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# Comparison of the efficiency of micro-pollutant removal from geothermal water on a laboratory and a semi-industrial scale

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## ABSTRACT

In recent years, there has been an increase in the demand for drinking water and also for water intended for agriculture, industry, and other purposes. Therefore, research is needed to find new technologies and methods for the comprehensive use of geothermal waters (GTs) to provide drinking water and water that can be used for other purposes in an environmentally-friendly way. The maximum permissible concentrations of inorganic micropollutants, including toxic constituents, both in drinking water and in wastewater discharged into the environment, are set by the World Health Organization, the Water Framework Directive, and relevant national regulations. The paper presents a comparison of the effectiveness of the removal of selected inorganic components from GTs on a laboratory and semi-technical scale. GT with mineralization of about 6 g/L was used in the research. Laboratory and semi-industrial tests were carried out with the use of NF270, NF90, ROBW30FR-400, and ROBW30HR-440i membranes from DOW FILMTEC Company. The research work carried out proved that the treatment of mineralized and salt-laden GT with increased content of micro-contaminants, including heavy metals, using a two-stage Nanofiltration-Reverse Osmosis system is an effective solution. Tests conducted on a laboratory (and semi-industrial) scale permitted micro-pollutant removal up to following values: B 96% (26%), $Cr^{3+}$ 86% (55%), $Pb^{2+}$ 94% (75%), $Ni^{2+}$ 67% (50%), $Fe^{2+}$ 99% (92%), and $As^{3+}$ 93% (67%). The use of membrane processes in water treatment can provide more or less selective removal of the target micropollutants.

*Keywords:* Micropollutants; Membrane processes; Geothermal water; Boron; Arsenic

## 1. Introduction

In many places around the world, the problems of access to drinking water and its limited resources present a serious challenge, which is compounded by population growth, urbanization, and economic development. Geothermal water (GT) gains attention as an efficient source of energy and also can be evaluated for other uses including bathing, agriculture, and balneology. Owing to the increasing usage of GTs, the management of possible environmental impacts and treatment of these waters is becoming more important day by day [1,2]. These waters, due to their specific physico-chemical parameters, can potentially improve the conditions for managing drinking water and increase its resources. A number of inorganic anions and metals are identified in surface and underground waters, including

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GTs. These include heavy metals and silica, which at certain concentrations have a detrimental effect on human health (inorganic micropollutants). Therefore, much research has been carried out aimed at seeking new technologies and methods to enable their comprehensive and multivariate management as a carrier of energy, as water intended for consumption, and as water that can be recycled in an environmentally friendly way [3]. The maximum allowable concentrations of inorganic components, including toxic ones, in both drinking water and wastewater discharged to the environment, have been defined by the World Health Organization (WHO) in the Water Framework Directive and in relevant national regulations. In many cases, they have been set at a very low level, even in the order of $\mu g/dm^3$. In different water sources, which include GTs, numerous inorganic compounds have been found in potentially harmful and unacceptable concentrations. The way of recognizing and removing these micropollutants from GTs is one of the main technological challenges [4]. To respect the proper concentrations of undesired components, the application of membrane processes, including nanofiltration (NF) as well as reverse osmosis (RO) and integrated systems, can be an effective method of reducing inorganic micropollutants in GTs. The high level of removal of dissolved inorganic compounds in water allows one to obtain high-quality products [5,6]. RO is a well-known technology which is increasingly being used to provide water intended for domestic consumption around the world due to its high efficiency, low energy consumption, and the improvements made in systems over years gone by [7,8].

