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Research on improving the composition of mineral water using nanofiltration

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ABSTRACT

In many commercial water treatment applications a reduction of sulphate ion content is needed to improve the taste of natural mineral water. This paper presents the results of nanofiltration (NF) process investigations to test sulphate ion reduction in natural waters. Commercial nanofiltration membrane NF-270 Dow Filmtec has been tested in this research project. NF tests were carried out at transmembrane pressure of 0.8–2.0 MPa in the dead-end filtration mode. In addition, in order to improve the composition of calcium ions in the final product, permeate obtained during the NF process was filtered through a $CaCO_3$ bed.

The Total Dissolved Solids (TDS) of tested raw mineral water was 2,176 mg L^{-1} and contained 798.7 mg L^{-1} of SO_4^{2-} and H_2S level was 2.0 mg L^{-1} on average. As a result of water improving in the NF process, high reduction of SO_4^{2-} ions has been obtained (more than 98%), while the TDS has been reduced by 61%–64% (dependent on transmembrane pressure applied). The NF process allowed for relatively high reduction of divalent ions; therefore, a significant reduction in calcium ion content (82%–84%) and magnesium (about 84%) has been also achieved. Monovalent ions have been reduced to a lesser extent, i.e., sodium by 42%–46% and bicarbonates by 42%–49%. NF permeate filtration in the $CaCO_3$ bed has increased calcium and bicarbonate ions concentration by 60.5% and 7%–8%, respectively.

Morphological assessment of the deposits using the Scanning Electron Microscopy (SEM) method and chemical composition analyses revealed the presence of gypsum crystals on the surface of the NF-270 membrane.

Keywords: Mineral water; Water composition improving; Nanofiltration; Hydrogeochemical type of water

1. Introduction

Mineral water is characterised by its purity at source, its mineral content, trace elements and other constituents, and its medicinal properties [1,2]. As the trend towards a healthy lifestyle becomes increasingly popular, many mineral water brands are marketed in developed countries [3]. In Eastern Europe, this sector is still developing. With growing public awareness of the role of healthy beverages and the effects of consuming carbonated soft drinks, interest in the consumption of bottled table and mineral water has increased. In Poland, an increase in the sales of these products was observed particularly in the first years of the twenty-first century [3].

In hydrogeology, generally accepted classification factor for naturally sourced water is also its mineralisation. On this basis groundwater is divided into three groups: (1) mineral waters, which contains not less than 1,000 mg L^{-1} dissolved

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solids; (2) acratopegae with mineralisation within the limits 500–1,000 mg L^{-1}, and (3) natural and fresh waters, containing less than 500 mg of mineral salts per litre.

In Poland, water intended for drinking and sold in packaging as natural water should comply with the requirements of the regulation of the Minister of Health of 31 March 2011 [4]. In consequence, natural waters are classified into water, mineral waters, spring waters and table waters. Taking into account mineral and gases composition, in some cases there is a need to improve the taste of mineral water before its bottling process, for example by reducing the sulphate ion content.

Nanofiltration (NF) is considered to be one of the most promising techniques for production of high quality water and many examples of its use exist, especially in the drinking water industry [5]. NF membranes are characterised by a high retention of divalent ions while the retention of monovalent ions is limited. They are usually polyamide-based, thin-film composite structures, relatively close in chemical structure to reverse osmosis (RO) membranes. Their pore size is 0.5–1.5 nm, ranging between that of ultrafiltration and RO membranes [5]. The membrane charge originates from the dissociation of ionisable groups at the membrane surface and from within the membrane pore structure [6]. In addition to the ionisable surface groups, NF membranes have a weak ion-exchange capacity and in some cases ions from the contacting solution may adsorb onto the membrane surface causing a slight modification to the membrane charge [7].

The aim of the study was to modify the physicochemical properties of mineral waters to achieve improvement in terms of water smell and taste. The research focused on efficacy of mineral water taste improvement using hydrogen sulphide rejection and sulphate ion content reduction methods.

2. Materials and methods

2.1. Water tested

The macro-composition of the natural mineral waters tested in this study showed occurrence of sulphate, chloride, sodium, calcium and magnesium ions with the presence of hydrogen sulphide. The TDS of tested raw mineral water was 2.176 g L^{-1} and contained 798.7 mg L^{-1} SO_4^{2-}, 145.3 mg L^{-1} Ca^{2+}, 93.5 mg L^{-1} Mg^{2+} and H_2S (average 2.0 mg L^{-1}). The temperature of the waters during test was 20°C, and pH of the water did not exceed the value of 7.

