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Fractionation of organic matter and validation of groundwater treatment technology

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ABSTRACT

Iron and manganese often exceed the acceptable concentrations in groundwater. Conventional technologies for the iron and manganese removal from groundwater (aeration and filtration) are inefficient when the groundwater contains high concentrations of organic matters. Usually organic substances that are in groundwater compose with iron organic complex matters, which are difficult to remove by conventional treatment. Coagulation is the most common method of organic compounds removal. In order to select proper treatment technology, the composition of organic compounds shall be determined in water. For this purpose, we used fractionation of organic compounds. This study analyses the types of organic compounds that are dominating in the particular groundwater, and how polyaluminium chloride affects organic and iron organic complex compounds that are present in groundwater under laboratory and pilot plant conditions. After fractionation of groundwater samples, it has been identified that the major fraction of organic compounds were very hydrophobic acids (69%), and major part of soluble divalent iron form complex compounds with these acids (81%). Results of research shows that concentrations of organic compounds, iron and iron organic complexes, and color of groundwater can be removed using polyaluminium chloride for coagulation process.

Keywords: Coagulation; Filtration; Fractionation; Groundwater; Iron; Organic matter

1. Introduction

Usually the acceptable concentrations in groundwater are exceeded by iron and manganese, and in some cases ammonium also. The conventional technologies (aeration and filtration through the granular filtration media) [1–3] are ineffective in elimination of iron and manganese compounds from groundwater when large concentrations of organic compounds are present. The excess of organic compound concentrations in groundwater appears in the well fields where the exploited aquifers have contact with surface water. High concentrations of organic compounds in water cause a hydrophobic film formation on the surface of filter media. It is difficult to remove hydrophobic film from filter by simple backwashing [4]. The removal of iron and manganese from water is limited, due to the formation of this film. Organic compounds are the first ones to react with oxygen, which is necessary for further oxidation of iron and manganese compounds. Metals can form complex organic matters and removal of iron complex organic compounds becomes complicated [3,5]. The taste and smell of water becomes unacceptable for consumption due to organic matters [6]. During the disinfection process, dissolved organic compounds form secondary substances, such as haloacetic acid and trihalomethanes [7–9]. Most of them are pharmacologically active and have a harmful effect on the human body [10]. In order to select the most proper method for

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organic compound removal, the dominating organic compounds in water should be identified. It has been found that using the physical and chemical fractionation of organic compounds at different pH values, the organic compounds can be divided into hydrophobic and hydrophilic substances [11]. Chow et al. [12] presented data of the fractionation research in which organic compounds are divided into four fractions: very hydrophobic acids (VHA), slightly hydrophobic acids (SHA), hydrophilic charged compounds (CHA) and hydrophilic neutral compounds (NEU) by using three different resins, i.e., DAX-8, XAD-8 and IRA-958. Researchers state that these fractions can be used to determine what functional groups are predominant in a certain fraction; for example, aromatic compounds are prevalent in hydrophobic fractions more often than in hydrophilic fractions. Chow with colleagues [12] performed fractionation of surface water samples after the coagulation process. It has been determined that slightly hydrophobic acids are easiest to remove and hydrophilic neutral compounds are most difficult to remove during the coagulation process. Soh et al. [13,14] identified that the percentage of very hydrophobic acid and slightly hydrophobic acid fraction compounds that are removed by means of aluminium sulphate is equal to 72% and 59%, respectively. Meanwhile, the percentage of hydrophilic charged and hydrophilic neutral fraction compounds removed through the coagulation process is as low as 38% and 16%, respectively. Since these compounds are not removed through the coagulation process, they have the potential to form disinfection by-products after disinfection. When groundwater is rich in organic substances and has high natural concentrations of iron, it is highly probable that iron organic complex compounds will be formed. Organic compounds are charged negatively, so they compose complexes with metals. Rahman with colleagues [15] have confirmed that iron usually binds to carboxyl groups. Yang et al. [16] have determined that metal complex compounds with humic material are more stable than metal complex compounds with fulvic acids. Munter with colleagues [5] have declared that trivalent iron's complex compounds with humic acids are stronger and more stable in comparison with divalent iron's complex compounds with humic acids. Iron is difficult to remove from water because dissolved iron is already oxidized. Dominating trivalent iron ions form complexes with fulvic acids, therefore, they cannot be hydrolyzed to $Fe(OH)_3$ compounds that precipitate easily.