The presence of inorganic micropollutants in drinking water has been recognized as a worldwide threat and problem imposing dangers to human health [9]. Membrane processes, including UF (ultrafiltration), NF, RO, and FO (forward osmosis), are mentioned as potentially beneficial methods but further investigation is needed to conduct micropollutant removal on an industrial scale [10]. The possibility of their removal from water which potentially can be considered as water intended for consumption by, for example, NF, is promising and is the subject of a number of research projects [3,11]. Van der Bruggen and Vandecasteele [3] indicate that NF is a suitable method for wide spectrum micropollutant removal, but points out that the use of a hybrid system of, for example, an NF-RO combination can significantly improve the results. Many works consider the problem of removing micropollutants from wastewater. In this case, technologies based on NF membranes are widely used due to their relatively high efficiency [11–14]. Moreover, the growing demand for water leads to considerations of the introduction of a water recovery system of GTs used for heating purposes, as well as wastewater and other spent waters. The presence of micropollutants in groundwater is also an emerging problem both in Poland and worldwide. Skoczko [15] and Skoczko et al. [16,17] investigated iron and manganese removal by the filtration method with the use of different filtration materials. In this case, the authors also suggest using a two-step filtration system to obtain satisfying rejection results. Szatyłowicz and Skoczko [18,19] tested another inorganic material such as activated alumina or activated alumina and a magnetic field for the removal inorganic impurities, including arsenic, fluoride, selenium, silicates, and heavy metals. The efficiency of iron and manganese removal was marginal when using activated alumina, however, the addition of a magnetic field caused a significant increase in heavy metal removal. They underline that the method of removal of emerging contaminants, especially manganese and iron, should be suitable for the type of water to be treated, and in some cases, combined systems should be used. Moreover, Zhang et al. [20] compared different membrane processes, including NF (negatively and positively with some modifications) and electrodialysis (simple binary or tertiary systems, actual brine systems). They indicated that membrane technologies are attractive methods for lithium and magnesium recovery from high salinity waters. However, a negatively charged NF membrane, such as NF90, represents the average rejection of these ions. The positively charged NF membrane permits a high separation efficiency of lithium and magnesium. Zhou et al. [21] indicated that integration of the NF process with RO, FO or electrodialysis [22], and multi-stage flash distillation, multiple-effect distillation, or membrane distillation/membrane crystallization (MD/MC) or an ion exchange process can be a promising technology, especially for cost reduction and rejection of ions. Albergamo et al. [23] investigated the removal of polar organic micropollutants by a pilot-scale RO treatment for drinking water. They indicated that tighter membranes and multi stage RO systems could cause higher efficiencies of removal. Research is being conducted on solutions based on NF, RO membranes [24–27], and FO [28] with different modifications. Fan et al. [29] proposed a novel nanofibre membrane with high efficiency in removing nanofibre organic micropollutants and heavy metal ions from water. Researchers testing micro-contamination removal using the photo-Fenton method with various solutions also obtained promising results [30–32]. The problem of removing micropollutants from groundwater, GTs, boiler water [33], and wastewater is discussed by many researchers all over the world and should be further explored.

The work presents the results of the assay designed to examine the efficiency of micropollutant removal from GT treated with a two-stage NF-RO system. The survey was carried out using the example of GT extracted from a well-located in central Poland. The water is characterized by elevated mineralization at a level of 6 g/L. The processes were conducted on a laboratory and semi-industrial scale and have allowed a detailed identification of the permeate physico-chemical composition, including the content of micropollutants, in the adopted process parameters.

## 2. Materials and methodology

### 2.1. Apparatus

The tests were conducted on a laboratory and semi-industrial scale. In the first situation, a two-step desalination NF-RO system was used for the tests. This included American Osmonics Inc., Company's SEPA CF-HP type membrane module, in cross-flow mode. A detailed description of the methodology and apparatus can be found in works by the other author Rajca et al. [6] and Tomaszewska et al. [34]. A schematic diagram of the apparatus is presented in Fig. 1 [6].

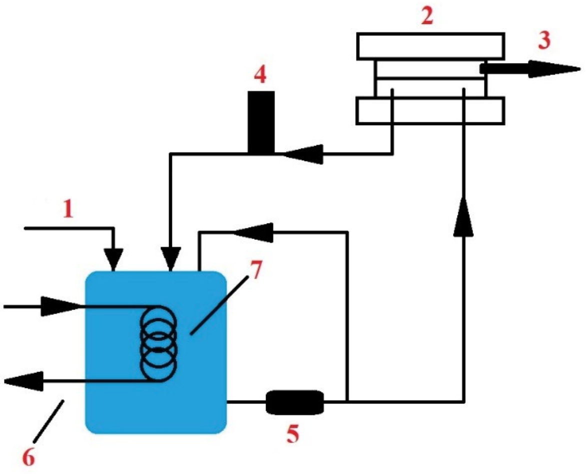

Fig. 1. Schematic diagram of the apparatus applied in the laboratory scale tests (1, raw water inlet; 2, membrane cell; 3, permeate outlet; 4, rotameter; 5, pump; 6, heat exchanger; 7, raw water tank) [34].

A volume of 5,000 mL of raw GT was placed in the water tank – 1, in which a heat exchanger – 6 – was also located. This was responsible for maintaining a stable water temperature during tests. A feed stream was pumped directly from the tank into the membrane cell – 2 – and therefore to the membrane. The water flowed tangentially across the membrane surface. The membrane, which was placed in the membrane cell, possessed an active area of 155 cm$^2$. Its task in the membrane process is to divide the inflowing stream into two separate streams. The first one is permeated and is part of the feed water, which permeated through the membrane surface. Permeate flowed out through the permeate outlet – 3 – and was collected in a vessel. The second stream is concentrate, which is a part of the feed water, which did not flow through the membrane. This part of the stream contained rejected dissolved compounds and was continuously recycled into the feed tank – 7.

