

Assessment of SW30 membrane for simultaneous removal of selected microelements from high-mineralized water

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ABSTRACT

Maximum permissible concentrations of inorganic elements, including toxic constituents (heavy metals), in drinking water, are established by the World Health Organization (WHO), EU Council Directive 98/83/EC of 3 November 1998, and relevant national regulations. The paper presents an assessment of reverse osmosis SW30 membranes for simultaneous removal of boron, copper, and lithium from two high-mineralized water. The experiments conducted allowed to gain removal up to the following values (retention coefficients): boron (30% and 8%), copper (89% and 69%), and lithium (39% and 8%), in permeates. Despite the quite promising removal ratios gained for copper and lithium, the value of reduction of mineralization, boron, and some of the major ions was insufficient and their concentration values exceeded the parametric value introduced in the mentioned Directive. In concentrates with these three parameters, negligible increases in concentrations were observed. The research work carried out provided that the treatment of high-mineralized water with increased content of microelements with the use of a one-step reverse osmosis system is not an effective enough solution. Due to the unsatisfactory boron removal and mineralization reduction being gained, further studies should be carried out to improve the efficiency of removal of these components, for example, the use of a multistage desalination process or secondary treatment.

Keywords: Seawater; Membrane; Desalination; Reverse osmosis; Copper; Boron; Lithium

1. Introduction

Effective and sustainable management of high-mineralized waters is a key aspect in the usage of these natural resources, in particular in the field of recovery, removing individual components from them, including copper, boron, and lithium. Highly mineralized waters can be both a source of ingredients desired in the industry and water intended for consumption. Drinking water shortages and

the growing industrial demand for certain elements lead such as boron, copper, and lithium, to search for new solutions aimed at meeting these needs as well as environmentally friendly management of waters with high salinity and mineralization. Several inorganic elements and metals, which at certain concentrations have a detrimental effect on human health, are identified in groundwaters, including high-mineralized waters [1].

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The maximum allowable concentrations of inorganic components, including toxic ones, in drinking water, have been defined by the World Health Organization (WHO), EU Council, and in relevant national regulations [2–4]. In many cases, they have been set at a very low level, even in the order of $\mu\text{g/L}$. The basis of the Polish national drinking water quality regulations (Polish Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption) were WHO Guidelines for drinking water quality (GDWQ) published in 2017 and the requirements of Directive 98/83/EC (Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption) [2–4].

The utilization and discharge of these waters to the environment are possible after prior treatment/desalination. Membrane processes, among others, reverse osmosis (RO), are tested for more complex use to remove or recovery microelements from seawater, wastewater, geothermal water, or high-mineralized water [5–7]. Present of inorganic pollutants in water, which even at low concentrations, can be dangerous for the human body and may cause serious illnesses due to their easy ability to accumulate in living organisms [8]. Copper is a very toxic metal, also at low concentration, and copper-contaminated water must be treated before using it for drinking or industrial purposes, and before discharging it to the environment [8]. Abdullah et al. [9] received a promising result for copper removal with the use of nanofiltration (NF) membranes and pressure forward osmosis (PFO) membranes, even up to 99.4%. On the other hand, lithium is the lightest alkali metal with high reactivity and is electrochemically active. Lithium is commonly obtained from brines (e.g., geothermal brine, seawater, and salt lake brine), clays, and recovered from waste lithium-ion batteries [10]. Lithium is an important element in industry and its demand in the global markets rapidly increases in recent years. This element is used in batteries, lubricants, refrigerants, ceramics, medicine, fusion, and electronics industries [11]. Roobavannan et al. [12] evaluated different methods for recovery of lithium from seawater, including evaporation/precipitation, selective membrane processes (pressure-driven nanofiltration), electrodialysis, electrochemical, and ion exchange adsorption. Nanofiltration membrane (positively charged) has been effective for elective Mg and Li separation from brine [11–13]. Somrani et al. [14] investigated the use of nanofiltration and low-pressure reverse osmosis membranes for efficient Li extraction from brine and seawater. The demand for this element exceeds the ore resources, therefore other sources such as brine are considered [11]. Boron is a component whose ability to be removed by membrane processes depends on the pH value of the feed water. Numerous studies on the effectiveness of removing boron ions from water and wastewater in the process of reverse osmosis show that a high degree of boron retention, at a level exceeding 98%, is possible in water with a pH value of at least 10 [15]. Koseoglu et al. [16] presented the results of the research with the use of NF90 membrane (pressure 15.5 bar) at pH 8. They received 60% of boron removal. Boron removal increases with the use of a more compacted membrane, and due to the narrowing pores of the membrane caused by the scaling phenomenon. Tomaszewska