For organic matter, removal methods such as coagulation, flocculation, filtration, oxidation, biological, and adsorption on activated carbon are used. Microfiltration and ultrafiltration membranes are considered ineffective in removing dissolved organic substances (between 5 and 30% efficiency). The nanofiltration membranes may reject 50–90% of humic substances, depending on the molecular weight cut-off membrane [17,18]. Coagulation is the most common method of organic substance removal [19–21]. The most common coagulants are: aluminium sulphate, iron(III) chloride, sodium aluminate, polyaluminium chloride, iron(II) sulphate, iron(III) sulphate, mixtures of aluminium and iron salts. Usually polyaluminium chloride is used in practice for its efficiency and low price [22–24]. Compared to aluminium sulphate, flakes form faster and are thicker [25]; compared to iron(III) chloride, doses are 10–30% lower. Also, polyaluminium chloride removes humic material more efficiently [26], and coagulation takes place in a more neutral pH interval 6.0–8.0 [27] compared to iron chloride pH operation interval 5.0–6.0 [28].

This study examines organic compounds' fractions' types dominating in a particular groundwater, whether the water contains iron organic complex compounds, and how polyaluminium chloride affects them under laboratory and production conditions.

2. Materials and methods

2.1. Water characterization

The raw groundwater of Nida wellfield is investigated (the groundwater quality indexes are presented in Table 1). Nida wellfield (55°33′N21°04′E) is in Curonian Spit with the Baltic Sea on one side of it, and the Curonian Lagoon on the other side. Nida wellfield belongs to the group of open water-places. This water-place exploits open layers of the groundwater (lagoon water). The water source of wellfield is the groundwater flowing through the aquifer which is constantly refilled by rainfall. Nida wellfield is located 3 km to the North from the city centre. The groundwater level of Nida wellfield settles in the depth of 2–5 m and practically coincides with the lagoon water level. The aquifer is made of medium and small marine-eolian sand, which is 14–20 m thick. This wellfield has increased concentrations of iron, manganese, ammonium, and organic substances. There is no pollution source around the wellfield; pollutants appear in water from the groundwater accumulated in marine sediments.

The drinking water treatment pilot plant (Fig. 2) is constructed at Nida wellfield. The water to the pilot plant supplied from well No. 2. The quality of the groundwater of this well is very similar to the mixture of Nida wellfield. The permissible rates are exceeded by the concentrations of iron, ammonium, manganese compounds, the permanganate index and color parameters. Water quality parameters of well No. 2 are provided in Table 1.

2.2. Fractionation

The fractionation procedure is based on the adsorption of different organic fractions by using different resins. Four different fractions (very hydrophobic acids, slightly hydrophobic acids, hydrophilic charged acids and hydrophilic neutral acids) can be separated using three different resins.

Table 1
Groundwater quality data average for the Nida wellfield (Courtesy of Neringa Water Utility, Ltd.), and for well No. 2

Water quality indicator, units	Wellfield average	Well No. 2
pH	7.45	7.39 ± 0.07
Permanganate index, mgO_2/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	34 ± 2

Fractionation was performed twice for each water sample. Three resins (DAX-8, XAD-8 and IRA-958) were used. Three glass columns 20 cm in height and 13 mm in diameter each were filled with 15 cm of resin (Fig. 1). 500 mL of water was filtered through 0.45 μm cellulose nitrate filter. Filtered sample was acidized to pH 2.0 using hydrochloric acid. Then sample was filtered through the first column containing DAX-8 resin. Filtration speed was 3 mL/min. The first 30 mL were discarded. After filtration was completed, 50 mL of water was taken to test the concentration of the dissolved organic carbon (DOC). The remaining part of the sample was filtered through the second column with XAD-8 resin. The pH index value of sample was kept equal to 2.0. The first 30 mL were discarded. After filtration of this sample was completed, 100 mL of water was taken to test the concentration of the dissolved organic carbon. The remaining water was alkalized with NaOH solution until the pH index value reached 8.0. Then sample was filtered through the third column with IRA-958 resin. The first 30 mL were discarded. After filtration, the testing for DOC was performed.