The NF-RO tests conducted on a laboratory scale included two main stages: (1) the NF process of raw GT with the use of either an NF270 or NF90 membrane, and (2) the RO process with the use of a BW30FR-400 membrane. The permeates obtained after the NF processes were used as the feed water for the second stage of the treatment system. For both the NF and RO processes, a 50% recovery rate of feed water (50% of permeate and 50% of concentrate to raw water volume) was obtained. The processes were carried out to obtain a specified value of recovery rate of permeate with measurement of the time required to gain each additional 50 mL of permeate. The accuracy of the volume measurement was 1 mL. Moreover, the cross-flow velocity used in these measurements was 1 m/s. The transmembrane pressure was determined to be 10 bar for the NF and 15 bar for the RO processes. In all the tests conducted, the temperature of the GT was 22°C. The electrical conductivity, pH, and temperature value of the raw GTs and concentrates were determined directly after the processes in the laboratory using the electrometric method. The temperature was kept constant to carry out tests at a temperature similar to that which GT possesses after cascade use. The temperature was stabilized at a given level by applying a heat exchanger. The accuracy of temperature measurement was 0.5°C and oscillated in the range of measurement error. Due to the purpose of the research, which was to investigate the effectiveness of removing selected micro-pollutants from GT for laboratory-scale tests, no chemical agents were used. After each process, one sample of permeate was collected and subjected to further analysis in an accredited laboratory to obtain a detailed physico-chemical description.

Due to the intended use of individual devices, the technological system of the semi-industrial scale water treatment plant included three basic stages: (1) preliminary water preparation, (2) the main treatment process in an NF-RO system, and (3) final treatment to produce water parameters enabling the water to be used as potable water. A basic schematic diagram of the semi-industrial-scale treatment plant is presented in Fig. 2. The preliminary water preparation was conducted using devices that included a mechanical filter, iron removal station, and an ultrafiltration module (devices marked in purple color, Fig. 2). These elements are designed to prepare chilled GT (raw), so as to enable the safe operation of membranes, which are very sensitive to solid pollutants during treatment processes. In order to remove contaminants accumulated during the operation, the iron-removal device periodically conducts the rinsing process. The initiation of the rinsing process, as well as its implementation, is executed automatically and in a fully automatic manner. In the last part of the pretreatment process (after mechanical filtration and iron removal), water is passed to an ultrafiltration module, which includes a UF membrane (eight inches in

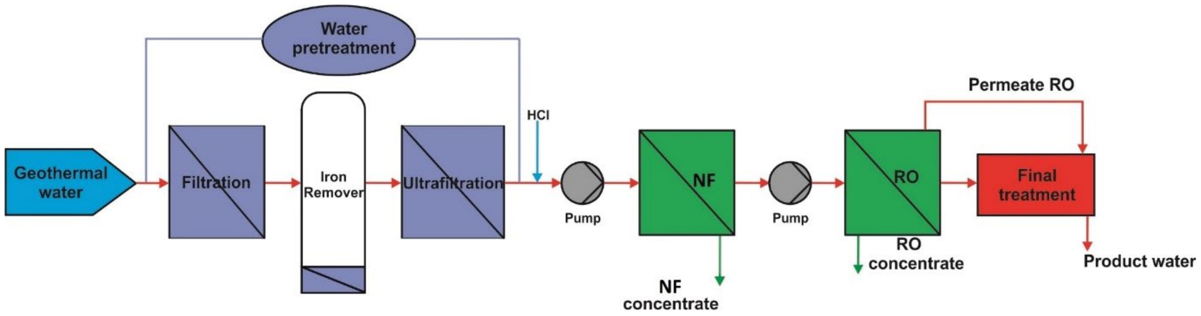

Fig. 2. Schematic diagram of the apparatus used in the test conducted on a semi-industrial scale.

diameter) with 0.03 μm pore size and an "out-in" flow from the DOW FILMTEC company. The second basic stage has been equipped with an NF-RO desalination system operating on NF-RO membranes in series and set for pH correction of the first permeate. The RO station was equipped with a DOW FILMTEC BW30HR-440i polyamide, thin-film, composite membrane, and NF station with an NF90 DOW FILMTEC membrane (Table 1) [35,36]. Two separate NF-RO units operated in a series system. Permeate from the first NF fed the RO station. The process was carried out with a 70% permeate recovery rate. The transmembrane pressure was set at 8 bar for NF and 11 bar for RO processes. The instantaneous GT flow rate feeding the desalination system was about 2–3 $m^3/h$ (average 1.5 $m^3/h$). At final treatment, the water permeate was subjected to further processes: (1) mineralization, consisting of filtration of water through a dolomite bed layer in order to increase the hardness of the, almost deionized water on the osmotic module, and (2) bacteriological sterilization with UV rays. After that, the GT treatment cycle was completed. The installation has been equipped with an automatic control system for individual processes that ensures the synchronization of the work of individual system components. In addition, due to the research character of the system, meters and stub tubes were installed at specific points of the installation, enabling the registration of basic water parameters and its collection for physicochemical laboratory tests. After each process (NF and RO), one sample of permeate was collected through a probe tap and subjected to further physico-chemical analysis in an accredited laboratory.