and Bodzek [15] received 96% and 97% rejection ratios for boron with geothermal water pH of 10 and 11 and up to 9.5 mg B/L. Yavuz et al. [17] also received high boron rejection (94.5%–95%) from geothermal water, when the pH of feed water was increased to 10.5. Landsman et al. [18] underlined that raising the pH of feed water to convert boric acid to borate ions to increase boron rejection can often cause calcite supersaturation. They proposed the application of electrodialysis pretreatment to enhance boron removal by nanofiltration/reverse osmosis as a promised novel approach.

The research aimed to present the results of experiments oriented towards examining the efficiency of boron, copper, and lithium removal from highly mineralized water on a laboratory scale with the use of one-stage RO modules and SW30 membrane. The tests were conducted based on two highly mineralized water from northern Poland. Naturally, these waters exhibit elevated concentrations of main ions, and consequently the elevated value of mineralization, which was more than 41 and 35 g/L. The evaluation of the simultaneous removal of copper, boron, and lithium was carried out based on the analysis of the obtained permeates (retention coefficients were calculated) and concentrates (the fold increase in the content of individual components was calculated). Moreover, the quality of the obtained products was assessed based on World Health Organization (WHO) guidelines, EU Council Directives, and relevant national regulations [2–4] for waters intended for consumption.

2. Materials and methodology

2.1. Method of water desalination

The desalination of high-mineralized waters was carried out on a laboratory scale using the reverse osmosis (RO) method. For the experiments was applied one-step desalination system operated in dead-end mode. The main part of the apparatus was a stirred cell device in a high-pressure version, inside which was placed feed water and membrane (Fig. 1). Produced concentrate remained in the cell while the simultaneously produced permeate was collected through an outlet in vessels. A more detailed description of the device scheme and procedure was described in the literature [19–22]. For the experiments, we have adjusted the process parameters due to water mineralization (membrane type, transmembrane pressure, water temperature, and permeate recovery rate) accordingly. Tests were carried out using SW30 DOW™FILMTEC membrane [23] at transmembrane pressure 28 bar, permeate recovery rate 50%, feed water temperature 22°C, and feed water volume 400 mL. The scheme of the apparatus is presented in Fig. 1 [19,22].

Physicochemical parameters (inorganic components) were identified in the samples of raw high-mineralized waters and permeates obtained in the tests in an accredited laboratory. The detailed characteristics of raw high-mineralized waters and permeates were established using inductively coupled plasma optical emission spectrometry (ICP-OES for Na, Ca, Mg, K, SO_4 , Li, Cu, and B) and titration method (for HCO_3 and Cl ion), under accredited testing procedures based on the Mohr's method, in the accredited laboratory under international standards.

For the research, the SW30 DOW FILMTEC™ membrane was used. According to the manufacturer's product information, the SW30 membrane offers the highest productivity while maintaining excellent salt rejection. This element has the highest flow rates available to meet the water demands of desalination facilities (inland or sea area), however, they may also be operated at lower pressure to reduce pump size, cost, and operating expenses. Seawater (SW30) membrane is a polyamide thin-film composite

type with 45°C of maximum operating temperature and 69 bar of maximum operating pressure. It is designed to work in pH continuous operating pressure from 2 to 11 with a stabilized salt rejection of 99.4%. SW30 membranes are produced with an automated fabrication process that ensures precision, consistency, and reliability [23].