Resins must be regenerated after completion of fractionation. DAX-8 and XAD-8 were regenerated at first with 60 mL 0.1 M NaOH solution, then 60 mL of deionized water, 60 mL 0.1 M HCl solution, and 60 mL of deionized water. IRA-958 was regenerated by pumping through the resin 60 mL of 1 M NaOH/NaCl solution, 60 mL deionized water, 60 mL 1 M HCl/NaCl solution, and 60 mL of deionized water. After regeneration, the concentration of dissolved organic carbon was assessed. Concentration should not exceed 0.2 mg/L. The concentration of fractions was calculated using formulas:

VHA = DOC (raw water) – DOC (DAX-8 effluent);
SHA = DOC (DAX-8 effluent) – DOC (XAD-8 effluent);
CHA = DOC (XAD-8 effluent) – DOC (IRA-958 effluent);
NEU = DOC (IRA-958 effluent).

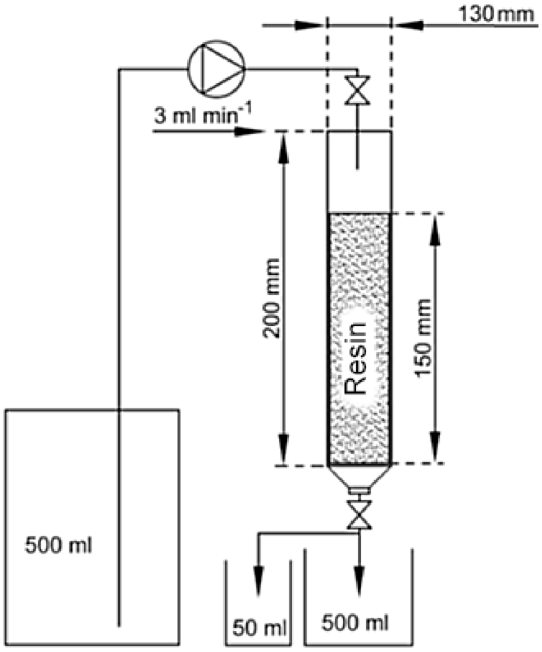

Fig. 1. Layout of fractionation setup.

Total organic carbon determination in underground drinking-water is based on standard LST EN 1484:2002 "Water analysis – Guidelines for the determination of total organic carbon (TOC) and dissolved organic carbon (DOC)". The tests were done using analyser Dohrmann Apollo 9000, Teledyne-Temar.

2.3. Chemicals and coagulants

Polyaluminium chloride (PAC18, 9% Al) was chosen for the research (wide pH interval, lower doses than other coagulants). Solution of polyaluminium chloride contains ~0.9 g/L aluminium. According to the analysis of scientific literature, and using practical knowledge, five doses of coagulants were selected: 3 mg/L; 5 mg/L; 7 mg/L; 10 mg/L; 15 mg/L (doses are calculated for milligrams of pure aluminium or iron per 1 L of water). To determine the most efficient coagulant dose, the identification of organic compounds and the color of water should be carried out after coagulation. The laboratory research was performed by mixing 1 L of sample, containing an adequate coagulant dose, for 1 min at the speed of 280 rpm, and for 20 min at the speed of 30 rpm; after this it was left to settle for 30 min. Such regimes of the coagulation process were selected in accordance with scientific literature. After the coagulation process, water was filtered through paper filters, and the quantitative analysis was performed. Each test was performed three times.

2.4. Analysis methods

Water quality assessment tests after coagulation were performed according to the following methodologies:

- permanganate index (PI) is determined according to LST EN ISO 8467:2002 "Water quality – Determination of permanganate index (ISO 8467:1993)".
- the color is determined according to ISO 7887:2011 "Water quality – Examination and determination of color".
- total iron in water is determined according to LST ISO 6332:1995 "Water quality. Determination of iron. Spectrometric method using 1,10-phenanthroline".

The obtained result of the analysis is the arithmetical average of concentrations of three samples, when distribution does not exceed 5%, if higher tested were repeated.