2.2. Apparatus

A diagram of the proposed process to improve water smell and taste is shown in Fig. 1. It is a feasible option for industrial applications. In this study, however, the second step (micro- and ultrafiltration) was omitted with the aim to assess NF performance in isolation. In order to remove hydrogen sulphide before carrying out a NF performance test, the water was degassed (aerated). It was obligatory first step to modify water's organoleptic properties and remove an unacceptable smell in the tested water.

The NF membrane process tests were conducted in the dead-end filtration mode. Pressure was applied to the membrane using a steel cell (volume: 400 cm^3) and a magnetic stirrer. The NF tests were carried out at a transmembrane pressure of 0.8–1.2 MPa. The active area of the membrane was 38.5 cm^2. NF-270 Dow Filmtec nanofiltration membrane, characterised by a negative load surface in a wide range of pH [8,9] was used. Membrane characteristics is shown in Table 1.

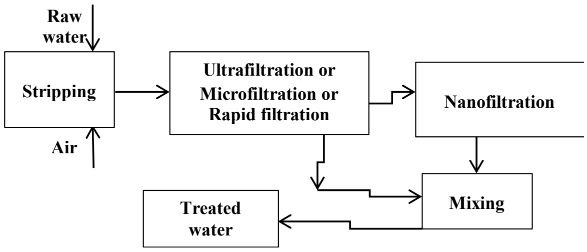


Fig. 1. Proposed process for mineral water treatment in industrial applications.

Table 1
Membrane characteristics: manufactures' data [10]

Membrane symbol	NF-270
Membrane material	polyamide thin-film composite
Mol. weight cut-off (Dalton)	200–400
Transmembrane pressure (max), MPa	4.1
pH range	2–11
Maximum temperature, °C	45
Retention coefficient	99.2% $MgSO_4$

During tests the changes of membrane effectiveness in time were observed. The NF permeate was filtered through a $CaCO_3$ bed column filled with natural limestone rock from Wierzbica Mine [11] with the purpose of improving composition of the mineral water. Aggregate fractions ranging from 1.0 to 3.0 mm were utilised in the tests. The permeate was not mixed with unfiltered water during tests.

2.3. Methodology of physicochemical analysis

Physicochemical analyses of the basic mineral components were carried out for to the raw tasted mineral water, NF permeate, retentate from the NF process, and the final effluent water saturated with calcium carbonate. , Inorganic constituents were determined in an accredited laboratory of the Department of Hydrogeology and Engineering Geology of the AGH University of Science and Technology in Krakow (PCA certificate No AB 1050) using the inductively coupled plasma mass spectrometry (ICP-MS) and inductively plasma optical emission spectrometry (ICP-OES) methods. Chloride ion content and water alkalinity were determined by titration in accordance with accredited testing procedures (PCA certificate No AB 1050). Sample preparation included filtration through a 0.45 μm membrane filter and acidification using 1 mL ultrapure nitric acid for each 100 mL of samples.

2.4. Methodology of membrane scaling analysis

The morphology and the chemical composition of the main mineral components of the materials examined in the micro area domain were determined using the Scanning Electron Microscope (SEM) [12]. The equipment used was

FEI Qanta 250 FEG scanning microscope equipped with a chemical composition analysis system based on Energy Dispersive X-Ray Spectrometer (EDAX).

3. Results and discussion

Hydrogeochemical characteristics of the raw mineral water analysed has classed the tested water as sulphate-chloride bicarbonate-sodium-calcium sulphide. It is a poly-ion water with increased major ion content: SO_4, Cl, HCO_3, Na and Ca. Substantial sulphate ion content (798.7 mg L^{-1}) caused bitter taste of the water. The tested process for adjusting composition of mineral water by using air stripping and nanofiltration has shown a very high retention coefficient of sulphates (98.2%–98.7%), and a significant retention of divalent cations and cations causing hardness. It was found that there was a low retention of chlorides (12.5%–18.1%) and boron (5.54%–9.64%), which was related to the fact that the pH of the raw water does not exceed the value of 7 [13,14]. Numerous studies devoted to the efficiency of boron ions removal from water and wastewaters using the reverse osmosis process demonstrate that a high retention rate for boron, at a level exceeding 98%, is possible at pH water value of at least 10 [13,14].

Physicochemical characteristics of raw mineral water and permeate obtained during nanofiltration process are presented in Table 2.