2.2. High-mineralized waters

For the experiments, two high-mineralized water obtained from wells located in the Poland area were used. Before testing on a laboratory scale, the detailed physico-chemical characteristics of raw waters were established. The first high-mineralized water (W1) is characterized by high total dissolved solids (TDS) (more than 41 g/L, mineralization 41.5 g/L), and an elevated content of sodium (more than 12 g/L) and chloride (more than 25 g/L). Other parameters, such as calcium (1,582 mg/L), magnesium (609 mg/L), and sulphate (332 mg/L) were established at lower concentrations. The second high-mineralized water (W2) is characterized by slightly lower TDS values (35 g/L, mineralization 35.1 g/L) than W1. As in the case of W1, the highest concentrations were found for sodium (more than 11 g/L) and chloride (more than 21 g/L). The specific water characteristic, including other micro-and macro-nutrients, is presented in Table 1. Both W1 and W2 were established as Cl-Na hydrogeochemical types, according to the Szczukariew–Prikłonski classification.

2.3. Analysis method of water quality

To analyze the quality of raw water and permeates obtained after laboratory-scale experiments, primarily to assess the efficiency of the desalination process in terms of

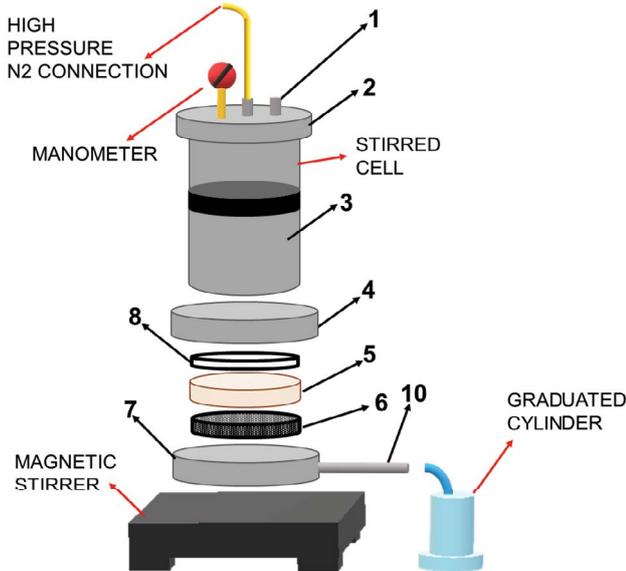


Fig. 1. Scheme of apparatus applied in the experiments (1 – raw water inlet; 2 – membrane cell; 3 – permeate outlet; 4 – rotameter; 5 – pump; 6 – heat exchanger; 7 – raw water tank) [19,22].

Table 1

Physicochemical parameters of raw water permeates and concentrates gained from laboratory-scale experiments and retention coefficients for permeates

Parameter	W1				W2			
	Raw water	Permeate	R (%)	Concentrate	Raw water	Permeate	R (%)	Concentrate
Mineralization (mg/L)	41,507.0	35,081.1	16	64,714.5	34,754.4	27,359.4	22	35,352.2
H-G type ^a	Cl-Na	Cl-Na	–	Cl-Na	Cl-Na	Cl-Na	–	Cl-Na
EC ^b (mS/cm)	88.0	61.7	–	107.8	66.2	53.5	–	71.1
pH	7.54	7.83	–	7.48	7.14	7.42	–	7.39
Na ⁺ (mg/L)	12,503.8	11,844.6	5	21,179.3	11,782.2	9,320.8	21	11,572.0
K ⁺ (mg/L)	314.9	205.2	35	NA ^c	91.7	77.0	16	98.5
Ca ²⁺ (mg/L)	1,582.3	1,028.6	35	2,201.6	789.4	629.7	20	781.5
Mg ²⁺ (mg/L)	609.3	367.8	40	813.5	426.3	349.7	18	433.1
Cl ⁻ (mg/L)	25,698.0	20,909.0	19	35,505.0	21,730.0	16,732.0	23	22,181.0
SO ₄ ²⁻ (mg/L)	332.4	172.8	48	463.1	26.3	24.2	8	31.3
HCO ₃ ⁻ (mg/L)	256.4	135.1	47	NA ^c	71.7	NA ^c	–	91.0
B (mg/L)	5.48	3.85	30	5.66	3.99	3.76	6	4.12
Cu ²⁺ (mg/L)	0.122	0.013	89	0.123	0.072	0.022	69	0.074
Li ⁺ (mg/L)	1.409	0.865	39	1.47	0.504	0.463	8	0.532