2.5. Water treatment pilot plant

The most efficient dose determined under laboratory conditions was used for groundwater treatment at pilot plant, where layout is presented in Fig. 2.

Water is lifted by a pump and fed to the open aerator (200 L tank). Water flow –100 L/h. Water is sprayed by a specially design sprayer with three weirs to improve the saturation of air oxygen, and for oxidation of hydrogen sulphide and iron. Water is pumped from the open aerator to the first filter, where filtration rate kept 3.0 m^3/

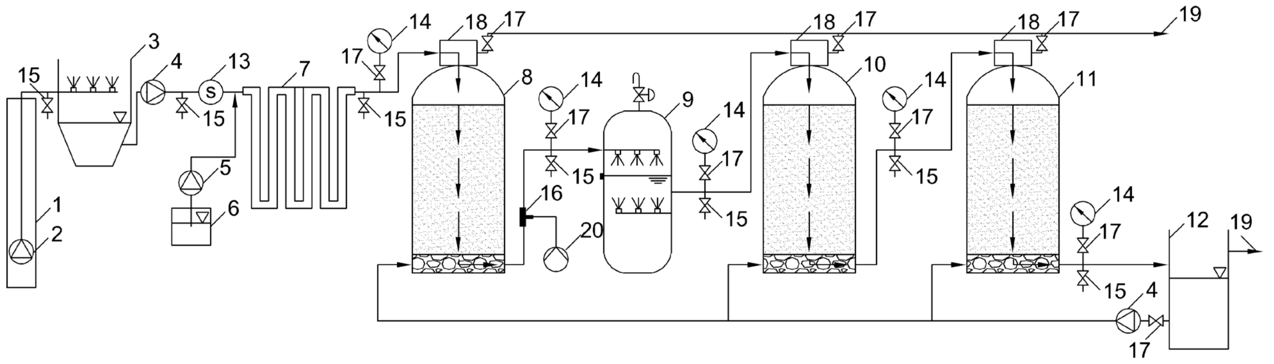

Fig. 2. Setup of the pilot plant for drinking water treatment: well (1); pump (2,4); open aerator (3); coagulant dosing pump (5); coagulant tank (6); reaction chamber (7); filter (8,10,11); closed aerator (9); clean water tank (12); water meter (13); pressure gauge (14); sample taking place (15); injector (16); valve (17); filter control valve (18); discharge into sewer (19); compressor (20).

m^2/h. Prior to the filter, 5 mgAl/L of coagulant polyaluminium chloride were added to the water. The coagulant gets into a plastic tube 50 m in length and DN25 in diameter. This tube is used as a reaction chamber to have time for the flakes to be formed. Duration time at the reaction chamber 22 min. During coagulation process, coagulant and organic compound flakes are formed, and they are removed by filtration through a sand filter. Water gets into the first pressure filter (height – 1200 mm, diameter – 250 mm, with quartz sand of 1–2 mm). This filter has to reduce the concentrations of iron and organic compounds. After this filter, the water flows into a closed aerator (height – 1100 mm, diameter – 200 mm). The aerator is necessary for the water saturation with oxygen which is necessary for further oxidation of ammonium ions and manganese compounds. The compressor was used for this purpose. After the aerator, water gets into the second pressure filter (height – 1200 mm, diameter – 250 mm), which is filled with natural zeolite (fraction 0.3–0.6 mm). After the second filter, water goes to the third filter (height – 1200 mm, diameter – 250 mm), which is filled with quartz sand containing oxidizing bacteria (fraction 1–2 mm).

1 L water samples were taken from 7 places: the well, after the open aerator, after the reaction chamber, after filter I, after the closed aerator, after filter II, and after filter III. Water samples were kept in refrigeration containers with temperature below 5°C . The samples were transported in 24-h period to the Drinking Water Laboratory of Ltd Vilnius Water Utility for the analysis.

