Research article

Water Softening by Nanofiltration – Case Study

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Abstract

In this research the object of the analysis was the improvement of a drinking water treatment plant with groundwater as the drinking water source. Improvements included the removal of magnesium and manganese. Improvements also mean choosing the proper water treatment technology that would meet the standards for drinking water quality. Technologies that are suitable for removal of these ions vary in many aspects, from technological challenges to cost analysis. After thorough analysis, the right choice, in this case, was a two-stage nanofiltration (NF) which has a removal rate of more than 90%. The analysis also included a detailed cost analysis.

Keywords: Drinking water; hardness; ion exchange; membrane technologies; nanofiltration.

Introduction

Raw groundwater usually does not meet the standards expected from drinking water with respect to water hardness (calcium and magnesium), sodium, nitrate, iron and manganese concentrations (Azimi et al. 2019). Water hardness is one of the issues that has been in focus from different aspects, which cover maintenance of the equipment and reliability of the water supply network. With increased consumption and demand for better drinking water quality, softening has become even more important (Boyd et al. 2016; Sanjuan et al. 2019). The choice and the application of technologies for softening differ according to the quality of raw water and specific demands (available space, cost, trained operators, etc.).

In this research the object of the analysis was the groundwater used for drinking in the existing water treatment plant in Serbia. Analysis showed that the concentration of magnesium and manganese exceeded the permissible values. The goal was to choose the proper water treatment technology which could meet the standards for drinking water quality.

Lime has been traditionally used for removing ions of calcium, magnesium. Cold lime softening has disadvantages (the consumption of the chemicals and disposal of sludge) that reduce the usage of this technology in comparison to other known technologies (Van der Bruggen & Vandecasteele 2003). Ion exchange has been successfully used for removal of calcium and magnesium ions and softening of groundwater, together with removal of organic substances (Levchuk et al. 2018). In the field of ion exchange sorbents are constantly improved and thoroughly studied. Different types of sorbents, such as zeolites, carbon nanotubes, activated carbon, graphenes, antibacterial hydrogel beads have been tested for softening of water (Fernandez et al. 2016; Shahmirzadi et al. 2018; Mohammadian et al. 2019). Ion exchange with natural zeolite as sorbent has many benefits, especially from a financial and environmental aspect (Hailu et al. 2019). Membrane technologies used for separation and removal of different ions from water have also been applied for water softening. When considering membrane technologies, both reverse osmosis and nanofiltration can be applied. Considering the task within this research, the removal of divalent ions such as magnesium and calcium, the most elegant is nanofiltration (Homayoonfal et al. 2010; Nanda et al., 2010; Rahimpour et al. 2010). The removal efficiency of different membrane technologies is presented in Figure 1.