^aHydrogeochemical (H-G) type according to the Szczukariew–Prikłonski classification;

^bElectrical conductivity;

^cNo Analyzed.

product quality gained, a detailed characterization of the concentration of the analyzed inorganic components, including microelements were specified. Successively, the retention coefficients R (%) for the permeates produced were calculated based on the following formula:

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

where R – retention coefficient (%); C_p – concentration of particular parameters in permeate (mg/L); C_n – concentration of particular parameters in raw water (mg/L).

The absolute permeate flux (J) was calculated based on the time needed to collect a set volume of permeate (5 mL) according to the formula as follows:

$$J = \frac{V}{F \times t} \quad (2)$$

where V – the volume of permeate (L); F – the active area of the membrane (m^2); t – filtration time (h).

Moreover, to analyze the process efficiency and quality of the concentrates obtained after tests conducted with the use of seawater SW30 membrane with the process parameters adopted, the increase in the content of the major ions and copper, boron and lithium components were calculated (concentration in the concentrate divided by the concentration in raw water).

3. Results and discussion

3.1. Performance of rejection of main ions, copper, boron, and lithium in the permeates

After the laboratory test with the use of reverse osmosis module and SW30 membrane raw waters, the permeates and concentrates were subjected to further analyzes. Table 1 shows the physicochemical compositions of raw high-mineralized waters used for desalination tests, permeate, and concentrates gained. Moreover, Table 1 also presents the retention coefficients (R) of the major ions, copper, boron, and lithium for the permeates.

Based on the results obtained, it can be seen that the concentration of almost all selected parameters, therein major cations (calcium, magnesium, potassium, and sodium), major anions (bicarbonate – only for W1, chloride, and sulphate) have decreased in varying amounts. The retention coefficient values for major ions range between 5% and 48%. The concentrations of copper, boron, and lithium decreased after the reverse osmosis process, and their values reduced compared to raw high-mineralized waters. The concentrations of boron in both permeates (W1 and W2) were reduced slightly to the values 3.85 mg/L in W1 and 3.76 mg/L in W2. The boron retention coefficient for W1 permeate was 30% and only 6% for W2 permeate. For both copper and lithium, the retention coefficients were calculated as higher values for W1 water, which was originally recognized as more mineralized water. The concentration of copper in W1 was reduced from 0.122 mg/L in raw water to 0.013 mg/L in W1 permeate (retention coefficient 89%), whereas in W2 from 0.072 mg/L in raw water to 0.022 mg/L (retention

coefficient 69%) in W2 permeate. In the case of lithium, the treatment of W1 resulted in the reduction of the content from 1.409 mg/L in feed water to 0.865 mg/L in permeate (retention coefficient 39%) and from 0.504 to 0.463 mg/L for W2 (retention coefficient 8%). The use of SW30 membrane caused mineralization reduction of about 16% for W1 and 22% for W2, respectively. Despite the lower mineralization reduction for W1, the experimental data indicated that for most of the parameters analyzed, the desalination of high-mineralized water marked as W1 resulted in the greater rejection of these parameters than for high-mineralized water marked as W2. This tendency was only not observed for sodium and chloride, for which greater rejection was observed for W2. It was apparent that the W1 permeate quality was slightly better than the W2 permeate (Table 1). The value of absolute permeate flux changes over time from 7 to 4 L/m²h (average 6 L/m²h) for W1, and from 10.5 to 6.5 L/m²h (average 9 L/m²h) for W2.

The basis of the Polish national drinking water quality regulations is the guidelines of the World Health Organization (WHO) and the requirements of Directive 98/83/EC (Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption) [2,3]. According to WHO Guidelines for drinking water quality (GDWQ) published in 2017 and Polish Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption [4], both permeates gained do not meet the requirements due to high content of boron and some desired and undesirable (toxic) components.