3. Results and discussion

The more organic compounds are found in water, the more difficult is the removal of iron and manganese compounds, and ammonium ions. In this case, the groundwater of Nida wellfield contains a lot of organic compounds (concentration of total organic carbon is 9.63 mg/L). Organic compounds must be removed from water in order to effectively remove iron and manganese compounds, and ammonium ions. The determination of dominating fractions of organic compounds in groundwater was needed to choose the most appropriate method for organic substance removal. The concentrations of organic compounds' fractions in the groundwater of Nida wellfield are presented in Table 2.

Table 2
Organic compounds' fractions in the groundwater of Nida wellfield

Water quality indicator, units	Average and standard deviation
Very hydrophobic acids (VHA), mg/L	5.62 ± 0.23
Slightly hydrophobic acids (SHA), mg/L	1.44 ± 0.02
Hydrophilic charged (CHA), mg/L	0.70 ± 0.04
Hydrophilic neutral (NEU), mg/L	0.31 ± 0.00

Fractionation was done for all samples, and examination of the dissolved organic carbon concentration was performed. From results are clear that main part of organic compounds in groundwater is a fraction of VHA (69%). It means that fulvic and humic acids dominate in groundwater. Those are high-molecular hydrophobic humic compounds could be removed by coagulation. Researchers claim that aromatic compounds in hydrophobic fractions are prevalent more often than in hydrophilic fractions. The organic compounds with higher molecular mass and more aromatic cycles are more hydrophobic. The amount of slightly hydrophobic acids in the investigative groundwater is considerably lower comparing to the fraction of very hydrophobic acid. Fraction of slightly hydrophobic acids in analyzed water samples reaches 18% of the concentration of all dissolved organic compounds. This fraction also consists of organic compounds containing higher molecular mass and more aromatic cycles. It means that this fraction of organic compounds is easily removable by coagulation process. The hydrophilic charged compound fraction in analyzed water samples reaches 9% of all dissolved organic compounds. The smallest part of organic matters is the hydrophilic neutral compound fraction (4%). These two fractions consist of short chains aliphatic amines, alcohols, ketones and esters. According to Chow and colleagues [12], removal of these organic compounds, using the coagulation process, is complicated, because these compounds have a small molecular mass and are hydrophilic. These matters tend to form disinfection by-products.

After fractionation analysis, it was found that 89% of all the organic matters were composed of VHA and SHA, and these fractions contain large molecular mass compounds. These compounds are effectively removable by coagulation method. And this technique of removal of organic matters is applicable to discussed water wellfield.

Humic acids have sorption properties, and as a result can form soluble and insoluble salts, and also complexes with organic and inorganic compounds. Organic compounds, specifically fulvic and humic acids, disturb removal of iron from groundwater. The concentration of humic acids in Lithuanian groundwater reaches 0.02–0.08 mg/L, and sometimes even up to 0.8–1.0 mg/L. To discover how much iron is in complex organic compounds the following tests were performed. The groundwater from Nida wellfield was fractioned to separate different organic compound's fractions, and then iron concentration was analyzed in each fraction. Before fractionation, water was aerated for 24 h, and then filtered through 0.45 µm size pores filter. Concentration of iron was analyzed in raw water, filtered water and in each fraction after fractionation. Ions of divalent iron form complexes with organic matters, and divalent iron compounds are soluble in water, so after filtration only divalent iron remains in the water. The data provided in Table 3 shows that the concentrations of divalent iron compounds dissolved in groundwater exceed the permissible norms of Directive 98/83/EB. Dissolved iron consist about 30% of the total iron concentration. During aeration, divalent iron should be oxidized to insoluble compounds of trivalent iron which can be removed by filtering. From results of the analysis we can make a conclusion that all divalent iron is in complexes with organic compounds.

The results in Table 3 suggest that the major part of divalent iron forms complexes with very hydrophobic acids (81%). 17% of divalent iron forms complex compounds with slightly hydrophobic acids. Such results illustrate that over 90% of divalent iron forms complex compounds with hydrophobic high-molecular organic matters. It means that complex organic compounds with iron can be eliminated using the coagulation process.

For efficient elimination of iron and organic matters from groundwater (to achieve the permissible hygiene norms), the optimum coagulant dose should be determined under laboratory conditions. The coagulation process test under laboratory conditions is performed for this purpose using polyaluminium chloride in different doses. The results are presented in Figs. 3–5.