Apart from the main ions (one- and two-valence), the following physicochemical parameters (inorganic components) were identified in the samples of raw GTs and permeates obtained in the tests: lithium, arsenic, antimony, iron, nickel, lead, mercury, cadmium, aluminum, chromium, and boron. The detailed physico-chemical characteristics of the raw GTs and permeates were established using inductively coupled plasma mass spectrometry (for determination of Al ion concentration, and others), inductively coupled plasma optical emission spectrometry (for determination of Na, Ca, Mg, K, Fe, B, $SO_4$, and other components) and the titration method (for chloride ions and water alkalinity, in accordance with accredited testing procedures based on Mohr's method), in the accredited laboratory in accordance with international standards.

Four types of DOW FILMTEC™ membrane were used in the research, the first commercially marked as NF270, second NF90, third ROBW30HR-440i, and fourth ROBW30FR-400. The basic membrane characteristics are shown in Table 1.

### 2.2. GT

GT obtained from a well-located in central Poland was used for the tests. Before testing on a laboratory and semi-industrial scale, the detailed physico-chemical characteristics of raw GT were established. The GT is characterized by high total dissolved solids (6 g/L) and silica concentration (35 $mgSiO_2/L$), and also by a quite elevated content of calcium (125 mg/L), and magnesium (21 mg/L). Other parameters, such as sulfates (854 $mgSO_4/L$), chlorides (488 mg Cl/L), and sodium (489 mg Na/L) were established at lower concentrations. The specific characteristics of the water, including other micro- and macro-nutrients, are presented in Table 2. GT was established as a Cl–Na hydrogeochemical type, according to the Szczukariew-Priklonski classification. In all the tests conducted, the temperature of GT was 22°C.

### 2.3. Method of analysis of water quality

A detailed description of the concentration of the inorganic components analyzed, including micropollutants, was specified to analyse the quality of the raw water and permeates obtained after both laboratory and semi-industrial scale processes. The prime aim was to recognize the differences between them. A series of retention coefficients $R$ [%] was calculated based on the following Eq. (1):

$$R = \left(1 - \frac{C_r}{C_n}\right) \times 100\% \tag{1}$$

where $R$, retention coefficient (%); $C_r$, the concentration of a particular parameter in permeate (mg/L); $C_n$, the concentration of a particular parameter in raw water (mg/L).

## 3. Results and discussion

### 3.1. The results of GT desalination conducted on a laboratory-scale

After the laboratory test with the use of a two-stage NF-RO module, raw water and permeates were subjected to further analyses. The detailed physicochemical characteristics of selected parameters of raw GT and permeates, which were obtained after both NF and RO processes with 50% recovery, are shown in Table 2. Based on the results obtained, it can be seen that the concentration of most of the selected parameters, including the main cations (calcium, magnesium, potassium, and sodium), main anions (bicarbonates, chlorides, and sulfates) and other factors have decreased in varying amounts. The concentrations of all of the micropollutants analyzed decreased after the NF process, and their values, after a two-stage test, reduced significantly compared to raw GT. At present, NF is considered as one of the most promising techniques for water desalination and meanwhile it is used for high quality water production [39,40]. The experimental data from the first test with a NF270 membrane indicated that poor rejection was observed of the main ions and selected micropollutants was observed. The treatment of GT in the NF process using the NF270 membrane resulted in a reduction in mineralization of about 13%. The reason for this phenomenon was that the GT tested possesses a high concentration of dissolved solids, and therefore a more compact membrane (NF90) was applied for further research. Using an NF90 membrane as the first step in the desalination of GT caused a greater reduction of monovalent and divalent ions, as well as iodide, bromide, arsenic, chromium, and boron. The reason is that the NF90 membrane provides a high productivity performance while removing a high percentage of salts, nitrate, and iron, and also organic compounds such as pesticides and herbicides [35]. This tendency was not observed for other micro-pollutants, such as lead, mercury, and iron. For the main mono- and divalent ions, the use of the NF90