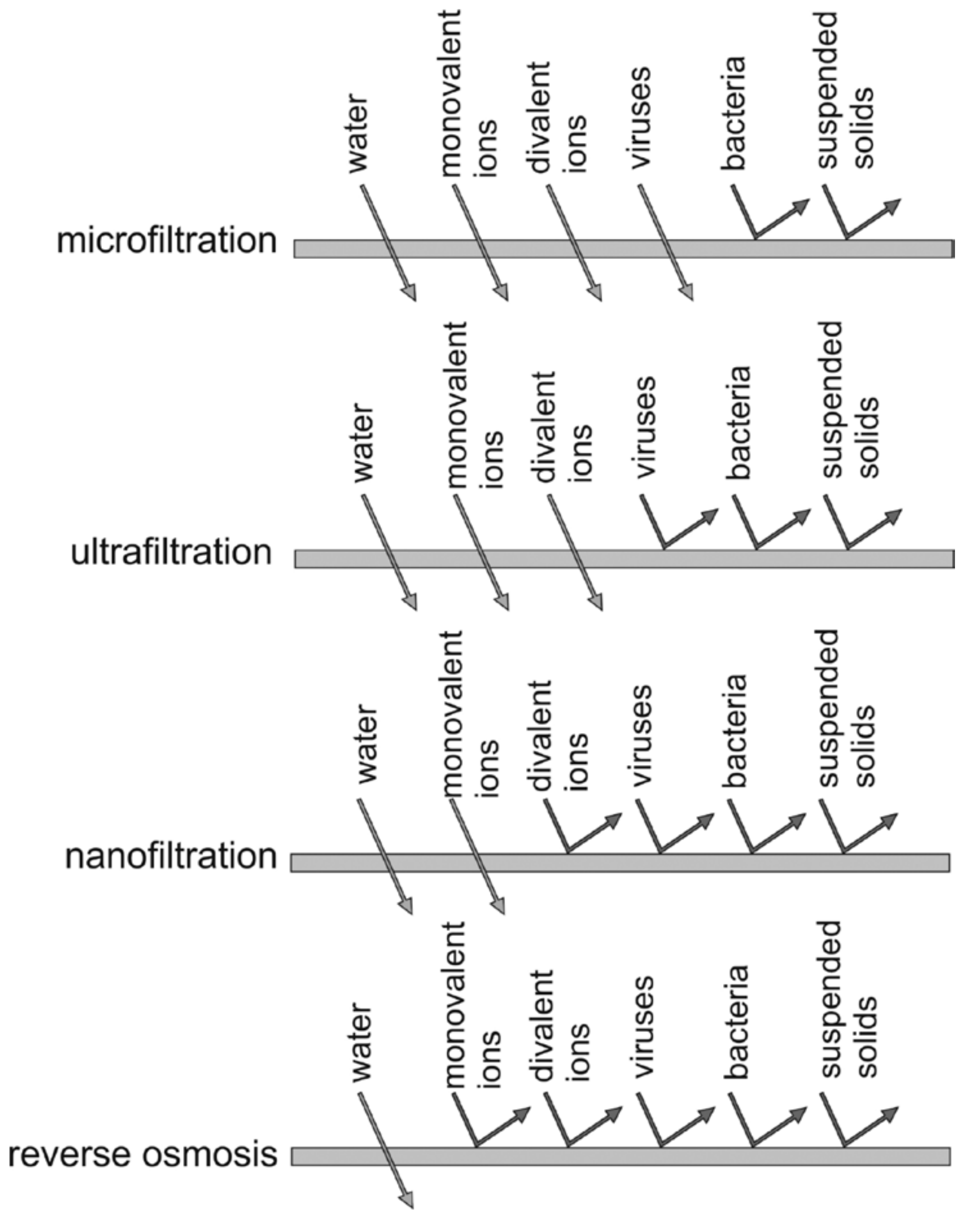

Figure 1: Comparison of removal efficiency of membrane technologies.

Methods

As mentioned, the goal of the research was the analysis of drinking water that is produced in the existing water treatment plant in Serbia.

A list of measured parameters, instrumental techniques and analytical methods are presented in Table 1. Currently water does not meet the standards for drinking water quality. The standard that is considered is the National Regulation on the Hygienic Quality of Drinking Water, published in the Official Gazette of the Republic of Serbia 42/98 and 44/99, published in Official Gazette of the Republic of Serbia 28/2019.

Table 1: The applied analytical methods.

Parameter	Applied analytical methods and standards	Instrumental technique
	Physical-Chemical parameters	
pH value	Electrometric method, 4500-H+ B *	WTW pHmeter 340i
Conductivity UV	EPA 120.1:1982 UV-Vis spectrometry	Conductivity meter UV-Vis Sp.photometer
p-alkalinity *m*-alkalinity HCO_3^- Total hardness	SMEW 22ND:2320B SMEW 22ND:2320B SMEW 22ND:2320B SMEW 22ND:2320B	Volummetric Volummetric Volummetric Volummetric
TOC		
Consumption of $KMnO_4$	SRPS EN ISO 8467:2007	Volummetric
Cations		
(Na^+, K^+, Mg^{2+}, Ca^{2+})	ISO 14911:1998	Ion Chromatography
Anions		
(Cl^-, SO_4^{2-})	ISO 10304-1:2007	Ion Chromatography
Ba^{2+}, Be^{2+}, B^{3+}, Cu^{2+}, Zn^{2+}, Si^{4+}, Se^{4+}, Sr^{2+}, Hg^{2+}, $As^{3,5+}$, Al^{3+}	Atomic absorption spectroscopy (AAS), SM 3111b:1999;	AAS, Perkin Elmer 4100ZL Agilent 7500ce ICP-MS system

* APHA, AWWA, WEF 2012 Standard methods for the examination of water and wastewater, 22nd edition

Results and Discussion

The results of the analysis of drinking water quality are presented within this section. The technological scheme and current treatment are described and illustrated in Figure 2, as well. In Table 2 the measured values of water quality parameters are presented together with the prescribed values. The values which exceed the maximum allowable values are presented in bold.

Table 2: Water quality in existing water treatment plant: current status.