Table 3
Concentrations of iron in different fraction of organic compounds

Fraction	Concentration of total iron and standard deviation, µg/L
Total iron	5650 ± 54
Soluble iron	970 ± 23
Iron in VHA	786 ± 14
Iron in SHA	165 ± 9
Iron in CHA	10 ± 3
Iron in NEU	9 ± 3

Figs. 3, 4 and 5 illustrate that the concentration of iron, organic compounds, and the color of water decrease as the coagulant doses are increased. Upon removal of iron, that is present in organic complexes, the iron concentration does not exceed the permissible rate of hygiene norm,when the coagulant dose is equal to 5 mgAl/L. During removal

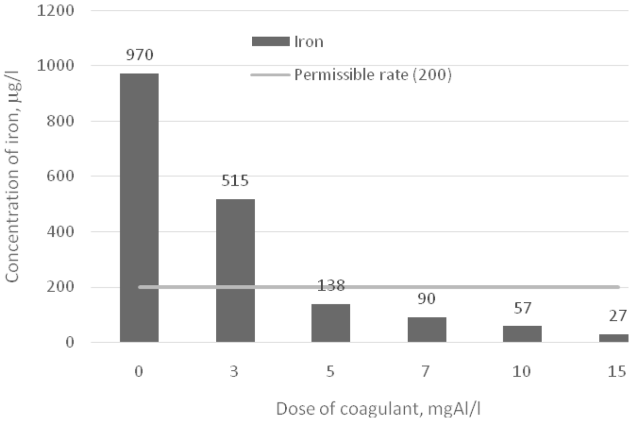

Fig. 3. Dependence of concentration of iron compounds on coagulant dose.

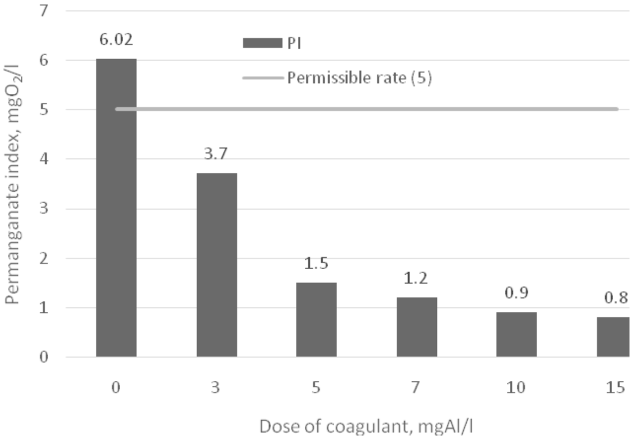

Fig. 4. Dependence of permanganate index on coagulant dose.

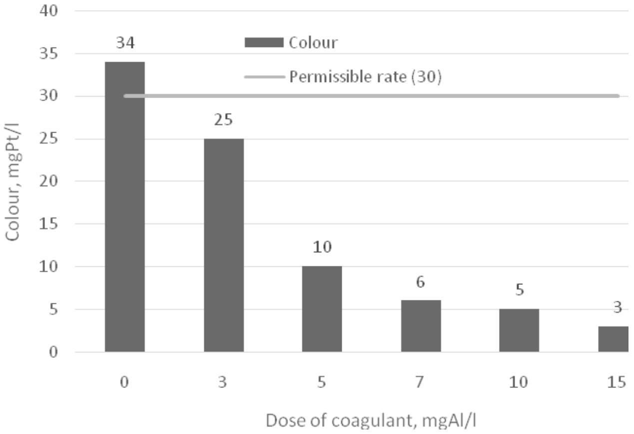

Fig. 5. Dependence of water colour on coagulant dose.

of organic compounds and color that is given by organic compounds, the permanganate index and color values do not exceed the permissible rate of hygiene norm, when the coagulant dose is equal to 3 mgAl/L. It shows that using 3 mgAl/L coagulant dose a part of organic compounds is removed, but the iron that forms complexes with organic compounds is not removed. Therefore, for further testing a polyaluminium chloride dose of 5 mgAl/L is used. This dose removes both iron and organic compounds from water, and their concentrations do not exceed the permissible rate of hygiene norm.

