is only efficient where the ammonium concentration is lower than  $2 \text{ mg/L}$ .

The filter filling of quartz sand with oxidizing bacteria removes manganese compounds most efficiently and its operational efficiency mostly depends on the consistent and sufficient amount of oxygen supplied.

It was determined that the removal of organic compounds is the most efficient after the coagulation process when the water is filtered through the first quartz sand filter. The permanganate index does not exceed the acceptable norms after the first filter. It was also determined that the efficiency of organic compounds removal remained stable over time and the concentration of organic compounds is not reduced by the second and the third filters.

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