Table 1
Characteristics of the membranes used [35–38]

| Parameter | NF270 | NF90 | BW30FR-400 | BW30HR-440i |
|---|---|---|---|---|
| Material | polyamide thin-film composite | polyamide thin-film composite | polyamide thin-film composite | polyamide thin-film composite |
| Maximum operating temperature (°C) | 45 | 45 | 45 | 45 |
| pH operating range | 2–11 (continuous operation) | 2–11 (continuous operation) | 1–13 (continuous operation) | 2–11 (continuous operation) |
| Maximum operating pressure (MPa) | 4.1 | 4.1 | 4.1 | 4.1 |
| Minimum salt rejection | – | – | 99.00% | 99.40% |
| Stabilised salt rejection | >97.00% | >97.00% | 99.50% | 99.70% |
| Stabilised $NO_3^-$ rejection | – | – | – | 98.50% |
| Stabilised $SiO_2$ rejection | – | – | – | 99.90% |
| Stabilised boron rejection | – | – | – | 83.00% |
| Application | Designed to permit the passage of medium to high concentrations of salts and hardness from water where good organic removal is desired with partial softening | Designed to provide high productivity performance while removing a high percentage of salts, nitrate, iron, and organic compounds | Designed to purify water with high biological and organic fouling potential in systems with well-controlled pre-treatment; described as an element which offers exceptional fouling resistance, cleanability and long-term efficiency | Designed to purify water with high-performance and productivity; a high rejection of the brackish water RO element combining the highest active membrane area available in the industry today; the membrane sheet sustains maximum rejection of critical solutes, including silica, boron, ammonium, and nitrate over the working life of the RO element |

Table 2
The physico-chemical parameters of raw water and the NF-RO system permeates obtained from laboratory-scale tests

| Parameter | GT | | | | | |
|---|---|---|---|---|---|---|
| | Raw water for NF270 (mg/L) | NF270 permeate (mg/L) | RO permeate (NF270 permeate as feed water) (mg/L) | Raw water for NF90 (mg/L) | NF90 permeate (mg/L) | RO permeate (NF90 permeate as feed water) (mg/L) |
| Mineralization | 6,251.2 | 5,444.4 | 198.4 | 6,029.1 | 867.3 | 22.6 |
| H–G type[a] | Cl–Na | Cl–Na | Cl–Na | Cl–Na | Cl–Na | Cl–Na |
| EC[b] (mS/cm) | 11.33 | 8.00 | 3.76 | 10.39 | 1.61 | 0.032 |
| pH | 7.30 | 7.42 | 6.08 | 7.39 | 6.98 | 6.13 |
| $Na^+$ | 2,132.0 | 1,989.0 | 67.4 | 2,061.1 | 327.8 | 4.2 |
| $K^+$ | 19.88 | 16.50 | 1.73 | 18.39 | 4.81 | 0.93 |
| $Ca^{2+}$ | 125.6 | 98.8 | 1.14 | 123.6 | 1.0 | 0.11 |
| $Mg^{2+}$ | 22.6 | 15.4 | 0.184 | 21.1 | 0.260 | 0.015 |
| $Li^{2+}$ | 0.178 | 0.142 | 0.005 | 0.170 | 0.020 | 0.005 |
| $Cl^-$ | 3,485.0 | 3,063.0 | 110 | 3,407.0 | 495.5 | 5.8 |
| $SO_4^{2-}$ | 83.1 | 17.7 | 3.00 | 70.45 | 3.00 | 3.00 |
| $HCO_3^-$ | 330.4 | 206.1 | 11.3 | 275.0 | 27.3 | 5.8 |
| $I^-$ | 0.306 | 0.126 | 0.044 | 0.085 | 0.010 | 0.010 |
| $Br^-$ | 5.357 | 1.501 | .107 | 6.018 | 0.360 | 0.100 |
| $As^{3+}$ | 0.014 | 0.006 | 0.001 | 0.015 | 0.001 | 0.001 |
| $Sb^{3+}$ | 0.0002 | 0.0002 | 0.0005 | 0.0002 | 0.0002 | 0.0002 |
| $Fe^{2+}$ | 1.644 | 0.018 | 0.010 | 0.480 | 0.014 | 0.010 |
| $Ni^{2+}$ | 0.003 | 0.002 | 0.001 | 0.003 | 0.002 | 0.001 |
| $Pb^{2+}$ | 0.0016 | 0.0001 | 0.0001 | 0.0003 | 0.0001 | 0.0001 |
| $Hg^{2+}$ | 0.0004 | 0.0001 | 0.0001 | 0.0003 | 0.0001 | 0.0001 |
| $Cd^{2+}$ | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0003 | 0.0003 |
| $Al^{3+}$ | 0.005 | 0.005 | 0.005 | 0.005 | 0.005 | 0.005 |
| $Cr^{3+}$ | 0.046 | 0.042 | 0.007 | 0.037 | 0.005 | 0.005 |
| B | 0.95 | 0.85 | 0.47 | 1.03 | 0.87 | 0.045 |