Analysed parameters	Unit	Proscribed values*	Inlet water	Outlet water
pH	-	6.8-8.5	7.25	7.66
Conductivity	μS/cm	<2500	1297	1387
UV	1/cm	/	0.048	0.062
p-alkalinity	mg $CaCO_3$/L	/	0	0
m-alkalinity	mg $CaCO_3$/L	/	555.5	580.0
HCO_{3-}	mg/L	/	677.7	680.8
Total hardness	mg $CaCO_3$/L	/	524.5	542.5
TOC	mgC/L	/	2.82	3.22
Consumption of $KMnO_4$	mg/L	<8	3.77	1.26
Cl^-		250.0	69.58	96.34
SO_4^{2-}		250.0	53.54	65.54
Ca^{2+}		200.0	131.14	133.15
Mg^{2+}		50.0	47.85	**51.01**
Na^+		200.0	/	111.0
K^+		12.0	3.99	4.16
$Fe^{2,3+}$		0.3	0.07	<0.005
$Mn^{2,4+}$		0.05	**0.11**	**0.09**
Ba^{2+}	μg/L	700.0	256.9	256.9
Be^{2+}		/	<5	<5
B^{3+}		1000.0	<20	<20
Cu^{2+}		2000.0	<2	4.6
Zn^{2+}		3000.0	11.6	19.6
Si^{4+}		/	29.6	29.3
Se^{4+}		10.0	<20	<20
Sr^{2+}		/	690.1	720.1
Hg^{2+}		1.0	<1	<1
$As^{3,5+}$		10.0	<20	<20
Al^{3+}		200.0	<40	<40

* National Regulation on the Hygienic Quality of Drinking Water, Official Gazette of the Republic of Serbia 42/98 and 44/99 and National Regulation on the Hygienic Quality of Drinking Water, Official Gazette of the Republic of Serbia 28/2019.

As presented in Table 2 the parameters that are above the maximum allowable values are: $Mn^{2,4-}$ content, Mg^{2+} content and even though the water hardness is not limited, it needs to be taken into account as it will affect the reliability of water supply networks and cause precipitation of $CaCO_3$. Also, it can be noticed that concentration of Na^+ is very high. A special task is to maintain sodium concentration below the limited values after the treatment.

The existing drinking water treatment plant is designed for a capacity of 70 L/s, with two parallel lines, each with a capacity of 35 L/s. The technological scheme and operations are described in the following paragraph. The feed water is groundwater which is pumped and stored in the tank for raw water. Before entering the tank, sodium-hypochlorite is added to the water due to the oxidation of iron (eq. 1-4) and manganese (eq. 5-6). The oxidation processes can vary, as described by equation (1-6):

$$2Fe^{2+} + ClO^{-} + H_2O \rightleftharpoons 2Fe^{3+} + Cl^{-} + 2OH^{-} \quad (1)$$

$$2Fe(OH)_2 + NaClO + H_2O \rightarrow 2Fe(OH)_3 + NaCl \quad (2)$$

$$2Fe^{2+} + 1/2O_2 + 5H_2O \rightarrow 2Fe(OH)_3 + 4H^{+} \quad (3)$$

$$2Fe^{2+} + HClO + 5H_2O \rightarrow 2Fe(OH)_3 + Cl^{-} + 5H^{+} \quad (4)$$

$$2Mn^{2+} + 1/2O_2 + 3H_2O \rightarrow 2MnO(OH) + 4H^{+} \quad (5)$$

$$Mn^{2+} + HClO + H_2O \rightarrow MnO_2 + Cl^{-} + 3H^{+} \quad (6)$$

Water from the tank is pumped further to the multi-layer filters. Before filtration, a 1% solution of sodium-hypochlorite and flocculant (if necessary) is added. Filtration consists of two pairs of filters: sand filters which have layers of quartz as a catalyst and anthracite and active carbon filters. After filtration, the water is stored in the water storage tank. Additional chlorination and control of residual chlorine are also part of the technological operation line.

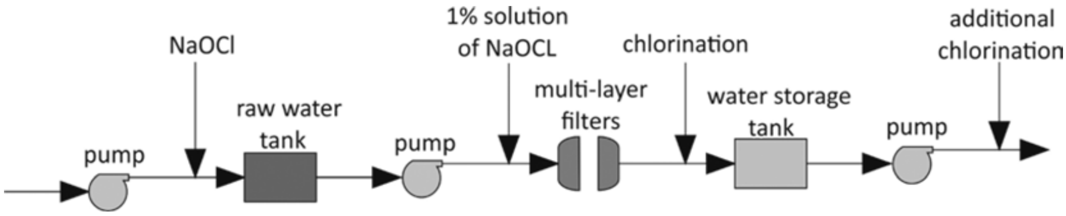

Figure 2: Existing drinking water plant technological scheme.