Boron is never found in the elementary form in nature and in different forms are used in glass manufacture (fiberglass, borosilicate glass, enamel, frit, and glaze), soaps and detergents, flame retardants, neutron absorbers for nuclear installations, mild antiseptics, cosmetics, pharmaceuticals (as pH buffers), boron neutron capture therapy (for cancer treatment), pesticides, and agricultural fertilizers [2]. In surface water and groundwater, the natural borate concentration is usually small. Boron, naturally occurring in groundwater, is present primarily as a result of leaching from rocks and soils containing borate and borosilicates. Unfortunately, the International Standards for Drinking-water from 1958, 1963, and 1971 did not refer to boron. However, in the Guidelines for Drinking-water Quality (first edition), which was published in 1984, it was introduced that no action was required for boron. The first guideline (health-based) value was introduced in 1993 in WHO Guidelines and amounted to 0.3 mg/L. Additionally, in 1993 guidelines it was pointed out that boron's removal by drinking water treatment appears to be poor. In the next WHO Guidelines in 1998, the value of boron was increased to 0.5 mg/L and was designated as provisional because, with the treatment technology available, the previously guideline value would be difficult to achieve in regions with high natural boron content in waters. In the third edition of the Guidelines, published in 2004, this guideline value remained without change. In the fourth edition of the Guidelines, published in 2011, the guideline value was increased to 2.4 mg/L and its provisional designation was deleted. Currently, according to the World Health Organization, the health-based guideline for boron level in drinking water is still 2.4 mg/L [2]. However, both Council

Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption [3] and The Polish Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption [4] introduced the guideline boron value of 1.0 mg/L.

The World Health Organization (WHO) Guidelines, the Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption and The Polish Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption did not establish any guideline value of lithium in drinking water [2–4].

Despite the promising rejection values gained for copper and lithium, the permissible value of boron was exceeded both regarding WHO, EU, and Polish Regulations in all permeates. Moreover, the mineralization value and some of the major ions also exceeded the parametric value introduced in the Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption and in the Polish Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption. It is advisable to use a secondary treatment to obtain a higher removal of ion content in the permeates.

3.2. Performance of retention of main ions, copper, boron, and lithium in concentrates

Table 1 shows the physicochemical composition of the concentrates gained in desalination experiments of two high-mineralized water (W1 and W2) with the use of SW30 membrane. Following the concentrate characteristics, the results showed that the treatment of selected waters increased the parameters in both concentrates.

An increase in the content of sodium, calcium, magnesium, chloride, and sulphate was gained in the W1 concentrate. In turn, the concentration of potassium, magnesium, chloride, sulphate, and bicarbonate slightly increased due to the desalination of raw W2. The increase of these values varies irrespectively for each selected parameter in both concentrates. The performance of retention of each element in concentrates W1 and W2 (concentration in concentrates divided by the concentration in raw water) was presented in Fig. 2. In W1 concentrate, the concentration of major cation increased around 1.3–1.7 (potassium parameter, in this case, was not analyzed) times compared to raw W1. No two-fold increase in concentration was obtained for any of the analyzed parameters. For W2, the concentrate produced some of the major cation (potassium and magnesium) values were around 1.1 times higher than for raw high-mineralized water. For W2 concentrate, the calcium and sodium concentrations slightly decrease after the conducted reverse osmosis process. Generally, a greater increase in the concentration of major cations was observed after the process with W1 water than W2. A similar tendency was also observed for sulphate and chloride, for which the increase in W1 concentrate was 1.4 times for sulphate and more than 1.5 times for chloride, in W2, 1.2 times, and slightly more than 1.0 respectively. For major ions, generally slightly more favorable values were obtained for W1, where raw water was characterized with higher value of mineralization. The values of potassium

and bicarbonate were not analyzed in concentrate W1 due to some analytical problems, while after the experiment with W2 content of these elements slightly increased 1.1 times for potassium and 1.3 for bicarbonate compared to raw W2 water.