[a] Hydro–geochemical (H–G) type according to the Szczukariew–Priklonski classification; [b] Electrical conductivity

membrane resulted in a significant increase in the reduction of these components in the permeate. After NF, permeate was used as feed water for the RO system for further GT treatment to increase the degree of rejection of undesirable components such as micropollutants. In the second stage of desalination (RO), after the process with the use of the NF90 membrane, most of the parameters analyzed were slightly reduced, except for micropollutants such as lead, chromium, mercury, and arsenic (remaining at a stable level after the NF process). After the process using an NF270 membrane, and after the RO process a significant decrease in the content of the main ions was observed, but the tendency relating to the micro-contaminants that were analyzed was maintained, in a similar manner to the process using the NF90 membrane. It was apparent that the permeate quality of the integrated NF-RO system was very high and slightly better than after the single processes with NF membranes (Table 2).

### *3.2. The results of GT desalination conducted on a semi-industrial scale*

In this study, a two-step NF-RO desalination module with 70% permeate recovery was employed. After analyzing the results from laboratory-scale tests it was decided that only the NF90 membrane would be used for the semi-industrial tests. Due to the equipment available, the laboratory scale tests were carried out with the use of a flat membrane, but on the semi-industrial scale a spiral membrane NF90 and ROBW30HR-440i were used, and also, of course, the values of the streams were much higher than on a laboratory scale. The detailed parameters of the permeates resulting from the NF and RO processes are presented in Table 3.

### *3.3. Comparison of the efficiency of micro-pollutant removal from GT*

To analyze the efficiency of the processes, the retention coefficients of the selected micropollutants and other parameters of the permeates obtained both after the first stage (NF) and after the two-stage NF-RO system was calculated (in accordance with the adopted methodology). Table 4 presents the calculated values of retention coefficients for all permeates obtained from both the laboratory and semi-industrial tests. By comparing the retention coefficients of the main bivalent ions, significant differences can be observed between the NF membranes applied. The

Table 3
The physico-chemical parameters of raw water and permeate streams obtained from tests conducted on a semi-industrial scale

| Parameter | GT | | |
|---|---|---|---|
| | Raw water (mg/L) | NF90 permeate (mg/L) | RO permeate (mg/L) |
| Mineralization | 6,305.2 | 2,155.9 | 97.6 |
| H–G type[a] | Cl–Na | Cl–Na | Cl–Na |
| EC[b] (mS/cm) | 11.39 | 4.35 | 0.141 |
| $Na^+$ | 2,177.6 | 803.7 | 34.06 |
| $K^+$ | 18.7 | 11.91 | 1.22 |
| $Ca^{2+}$ | 120.48 | 2.68 | 0.30 |
| $Mg^{2+}$ | 22.39 | 0.428 | 0.045 |
| $Li^{2+}$ | 0.184 | 0.069 | 0.005 |
| $Cl^-$ | 3,543.0 | 1,293.0 | 40.7 |
| $SO_4^{2-}$ | 84.33 | 1.64 | 0.49 |
| $HCO_3^-$ | 295.7 | 27.8 | 13.2 |
| $I^-$ | 0.25 | 0.16 | 0.08 |
| $Br^-$ | 5.3 | 2.99 | 1.73 |
| $As^{3+}$ | 0.015 | 0.008 | 0.005 |
| $Sb^{3+}$ | 0.0078 | 0.0006 | 0.0045 |
| $Fe^{2+}$ | 0.123 | 0.04 | 0.01 |
| $Ni^{2+}$ | 0.002 | 0.001 | 0.001 |
| $Pb^{2+}$ | 0.0008 | 0.0005 | 0.0002 |
| $Hg^{2+}$ | 0.0001 | 0.0001 | 0.0001 |
| $Cd^{2+}$ | 0.0003 | 0.0003 | 0.0003 |
| $Al^{3+}$ | 0.005 | 0.005 | 0.005 |
| $Cr^{3+}$ | 0.011 | 0.006 | 0.005 |
| B | 1.59 | 1.53 | 1.17 |

