

REMINERALIZATION OF NANOFILTRATION PERMEATE

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Abstract: Nanofiltration is widely used for drinking water preparation as well as for water softening. When used for filtration of naturally low mineralized water it decreases mineralization of obtained permeate additionally. This paper shows the possibility of permeate remineralization in order to increase the total hardness and calcium and manganese levels in the permeate. For the purpose of the experiments, dolomite rock acidic solution was created and added in different amounts to the nanofiltration permeate obtained on self-made nanofiltration pilot plant. It was shown that calcium and manganese concentrations exhibited linear increase with regard to the inlet concentrations. Water hardness was also elevated to up to 10.845 °dH. Experimental procedure presented in this paper can be successfully used for elevating nanofiltration permeate water hardness and total mineralization.

Key words: nanofiltration, remineralization, total hardness, pH value, calcium, manganese

1. INTRODUCTION

Calcium and magnesium are both essential for biochemical processes in the human body. Calcium is a key component of bones and teeth and plays an important role in reducing neuromuscular stimuli, proper functioning of the cardiovascular system, heart and muscle contractility, information transfer between cells, and blood coagulation. Osteoporosis and osteomalacia are common manifestations of calcium deficiency. A less common but proven disorder due to calcium deficiency is hypertension. The recommended daily intake of calcium, as per WHO, for adults is between 1000 mg and 1300 mg, depending of the age [1]. Magnesium is a cofactor and activator in over 300 enzymatic reactions, including glycolysis, adenosine triphosphate mechanisms, transport of cations such as Na, K, and Ca across cell membranes, protein and nucleic acid synthesis, and muscle contraction [2]. Mg is a natural antagonist of calcium. As a result of magnesium deficiency in the human body, disorders such as cardiovascular diseases, type II diabetes, osteoporosis, and eclampsia may develop [2-4]. Also the deficiency of Mg in human body increases risk of developing serious diseases such as depression, addictions, memory disorders, anxiety states and other [5]. Recommended daily intake of magnesium for adults is 300 - 400 mg [6, 7]. There are no health-related standards that define Total Hardness (TH) in drinking water. The WHO guide identified that water with a TH value of 200 mg CaCO₃/L (11.2 °dH) or higher promotes scale formation, while soft water with a TH of 100 mg CaCO₃/L (5.6 °dH) or less has a low buffering capacity and becomes corrosive to plumbing installations. For these reasons, water softening is recommended to be limited to 150 mg CaCO₃/L (8 °dH) [8]. There are opposing views on the necessity of Ca and Mg presence in drinking water, and there is very little scientific literature on the subject. Advocates of the thesis that elements forming TH are essential in drinking water due to their beneficial effects on health rely on the premise that very soft waters negatively impact the mineral balance in the human body, which may be related to strokes and the formation of vascular spasms in the heart. As general food components, Ca and Mg supply the human body with [8] the largest required daily intake of these minerals in amounts ranging from 80 to 95%. In any case, there is no direct evidence that soft water explicitly causes certain human diseases, but it has been shown that the deficiency of Ca and Mg negatively affects the development of certain diseases. Although most of the world's drinking water sources contain Ca and Mg, there are many areas where rainwater or demineralized water obtained from desalination plants of seawater or brackish water is used for drinking. Groundwater sources in the Pannonian Plain, including the municipality of Kikinda, contain low concentrations of Ca and Mg, resulting in very low total hardness. According to the current regulation on drinking water quality, neither minimum nor maximum values for total hardness are defined, although the maximum values of total hardness are indirectly determined by limiting the values of Ca to 200 mg/L and Mg to 50 mg/L.

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Nanofiltration systems operate according to a tangential hydraulic configuration called cross-flow (CF) filtration. In tangential filtration, the influent continuously moves across the membrane surface, resulting in permeate and concentrate, which are removed from the system through special pipelines. In CF filtration, directing the flow of the influent tangentially to the membrane surface increases the permeate flux, as the influent helps to remove some of the accumulated substances from the membrane surface during flow. By continuously removing the concentrate, the formation of a cake layer on the membrane is significantly reduced, thus extending the membrane's operational lifespan.

Nanofiltration is widely used membrane filtration process for drinking water preparation and brackish water filtration [9]. It is commonly used for water softening but it can be also very successfully used for removal of humic matter [10], arsenic [11] and sodium as well [12].

The goal of the remineralization study was to investigate possibility of nanofiltration permeate total water hardness increase in order to produce water with increased mineralization.