In the case of copper, boron, and lithium, a different tendency was observed. For these three parameters, negligible increases in concentrations were observed in the concentrate obtained from the test with W1 and W2 water. A high degree of rejection of the analyzed parameters, found in trace amounts in raw waters W1 and W2, was obtained in permeates, while in the concentrates, no significant increases in the content were obtained.

Concentrates as desalination by-products are generally considered waste. However, the concentrates obtained as a result of the experiments, due to their high mineralization, can potentially be considered a source of useful products and desired elements. One of such possible directions is the use of concentrate as a concentrated product used for therapeutic purposes. The possibility of using concentrate as a concentrated source product in treatments (among others in health baths), in Poland, is decided by the Regulation of the Ministry of Health, which determines the highest acceptable amounts of undesirable and toxic components in therapeutic waters used for drinking treatment, inhalations and external use [24]. The regulation does not define the permissible level of concentration of the main ions, copper and lithium as a condition for the possible use of water in drinking treatment, inhalations, and external use, but regulates it for boron. The permissible value of boron for the solution used for drinking treatment is 5.0 mg/L, while for inhalation is 30 mg/L. According to the boron concentration in concentrates, only in the case of W1 concentrate, the permissible value of boron in drinking treatment was exceeded. Further research of the concentration of barium, antimony, arsenic, chromium, cadmium, nickel, lead, mercury, and aluminium boron in the concentrates gained will determine the possibility of their reuse in other applications and then external treatment, which is not limited by the concentration of individual components [24]. Considering WHO guidelines suggesting acceptable concentrations of copper in water, the proposed RO system for desalination of water mineralized up to about 41 g/L would be sufficient to remain beneficial drinking water parameters in the produced concentrates [2]. However, other techniques should be introduced to reduce the content of other parameters which exceed the permissible values, such as boron.

As was mentioned before, concentrates can be also considered as a source of useful products, including heavy metals, salts, and others. Copper, as a metal with very high thermal and electrical conductivity, is used, among others, as a conductor of heat and electricity. Occurred various copper concentrations in high-mineralized geothermal waters and wastewaters lately are becoming the subject of research for its recovery. Pires da Silva et al. [1] presented research of application reverse osmosis process for nickel and copper removal from wastewater. They presented the results of experiments made at different pressures and they showed that the increase in pressure affects increasing rejection and permeate flow. They achieved 98.5% removal