Several technologies have been considered for the improvement of the existing water quality. The goal of the improvement was to reach the water quality according to standards for drinking water.

Since manganese concentration and magnesium concentration are above the maximum permissible value and sodium concentration and water hardness are very high (over 500 mg $CaCO_3$/L), one of the options for improved water treatment is the ion exchange technology. Standard water softeners are cation exchange devices. Cations refer to positively charged ions dissolved in the water. Cation exchange involves the replacement of the hardness ions with a nonhardness ion. Water softeners usually use sodium (Na^+) as the exchange ion. Sodium ions are supplied from dissolved sodium chloride salt, also called brine. In the ion exchange process, sodium ions are used to coat an exchange medium in the softener. As hard water passes through a softener, the calcium and magnesium trade places with sodium ions. Sodium ions are held loosely and are replaced easily by calcium and magnesium ions. During this process, “free” sodium ions are released into the water.

As mentioned before, water hardness is not a parameter that has a defined maximum value, but what is important is that a high value of water hardness has numerous negative effects (Van der Bruggen et al. 2009). The most pronounced are negative effects on:

- the functionality of process equipment (it is rapidly destroyed),
- the distribution network that is manifested in the form of precipitation of carbonates on the surface of pipes, and
- the quality of drinking water, which can be observed by the complaints of the consumers.

One of the technologies that is often used is the ion exchange process. In the ion-exchange process Mg^{2+} and Ca^{2+} ions are substituted by Na^+-ions, as presented in equation (7):

$$2NaCl + CaCO_3 \rightleftharpoons Na_2CO_3 + CaCl_2 \quad (7)$$

From equation (7) it can be calculated that the number of moles in 17.9 mg $CaCO_3$, as presented by equation (8):

$$n(CaCO_3) = \frac{m(CaCO_3)}{M(CaCO_3)} = \frac{17.9mg}{100\frac{g}{mol}} = 0.000179mol \quad (8)$$

where n is the number of moles of $CaCO_3$, m is the mass of $CaCO_3$, and M is the molar mass of $CaCO_3$. To remove 1 mol of Ca^{2+} ($CaCO_3$), it is necessary to add 2 mols of Na^+ (NaCl), as presented by equation (9):

$$N(NaCl) = 0.000358mol \quad (9)$$

Required mass of Na^+ (NaCl) for removal of 1 mol of Ca^{2+} ($CaCO_3$), is presented by equation (10):

$$m(Na^{+}) = n(Na^{+}) \cdot M(Na^{+}) = 0.000358mol \cdot 23\frac{g}{mol} = 8.2mg \quad (10)$$

Based on the previous calculations, it can be concluded that by removing 17.9 mg/L of $CaCO_3$ (1.0 °dH) the concentration of Na^+ increases for 8.2 mg/L.

When these calculations are applied to the present research, the efficiency of softening by ion exchange can be illustrated, as presented in Figure 3.

As seen from Figure 3 it can be observed that for water flow through an ion exchange resin of 15.37 L/s the water hardness is 19.02 ºdH and the concentration of Na^+ is 200 mg/L. The optimal recommended value of hardness, based on the utilities' experience, is around 10 ºdH. If that recommended value was achieved, the value of Na^+ would be far above the regulated value.