2. MATERIALS AND METHODS

2.1. Water source characterization

Determination of optimal nanofiltration process parameters of deep well groundwater from the aquifer of the city of Kikinda (45° 49' 46" N, 20° 27' 55" E) was examined as a part of separate experiment. Groundwater found in northern parts of Serbia have characteristic yellow color due to the presence of organic humic matter, are rich in sodium, ammonia and arsenic ranging from 0.040 to 0.380 mg/L [13, 14] as well as elevated ammonia and sodium level. Selected physicochemical parameters of groundwater from city of Kikinda are presented in Table 1. The groundwater was treated on a self-made NF pilot plant (NFPP), shown on Figure 1, at different transmembrane pressures and flux conditions. NFPP has been designed for optimal permeate flow rate of 700 L/h and flux of approximately 30 L/hm², according to number of membrane elements and inlet water type. NFPP contained three NF membrane elements (CSM NE4040-90, manufactured by Toray Chemical Korea Inc. [15]). Upon determination of optimal process parameters such as permeate and concentrate flows, transmembrane pressure and flux, pilot plant was left to operate under these conditions.

Obtained permeate parameters were in accordance with European regulations [16] as well as local regulations for drinking water [17]. The average total hardness of tap water was ~1.4 °dH. 98.75% of the total hardness was removed from well water using membrane technology, with the concentrations of Ca and Mg individually being less than 2 mg/L and less than 0.3 mg/L, respectively.

Table 1 – Selected physicochemical parameters of groundwater from city of Kikinda and obtained experimental NF permeate

Parameter	Groundwater from the city of Kikinda	NF3-90 permeate
pH	8.34	7.43
Electrical conductivity (μS/cm)	856	26.95
NOM (mgKMnO ₄ /L)	28.65	0.3
TOC (mg/L)	3.52	0.23
As (μg/L)	18.07	4.12
Na (mg/L)	206.90	6.91
NH ₄ -N (mg/L)	2.07	0.11
Ca (mg/L)	9.27	<2
Mg (mg/L)	0.3	<0.3
Total hardness (°dH)	1.37	<0.5

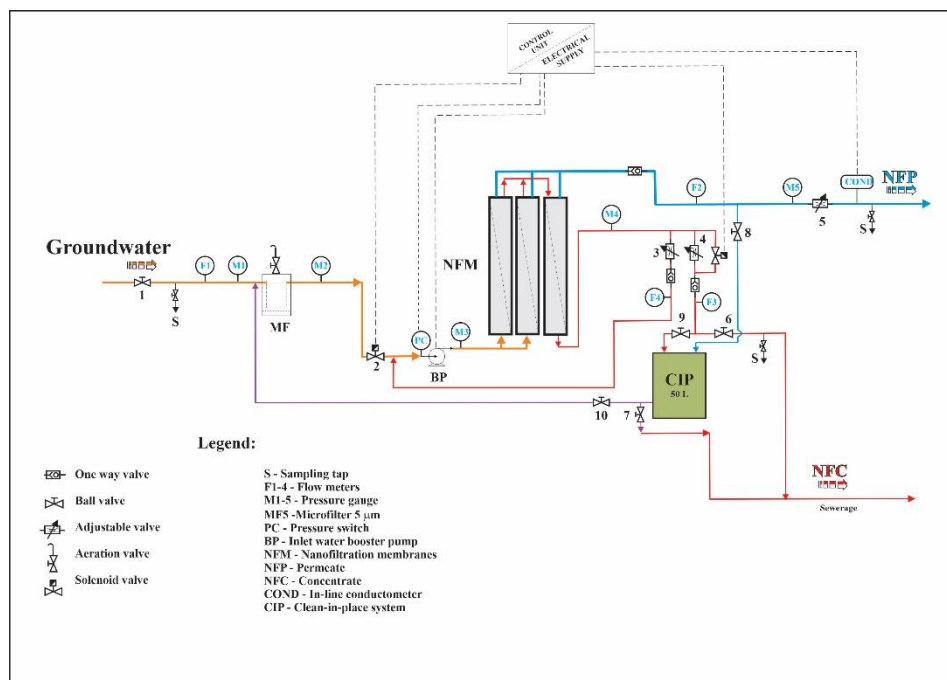


Figure 1 - Schematic presentation of NF pilot plant; MF-Protective 5 μ m microfilter, NFM – Nanofiltration membranes, M–Pressure gauges for water pressure measuring at the next points: M1- Before MF, M2-After MF, M3-Before membrane modules, M4-Concentrate branch, M5-Permeate branch, F– Flowmeters for water flow measuring of F1-Feed water, F2-Permeate, F3-Concentrate, F4 – Recirculation, PC- Pressure switch, BP-Booster pump, COND-Conductivity meter, CIP-Clean in place unit, S-Sampling tap

During the operation of nanofiltration pilot plant permeate and concentrate are produced simultaneously. The concentrate composition is such that it can be discharged into the local sewerage. Besides liquid concentrate, nanofiltration process is a process where no waste is generated (sludge, mud, etc.) during the operation.