The TDS of water has been reduced by 61%–64% using the NF process. NF allows a relatively large reduction in the concentration of divalent ions and a significant reduction in the calcium (83%–84%) and magnesium (84%) ion content has also been obtained. Monovalent ions have been reduced to a lesser extent, i.e., sodium by 42%–46% and bicarbonates by 42%–49%. The hydrogeochemical characteristics of mineral water after NF has changed from sulphate-chloride bicarbonate-sodium-calcium to chloride-sodium water. Despite obtaining a beneficial effect in reducing the concentration of sulphate ions, the NF process has significantly changed the mineral composition of the water (Table 2).

Despite high level of calcium retention, the NF permeate has not met the total hardness standards for drinking water required by law in Poland and the European Union [15]. For this reason a polishing step involving filtering the NF permeate through a $CaCO_3$ bed was proposed and tested. The main aim of conducting this experiment was improvement of hydrogeochemical characteristics of the final effluent water from chloride-sodium to chloride-bicarbonate-sodium water. The concentration of calcium ions has been increased by 60.5% while bicarbonate ions increased only by 7%–8% (Table 2).

Permeate flux changes in time during the NF process are presented in Fig. 2. This study has shown a minimum loss of membrane efficiency with time, which indicates the absence or limited effect of fouling and scaling phenomena on the NF process efficiency.

The morphological assessment of the NF-270 membrane deposits using SEM method and the chemical composition of

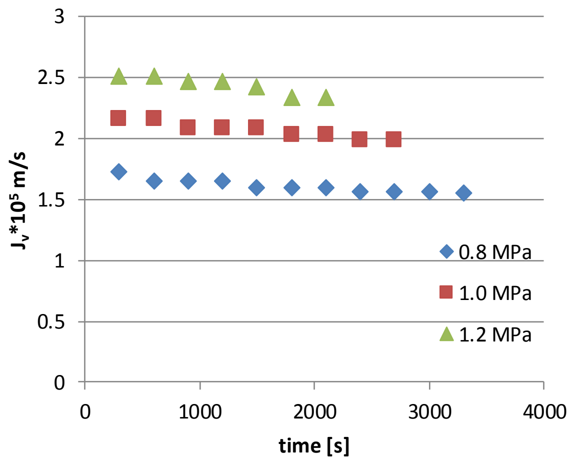
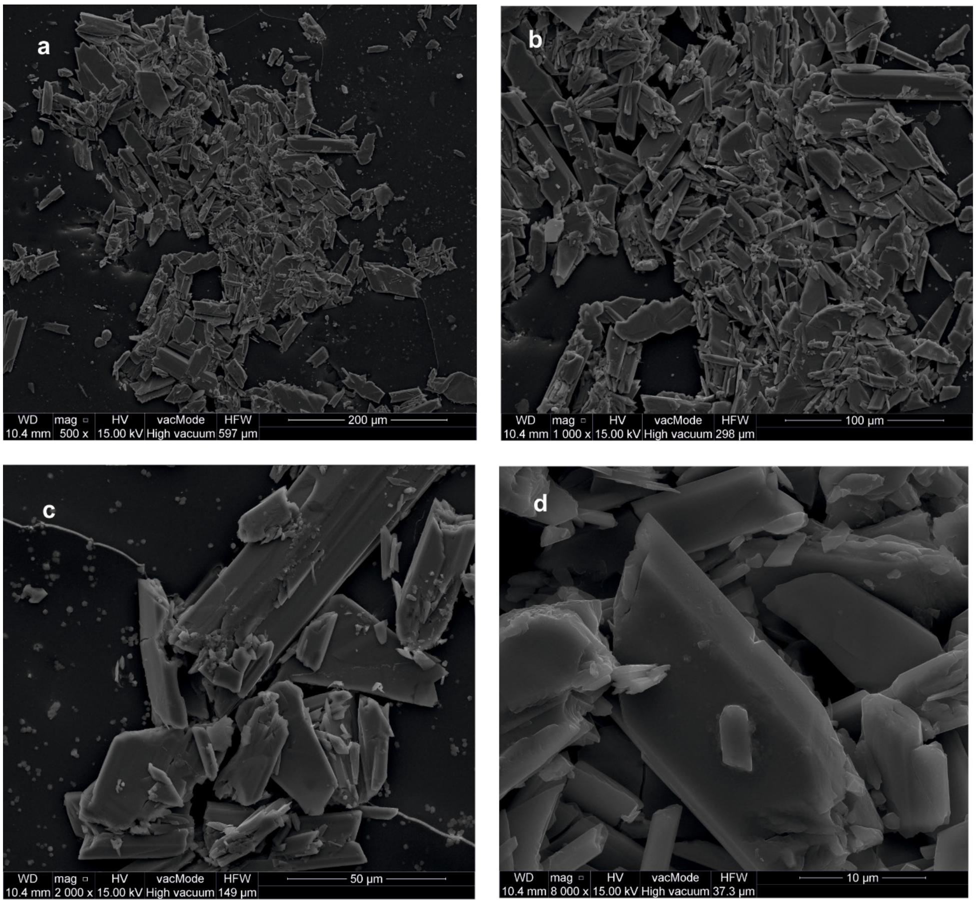