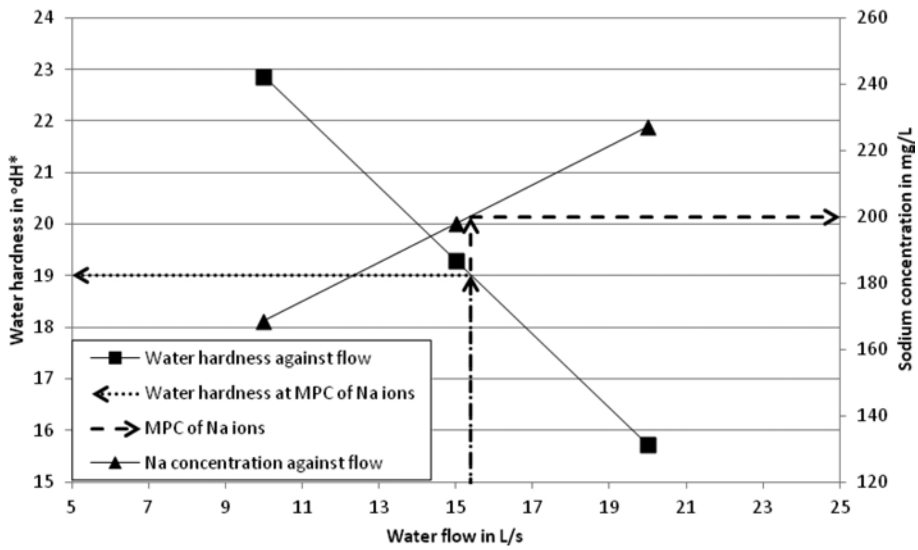

Figure 3: Calculations based on the effect of ion exchange for existing water quality on water hardness and sodium concentration depending on the water flow.

*1°dH = 17,9 mg $CaCO_3/dm^3$

The option of using ion-exchange technology for removal of water hardness has been rejected. As mentioned in the introduction, the membrane filtration processes can be applied to water softening. Reverse osmosis (RO), was one of the considered options. RO is a technology used in the desalination process of sea water, as well as for water treatment in the pharmaceutical and electronics industry (Magara et al. 2000; Le & Nunes 2016; Tang et al. 2017). The reverse osmosis process allows for the removal of almost all ions from the water. Separation is based on the pore size and also on the interaction between charged particles and membrane material. RO requires high pressure. RO in water treatment is very expensive, therefore nanofiltration (NF) was also considered. NF is a membrane filtration process widely used for removal of multivalent ions from solutions, which is exactly the case in this research. And NF, unlike RO, requires low pressure (Labban et al. 2017). NF is a separation process that is finding widespread use in water (drinking water, wastewater or seawater) treatment, particularly for water-softening applications (Mohammad et al. 2015; Su et al. 2015).

The proposed technological scheme with recommended treatment is illustrated in Figure 4.

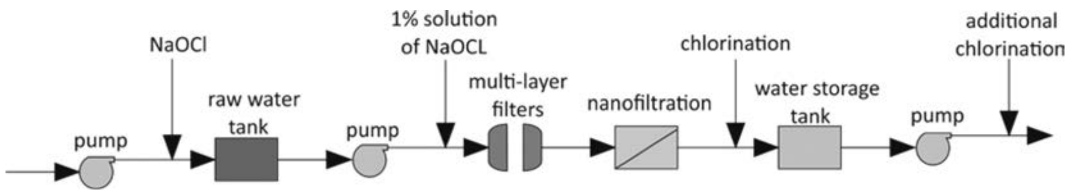

Figure 4: Recommended treatment for drinking water plant - technological scheme.

The entire flow of 35 L/s water (for one line of the treatment plant) goes through NF membranes. The NF system is designed in a way that 85% of water is treated and passes through the membranes and the rest, 15% of the input water, is rejected, as a concentrate.

To get an even higher percentage of removal and better efficiency of the treatment process, a two-stage membrane filtration system is recommended. The input water in the second stage is the outlet water from the first stage. In this way, the concentrate from the first stage goes through one additional treatment. With additional removal, the degree of the purification is usually higher than 90%. The two-stage NF system is schematically presented in Figure 5.