To determine the organic compound fractions, that are removed most efficiently through the coagulation process, fractionation is performed after the coagulation. Analysis of coagulation is done using a polyaluminium chloride dose of 5 mgAl/L in the groundwater of Nida wellfield. The results are presented in Fig. 6.

After fractionation before and after coagulation it has been determined that during coagulation all organic compound fractions were removed except the hydrophilic neutral compound fraction. As seen in Fig. 6, the very hydrophobic acid fraction is the largest organic compound fraction in water, and their concentration is reduced from 5.42 to 2.03 mg/L after coagulation. The removal efficiency of the organic compounds of very hydrophobic acid fraction equals to 63%, and the removal efficiency of slightly hydrophobic acid fraction equals to 39%. The removal efficiency of hydrophilic charged compounds is 50%. Hydrophilic neutral compounds are not removed from water by the coagulation method. The results of this testing suggest that the compounds of very hydrophobic acid fraction are most effectively removed by the coagulation. Since the compounds of very hydrophobic acid fraction dominate in groundwater of the wellfield investigated, coagulation is an appropriate method for removal of organic compounds from groundwater.

The main task of these water treatment systems is to remove ammonium ions, iron, manganese, and organic compounds from water, and to reduce the color of water by applying as few chemical reagents as possible. The following test results illustrate how concentrations of iron and organic compounds, and the intensity of water color change in all stages of water treatment systems. During water treatment technology stages, organic compounds are removed and the color of water is reduced first. In Figs. 7 and 8 the deviations of permanganate index and color in water treatment systems are presented.

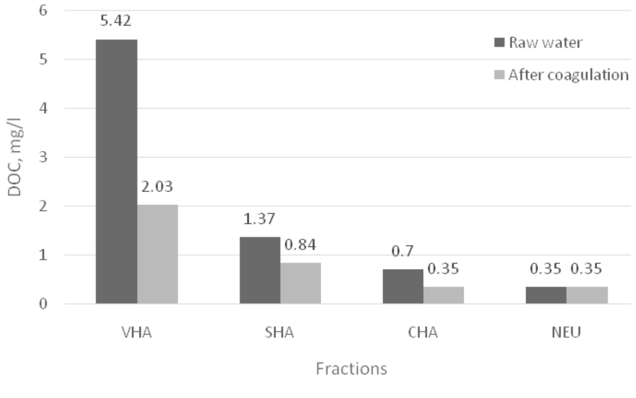

Fig. 6. Fractionation data before and after coagulation.

The permanganate index of untreated groundwater exceeds the permissible rate of hygiene norm (5.0 mgO$_2$/L). The permanganate index decreases after the coagulation process. Using 5 mgAl/L of coagulant, and after water flows through the first filter, the permanganate index is decreased by 81%, and does not exceed the permissible rate anymore. Further the permanganate index in water treatment systems remains almost unchanged. The results of the research illustrate that organic compounds are efficiently removed by the method of coagulation. The efficiency of this technology for organic compound removal is ~80%.

The water color intensity is decreased by 79% after the coagulation process and filtration through the first filter. In the following stages of water treatment, the intensity of water color remains unchanged.

After organic compound removal, iron compounds should be removed. The variation of concentration of iron compounds in all stages of water treatment is presented in Fig. 9.

After the open aerator, the total iron concentration is decreased by 20%. It means that a portion of divalent iron ions is oxidized to trivalent iron ions, and hydrolyzed to trivalent iron hydroxides that are insoluble and settle to the bottom of the aeration tank. The sediments were taken out from the tank once per month. However, only a small portion of iron compounds is oxidized. The concentration of dissolved oxygen in water after the open aerator is over 6 mgO$_2$/L. The results of fractionation illustrate that iron

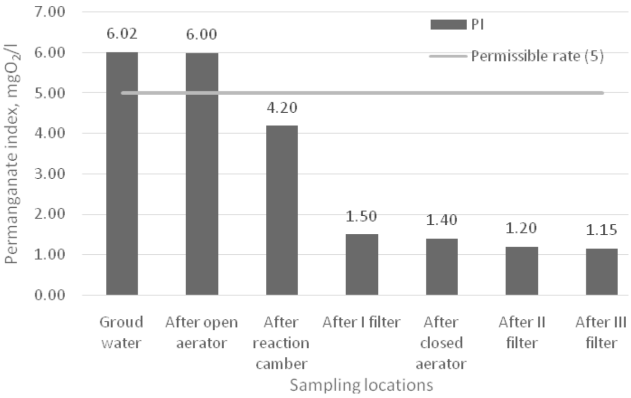

Fig. 7. Permanganate index at different sampling locations.