2.2. Experimental procedure

The experiment was designed to dose the permeate with a dolomite solution of known concentrations of Ca and Mg. The dolomite, whose composition is shown in Table 2, was obtained from the Ibarski mines. The Ca and Mg solution was prepared via dissolving process of 3.5 kg of dolomite in 2 L of 13% HCl. The total hardness of obtained solution was $\sim 10,000$ $^{\circ}$ dH. Using the Grundfos DDE 6-10 dosing pump, a mixture of water and solution (in a ratio of 8 parts water to 3 parts solution) was added to the homogenization tank (Type: C-2160-F7, V=410 L, Structural, Belgium), where the permeate was mixed with the remineralization solution. The dolomite solution was added in varying portions for each test point during the experiment while maintaining a constant flow of permeate.

Table 2 – Mineral composition of the dolomite rock

CaO	MgO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃
30.57	21.38	1.57	0.57	0.20

The first point of the experiment was defined by adjusting the parameters on the dosing pump, selecting the minimum possible value for the amount of solution dosed and the dosing frequency. The dosing frequency was maintained at 25% during the experiment, while the dosing pump

stroke for each experimental point is shown in Table 3. The addition of the solution caused an increase in the electrical conductivity of the permeate at the outlet of the mixing tank due to the dissolution of minerals. When the electrical conductivity value remained constant for 10 continuous minutes, the first sample was taken. Subsequent experimental points were defined by increasing the dosed volume of the solution over time, and samples were taken after the electrical conductivity values of the permeate stabilized.

Table 3 – Dosing pump stroke per experimental point

Experiment number	Stroke
T1	30%
T2	45%
T3	70%
T4	100%

3. RESULTS AND DISCUSSION

Empirically obtained values of amount of dosing solution, electrical conductivity, water hardness, pH value and chloride concentrations in four experimental points is presented in Table 4.

It can be seen from Table 4 that a successful increase in the total hardness of the permeate was achieved. Electrical conductivity shows an increasing trend with the rising amount of minerals in the permeate, while a decrease in pH value is observed. Since in sample T4 the pH value was very low and close to the lower prescribed limit [17], the addition of the solution to the permeate was not continued, as further increase would result in a pH value outside the maximum tolerable level according to local regulations. The exhibited decrease in pH value was the consequence of the composition of the dosing solution that was of acidic nature. Chloride concentration as presented in Table 4 shows increasing trend with regard to the amount of the dosing solution increase. The concentration of chlorides at all experimental points did not exceed the maximal tolerable limit of 250 mg/L [17].

Calcium and magnesium levels during the experiment exhibited linear increase with $R^2 = 0.9617$ and 0.9598 , respectively (Figure 2) thus exhibiting direct correlation with the increase of the dolomite solution. Increase of calcium with regard to the values in the permeate was ~22 times while increase of magnesium concentrations with regard to the values in the permeate was ~11 times.

Water hardness was increased in the first experimental point 3.35 times with regard to the inlet permeate value. With the increase of the dosing solution amount water hardness continued to exhibit increase to up to 10.845 °dH at the last experimental point.

Table 4 – Empirically obtained results per experimental point

Experiment number	Amount of dosing solution (mL/h)	EC (µS/cm)	Water hardness (°dH)	pH	Cl ⁻ (mg/L)
T1	157.50	230.8	4.587	7.4	54.95
T2	236.25	250.5	5.326	7.2	56.72
T3	367.50	402.0	7.025	7.1	108.13
T4	525.00	514.3	10.845	7.0	136.49