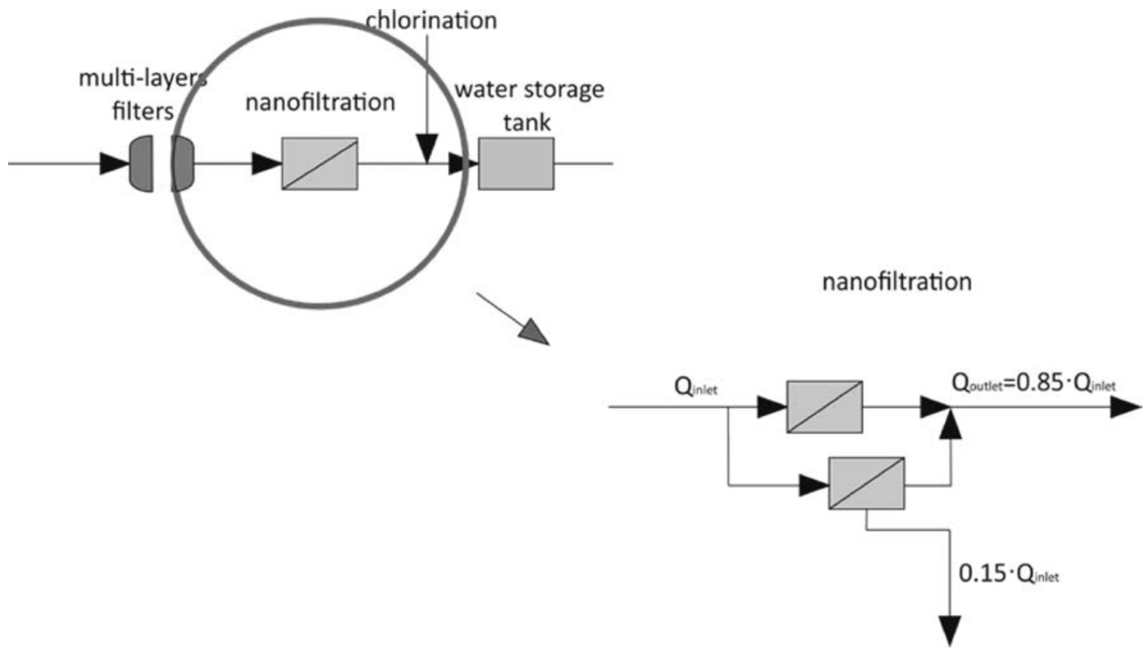

Figure 5: Recommended two-stage nanofiltration system.

When described by the equations which consider flow rate the NF process can be presented by equation (11):

$$0.85 \cdot Q_{inlet} = Q_{outlet} \quad (11)$$

where:

Q_{inlet} – flow rate of water that passes through the membranes,

Q_{outlet} – output flow values.

Output flow value for one line of the treatment plant is lower then the input flow values (Q_{inlet}), due to the loss of water that stays with the concentrate after NF treatment.

Values for Q_{inlet} depend on different parameters, and concentrations of parameters that need to be reduced.

In our case the maximum output flow value for one line is exactly 35 L/s and the input flow, calculated from the equation (11), is 41.2 L/s.

The calculation necessary for decreasing the concentration for any parameter is presented in (12):

$$(0.1 \cdot c_{inlet}) \cdot (0.85 \cdot Q_{inlet}) = c_{outlet} \cdot Q_{outlet} \quad (12)$$

where:

c_{inlet} - concentration of analysed parameter in the inlet water (after NF),

c_{outlet} - concentration of analysed parameter in the outlet water (after NF).

When the cost analysis is considered, investment in the technology that is considered most appropriate is approximately 15000 euro for each installed L/s (Shahmansouri & Bellona 2015; Tang at al. 2019). In this case, the investment cost (IC) for one water line would be 617700 euro, as presented by the equation (13):

$$IC \cdot Q_{inlet} = 15000 \frac{€}{\mathrm{L/s}} \cdot 41.2 \frac{L}{s} \approx 617700€ \quad (13)$$

Apart from investment costs, there are also operational and maintenance costs for NF (MCNF). These costs are expressed per unit of purified water, and those are 0.25 euro per m^3. Other maintenance costs (OMC), for the rest of the treatment plant are considered to be 0.15 euro per m^3 of treated water. The ratio of the mean annual flow and maximum daily flow is 0.75. The operating costs are calculated on an annual basis as presented by equation (14):

$$MCNF \cdot 0.75 \cdot Q_{inlet} + OMC \cdot 0.75 \cdot Q_{inlet} = 0.25 \frac{€}{\mathrm{m}^3} \cdot 0.75 \cdot 41.2 \frac{L}{s} + 0.15 \frac{€}{\mathrm{m}^3} \cdot 0.75 \cdot 41.2 \frac{L}{s} \approx 389600€ \quad (14)$$

Conclusions

In this research the goal of the analysis was the improvement of the existing drinking water treatment plant. The improvements, in this case, had to involve technologies that are applied for removal of magnesium and manganese. Both of these ions are divalent ions. Technologies that are suitable for removal of these ions vary from classical to modern. One of the options was the ion exchange process, but, since there is an increase in sodium concentration after ion exchange treatment, this technology had to be rejected. Membrane technologies were fulfilling all the expectations. Nevertheless, these technologies are very expensive, and reverse osmosis was rejected, but nanofiltration meets the required removal demands and it has been selected as the right choice in this case. Cost analysis was also included to get a better perspective when deciding on an optimal technology choice.

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