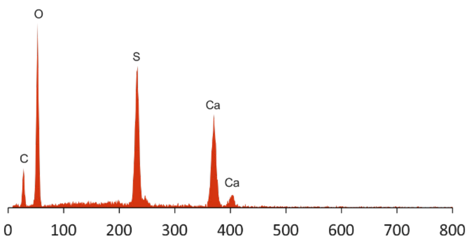
Fig. 2. Changes of permeate flux during nanofiltration of mineral water using the NF-270 membrane.

Table 2
Results of treating mineral water using a NF-270 Dow Filmtec nanofiltration membrane (ΔP- transmembrane pressure, *R*-retention coefficient)

Parameters	Mineral water (Raw water)	Permeate ΔP = 0.8 MPa	*R* [%]	Permeate ΔP = 1.0 MPa	*R* [%]	Permeate ΔP = 1.2 MPa	*R* [%]	$CaCO_3$ filtration effluent
[a]TDS	2176	780.4	64.1	827.5	62.0	848.0	61.0	897.2
[b]Total hardness	747	117	84.3	123.9	83.4	125.0	83.3	118.1
[a]Na^+	456.1	243.5	46.6	257.1	43.6	263.8	42.2	277.06
[a]Ca^{2+}	145.3	22.7	84.4	24.7	83.0	25.0	82.8	28.23
[a]Mg^{2+}	93.5	14.87	84.2	15. 2	83.8	15.2	83.7	11.57
[a]Cl^-	459.1	376.2	18.1	401.5	12.5	400.1	12.85	402.4
[a]Br^-	0.50	0.467	6.62	0.482	3.64	0.50	0.00	1.1
[a]SO_4^{2-}	798.7	10.4	98.7	11.5	98.6	14.1	98.2	45.43
[a]HCO_3^-	369.4	186.8	49.4	191.0	48.3	213.7	42.15	195.3
[a]CO_3^{2-}	<0.50	<0.50	0.00	<0.50	0.00	<0.50	0.00	<0.50
[a]B	0.99	0.90	9.64	0.98	1.68	0.99	–	0.9

[a]In mg L^{-1}.
[b]In mg $CaCO_3L^{-1}$.





Element	Mol %
SO_3	59.62
CaO	40.38

Fig. 3. SEM-EDS images of the NF-270 membrane surface in membrane autopsy revealing the formation of gypsum scale. Explanations: (a) magnification 500x; (b) magnification 1000x; (c) magnification 2000x; (d) magnification 8000x.

the deposits crystallised on membrane's surface has shown the presence of gypsum ($CaSO_4 \cdot 2H_2O$) crystals (Fig. 3). Multiple aggregates of the minerals are visible in microscopic images of the NF-270 membrane in place of a background of the membrane itself and in some micro-areas these aggregates have the form of a solid layer. It has been concluded that an intensive concentration polarisation process, membrane characteristics and the mass transport mechanism could have affected the precipitation of these crystals on membrane's surface.

4. Conclusions

This research study has demonstrated that the nanofiltration process using the NF-270 membrane can be applied as an effective method to reduce sulphate ions content in mineral waters. The results have demonstrated that the NF process has changed the mineral hydrogeochemical type of tested mineral water from sulphate-chloride-sodium-calcium-magnesium to chloride — sodium water type. NF permeate water quality has been improved by a filtration process using a $CaCO_3$ bed. This has resulted in the second correction of the hydrogeochemical composition of water from chloride-sodium to chloride-bicarbonate-sodium water type.

Presence of gypsum ($CaSO_4 \cdot 2H_2O$) crystals has been detected by the SEM equipped with a chemical composition analysis system based on Energy Dispersive X-Ray Spectrometer (EDAX). It has been found thatthe entire NF-270 membrane surface has to be susceptible to scaling, which resulted in the formation of a layer that decreased the NF process performance over time.

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