[a]Hydro–geochemical (H–G) type according to the Szczukariew–Priklonski classification; [b]Electrical conductivity

rejection ability of the NF membrane depends primarily on its pore size, and consequently on its compaction [41–43]. For NF270, the decrease in the content of these components was three times smaller. On the other hand, by comparing their retention coefficients between the laboratory and semi-industrial processes using the NF90 membrane, only small differences can be observed, with their values oscillating between 98% and 99%. Comparing the processes, the worst retention coefficients were obtained as a result of the desalination process on a laboratory scale using the NF270 membrane. For almost all the parameters analyzed (including micropollutants), the reduction of the main cations did not exceed 32% and their values oscillated between 7% and 32%. On the other hand, a high level of reduction of iron was obtained (99%). The concentration of antimony, cadmium, and aluminum was not reduced during the process, while the lead and mercury content is reduced by 94% and 75%, respectively, compared to raw water. Due to such poor values of the retention coefficients of the parameters considered when using an NF270 membrane, the comparison will mainly concern the processes carried out with the use of the NF90 membrane on a laboratory and semi-industrial scale. The retention coefficient for mineralization significantly increases after the NF process (NF90 membrane) and after the RO process sequentially increases from 86% to almost 100% for the laboratory scale process and from 66% to 98% for the semi-industrial scale, respectively. After laboratory-scale tests, the retention rates for the main ions after the NF process range from 74% to 99%, after RO from 95% to almost 100%, while on a semi-industrial scale from <36% to 98% and from 93% to almost 100%, respectively. For iodide, the value of the retention factor was also reduced after the NF process was carried out on a laboratory-scale and it was 88% (application of the RO process did not increase this value), whereas in the process using semi-industrial equipment this parameter decreased by up to 0.08 mg/L. Bromides were also reduced on a semi-industrial scale, but their rejection rate in permeate in laboratory-scale tests increased from 94% to 98%. For laboratory-scale tests, the retention coefficients for arsenic, chromium, lead, and mercury after the first and second stages of desalination were constant and amounted to 93%, 86%, 67%, and 67%, respectively. For the semi-industrial scale tests for chromium and arsenic, these values change from 45% and 47% to 55% and 67%, respectively. The reduction of nickel content was observed only in the process performed with the use of semi-industrial apparatus and was not increased after the RO process, amounting to 50% (after NF and RO processes).

The treatment of water from the GT well-using the NF90 membrane resulted in a reduction in mineralization of about 66%. Compared to laboratory-scale tests, the impact of the second desalination step for the semi-industrial system

Table 4
Retention coefficients of the parameters investigated in permeates obtained after two-stage NF-RO processes conducted on a laboratory and semi-industrial scale

| Parameter | GT | | |
|---|---|---|---|
| | Retention coefficient after NF270/RO (laboratory scale) R (%) | Retention coefficient after NF90/RO (laboratory scale) R (%) | Retention coefficient after NF90/RO (semi-industrial scale) R (%) |
| Mineralization | 13/97 | 86/100 | 66/98 |
| EC[a] (mS/cm) | 29/67 | 85/100 | 62/99 |
| $Na^+$ | 7/97 | 84/95 | 63/98 |
| $K^+$ | 17/91 | 74/95 | 36/93 |
| $Ca^{2+}$ | 21/99 | 99/100 | 98/100 |
| $Mg^{2+}$ | 32/99 | 99/100 | 98/100 |
| $Li^{2+}$ | 20/97 | 88/97 | 63/97 |
| $Cl^-$ | 12/97 | 85/100 | 64/99 |
| $SO_4^{2-}$ | 79/96 | 96/96 | 98/99 |
| $HCO_3^-$ | 38/97 | 90/98 | 91/96 |
| $I^-$ | 59/86 | 88/88 | 36/68 |
| $Br^-$ | 72/98 | 94/98 | 44/67 |
| $As^{3+}$ | 57/93 | 93/93 | 47/67 |
| $Sb^{3+}$ | –/– | –/– | 92/42 |
| $Fe^{2+}$ | 99/99 | 97/98 | 67/92 |
| $Ni^{2+}$ | 33/67 | 33/67 | 50/50 |
| $Pb^{2+}$ | 94/94 | 67/67 | 38/75 |
| $Hg^{2+}$ | 75/75 | 67/67 | –/– |
| $Cd^{2+}$ | –/– | –/– | –/– |
| $Al^{3+}$ | –/– | –/– | –/– |
| $Cr^{3+}$ | 9/85 | 86/86 | 45/55 |
| B | 11/51 | 16/96 | 4/26 |