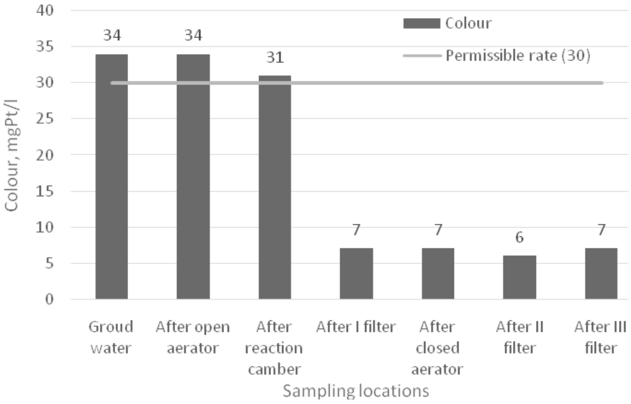

Fig. 8. The colour of water at different sampling locations.

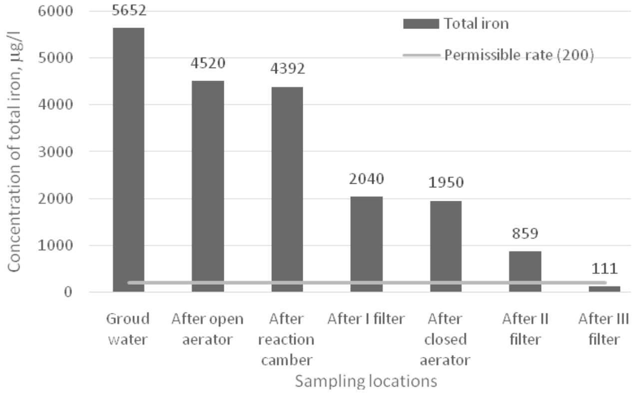

Fig. 9. Total iron concentration at different sampling locations.

is bound in complex organic compounds, and iron is not oxidized. Using 5 mgAl/L coagulant doses after the first quartz sand filter, the iron concentration is decreased by 63% compared to the primary concentration. However, the total iron concentration exceeds the permissible rate of hygiene norm. After the second filter, which is filled with zeolite, the total iron concentration is decreased. However, the total iron concentration still exceeds to permissible rate of hygiene norm. After the third filter, which is filled with quartz sand containing oxidizing bacteria, the total iron concentration is decreased down to acceptable level. The efficiency of iron compound removal reaches 98%. This research suggests that using coagulation and filtration through quartz sand filters, organic substances are removed together with iron organic complex compounds. If these compounds would not be removed in the first filter, other filters would fail to remove iron and manganese. The first and second filters does not affect the manganese content. The content is substantially decreased below the limit of the water quality standards only in the third filter containing sand with oxidizing bacteria.

4. Conclusions

- Fractionation of Nida's wellfield groundwater samples show that the biggest part of organic compounds is the very hydrophobic acid fraction (69%).
- The organic compounds of very hydrophobic acid fraction are most efficiently removed through coagulation (63%).
- It is clear from iron concentration measurements in different fractions that the biggest part of soluble divalent iron forms complex compounds with very hydrophobic acids (81%).
- It is found that minimal dose of polyaluminium chloride, used to remove iron and organic compounds from groundwater by coagulation, is 5 mgAl/L, when raw water contains 6 mgO_2/L of permanganate index.
- Analysis of coagulation process using polyaluminium chloride under laboratory and pilot plant show that color of water, concentrations of organic substances, iron and iron organic complexes in groundwater are reduced to the permissible rate of hygiene norm. The organic compound concentration and the color of water meet the permissible rate of hygiene norm after the first filter already, and the iron concentration does not exceed the permissible rate after the third filter.

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