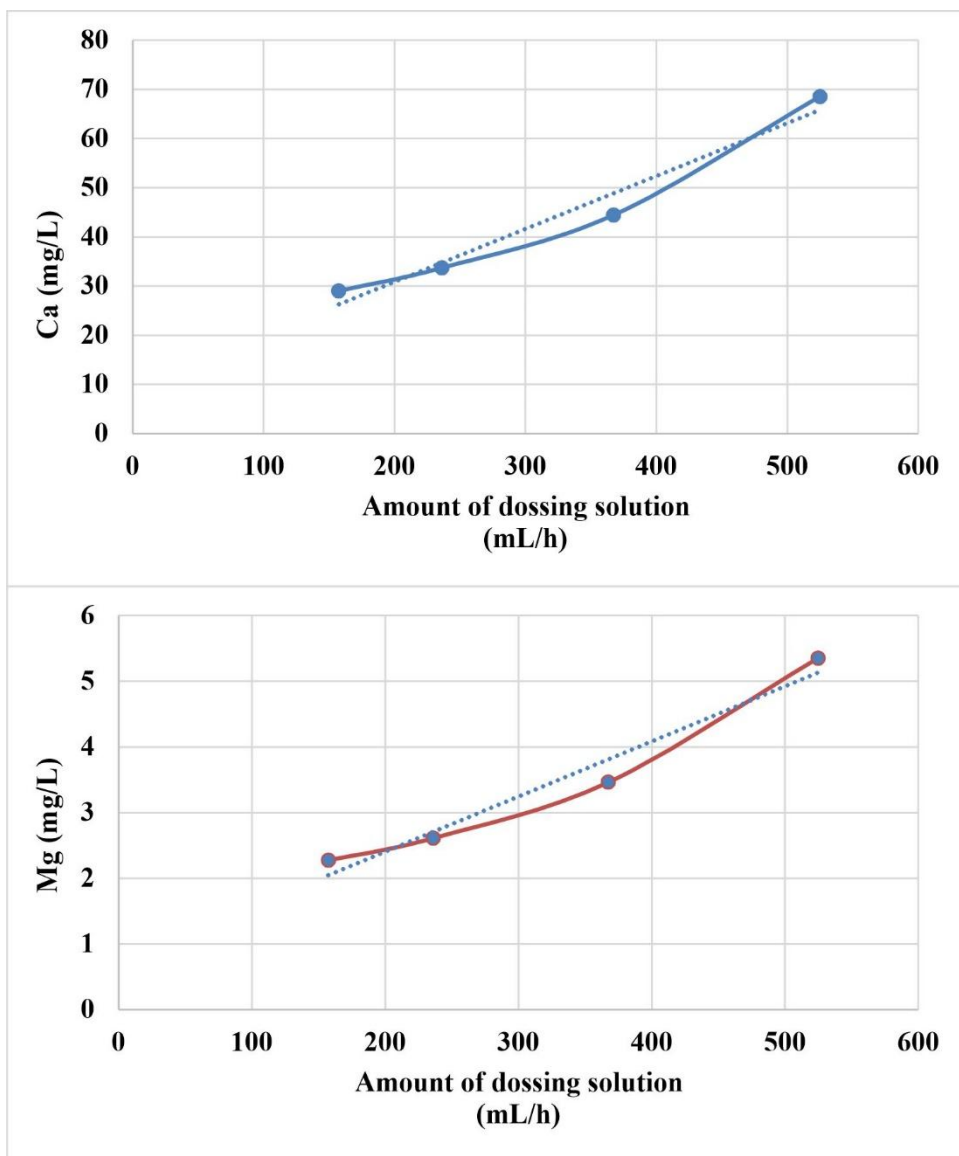


Figure 2- Influence of the amount of dosing solution on calcium (A) and magnesium (B) levels

Number of published scientific papers, that authors could find in the literature regarding the remineralization of nanofiltration permeate was very poor. Namely, all papers that could be found are concerning the topics of reduction of total hardness and/or calcium and magnesium removal from groundwater using nanofiltration. On the other hand, papers concerning reverse osmosis permeate remineralization can be found in great number. Philiber et. al (2022) conducted experiments on surface water RO permeate remineralization through minerals recovery from brines and obtained permeate hardness increase from 20 to 553 mg/L CaCO_3 [18]. Biyoune et. al (2017) explored remineralization of reverse osmosis permeate water by calcite bed in the Daoura's plant (south of Morocco) and managed to bring to water back its entire calco-carbonic balance to measure up to the Moroccan standards of drinking water [19]. One study also considered the way to adequately remineralize desalinated water for a range of temperatures of between 14°C and 25°C [20].

All of the above indicates that this paper is probably one of the first concerning remineralization of nanofiltration permeate.

4. CONCLUSION

The main goal of this investigation was reached i.e. it was shown that low values of nanofiltration permeate water hardness can be elevated using the dolomite acidic solution. Water hardness was increased as up to 7.91 times in the last experimental point with the largest amount of dosing solution. Calcium and magnesium levels exhibited linear increase with regard to amount of dosing solution reaching up to 68.53 mg/L and 5.35 mg/L in the last experimental point, respectively. Presented experimental procedure can be successfully used for low mineralized nanofiltration permeate water hardness increase thus obtaining water with increased mineralization and of better sensory characteristics. This was a success from the point of designing the drinking water plants for settlements with similar groundwater composition.

5. REFERENCES

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