can be observed to be more significant. Only for nickel and antimony, the content of which significantly increased after the second stage of the process (after RO), was this dependence not observed. After a two-stage desalination process, permeates were obtained in which the content of the main ions and some of the micropollutants analyzed were significantly reduced. Small differences in concentrations of selected components in the permeate obtained from the RO processes carried out on a laboratory and on a semi-industrial scale may result from the fact that different RO membranes (with similar filtration parameters) were used. Moreover, the pre-treatment of raw water applied in the semi-industrial process has an influence on the degree of retention of the components investigated. The reductions in the concentration of key constituents of the GT were at a sufficient level in relation to the legal requirements for water intended for consumption. In no case was the permissible content of hazardous substances exceeded [44,45]. Taking into account WHO guidelines suggesting acceptable concentrations of boron and other micro-pollutants in water, the proposed two-step NF-RO system for the desalination of water mineralized up to about 6 g/l would be sufficient to achieve beneficial drinking water parameters [9]. Other researches also indicated that the two-stage NF-RO system can be successfully used to increase water purification [46]. Cartagena et al. [47] present research oriented toward reducing contaminants emerging from wastewater by combined MBR-NF/RO treatment. Macedonio et al. [48] analyzed seven different integrated membrane systems for seawater desalination marked as: (1) only the RO unit, (2) NF-RO, (3) MF-NF-RO, (4) MF-NF-RO and a membrane crystallizer module on NF brine, (5) MF-NF-RO and a membrane crystallizer module on RO brine, (6) MF-NF-RO and a membrane crystallizer module on both NF and RO brines, and also (7) MF-NF-RO and a membrane crystallizer module on NF brine and MD on RO brine. Research results indicate that applying integrated membrane systems appears to provide interesting and efficient possibilities for enhancing desalination operations and meeting the increasing demand for water intended for drinking purposes [48]. Moreover, rejection of organic micropollutants by NF/RO membranes has also been investigated [49]. Shen and Schafer [39] analyzed the possibility of using NF and RO to remove micro-contaminants from drinking water, such as uranium and fluoride. Membrane processes, including UF, NF, RO, and FO are potentially treated as beneficial methods for micropollutant removal, but further tests should be done in order to develop the most beneficial systems so that they can work efficiently on an industrial scale [14]. Other methods are also considered as promising techniques for iron and manganese removal with filtration from 20% to more than 70% [15–17], however, with the two-step NF-RO system presented here, these values oscillate by up to 99%. Groundwater treatment processes using activated alumina and a magnetic field resulted in the removal of more than 90% of lead and copper [19], in the research presented these values ranged from 38% up to 94%. Tests conducted using asymmetric polyelectrolyte multilayer membranes with ultrathin separation layers resulted in 98% micropollutant retention. Authors underline that this new membrane can be turned to other applications, including water desalination and ion recovery [26]. Other researchers also indicated that a combined system of water purification results in higher values of micropollutant rejection [28–31]. The combination of membrane processes with other treatments provides a significant increase in micropollutant removal [22–27]. The proposed two-stage NF-RO system results in higher rates of rejection of some of the micropollutants investigated with relatively low energy consumption and a high rate of rejection of other ions [21,23]. Moreover, the permeates obtained from the processes conducted on a laboratory and semi-industrial scale meet the requirements of drinking water.

## 4. Summary and conclusions

This work aimed to present the results of assays designed to examine the efficiency of micropollutant removal from GT on a laboratory and semi-industrial scale with the use of a two-stage NF-RO module. The tests were conducted based on GT extracted from a well-located in central Poland. Naturally this water exhibits elevated concentrations of the main ions, and consequently has an elevated value of mineralization, which was more than 6 g/L. The processes conducted on a laboratory and semi-industrial scale have allowed a detailed recognition of the level of retention of selected parameters. The results indicate that the two-stage NF-RO treatment technique can be a promising solution for increased removal of some of the micropollutants occurring in GT. Moreover, the study results revealed that the use of an NF270 membrane for such highly mineralized water is not an effective solution. Generally, the assay has shown that the proper selection of membrane-type can lead to significant growth in micropollutant removal. The pre-treatment of raw water applied in the semi-industrial process played an important role in the assessment of the degree of retention of the components investigated. Tests conducted on a laboratory scale permitted micropollutant removal to reach the following values: 96% (B), 86% ($Cr^{3+}$), 94% ($Pb^{2+}$), 67% ($Ni^{2+}$), 99% ($Fe^{2+}$), and 93% ($As^{3+}$). For experiments carried out on a semi-industrial scale these values ranged up to: 26% (B), 55% ($Cr^{3+}$), 75% ($Pb^{2+}$), 50% ($Ni^{2+}$), 92% ($Fe^{2+}$), and 67% ($As^{3+}$).

Additionally, treated waters (permeates) meet the criteria specified in the Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption (Journal of Laws of 2017, item 2294), the criteria contained in the Regulation of the Minister of Health of 13 April 2006 on the scope of tests necessary to determine the therapeutic properties of natural medicinal materials and the therapeutic properties of climate, the criteria for their assessment and the model certificate confirming these properties (Journal of Laws of 2018, item 605) and also the WHO guidelines on the quality of waters intended for consumption. The research work carried out proved that the treatment of mineralized and salt-bearing GT with increased content of micro-contaminants, including heavy metals, via the use of membrane processes, especially a two-stage NF-RO system, is an effective solution. The use of membrane processes in water treatment can provide more or less selective removal of the target pollutants, especially when the separation of mono- and multi-valent ions is desired.

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