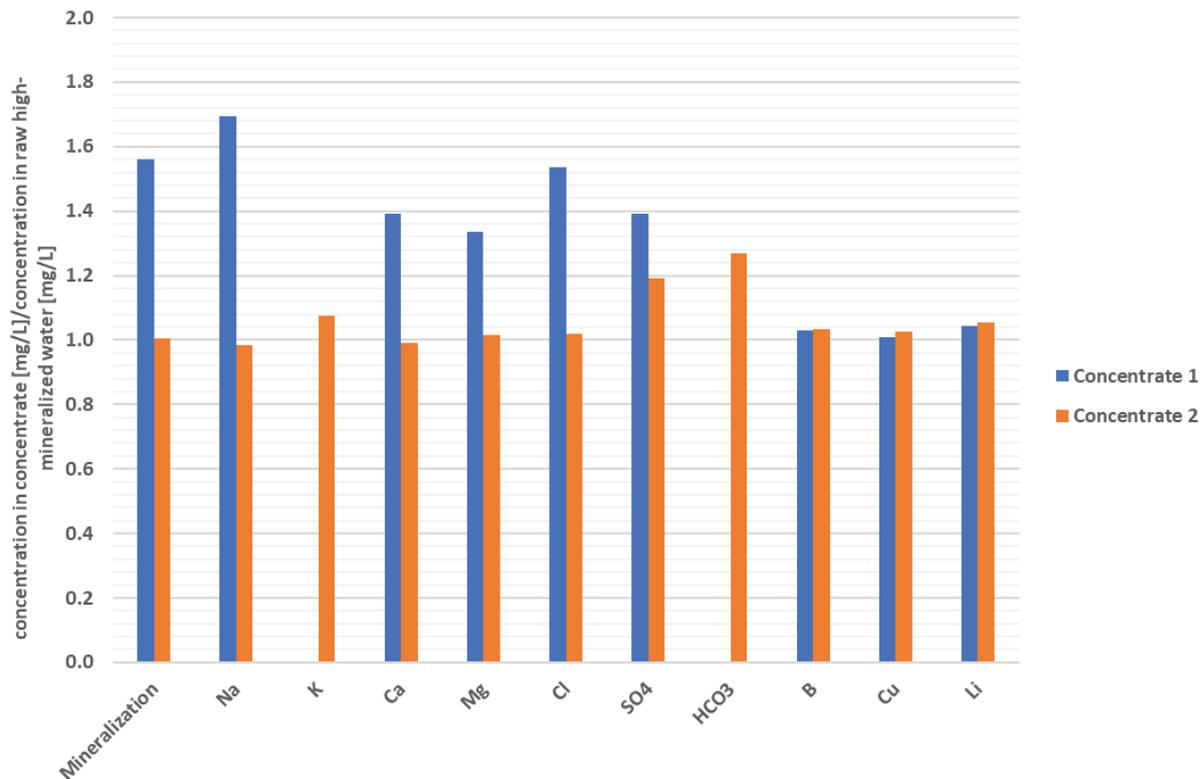


Fig. 2. Graph of the performance of retention of each element in concentrates W1 and W2 (concentration in concentrates divided by the concentration in raw water).

of metal ions and a flow of about 13 L/h m² at a pressure of 0.5 MPa. Eberhard and Hamawand [25] presented the research-oriented towards copper removal from brackish water by selective electrodialysis. They received removal rates of around 98% for copper. They presented a model that can be used to customize nutrient concentration in the water end product. Bandehali et al. [26] conducted experiments with the use of a new PEI-based NF membrane modified by functionalized POSS nanoparticles with copper and lead ions in water. The applied membrane allows receiving a copper rejection of 86% for the proposed new membrane and 40% for the neat membrane. The results showed the high capacity of blended nanocomposite membranes for copper removal from water compared to other reported ones. Al-Saydeh et al. [8] made a comprehensive review about copper removal from industrial wastewater. Among different copper removal techniques, they considered membrane filtration including reverse osmosis. After other researchers, they indicated the copper removal efficiency range from 47% to 99.5% depending on the initial concentration and process parameters (type of membrane and operational conditions) of NF, RO, and NF+RO. Teow and Mohammad [27] presented a review of a new generation of nanomaterials such as carbon nanotubes, graphene, zeolites, aquaporins created to improve water desalination efficiency. Authors underlined that despite the benefits which they bring, the environmental risk and public health impact due to the accidental or incidentally release of nanomaterials are still the major concern. Lithium

recovery from the desalination concentrate was a subject of Joo et al. [28] research. They proposed electrochemical systems equipped with lithium-ion battery electrode materials (λ -MnO₂ and Ag electrodes) that enable highly selective electrochemical capture and release of lithium. Li et al. [10] presented a review of membrane-based technologies for lithium recovery from water. They indicated that the extraction of lithium from aqueous sources, particularly salt lake brine, has become a trend in the lithium recovery industry because of its low cost and abundant reserves. Membrane processes driven by pressure, electric field, and thermal gradients, among the various technologies applied for lithium recovery, have received considerable attention in the past few decades because of their high energy efficiency and low environmental impact. They highlighted that the combination of membrane processes with a conventional lithium precipitation process will lead to higher performance, efficiency, and lower cost. Li et al. [10] indicated that further development should be oriented towards separation efficiency and process optimization. Improving the performance of membrane distillation and ion-exchange manganese oxide for the recovery of lithium from seawater was investigated by Roobavannan et al. [12]. They examined the potential of enhancing Li recovery from seawater by acid-treated manganese oxide ion sieve (HMO) by increased Li concentration in seawater using direct contact membrane distillation (DCMD) and reducing competitive ions. With the proposed multistep process, they achieve favorable high selective Li recovery from

seawater as well as for recovering fresh water and other valuable products – Ca and Mg. Somrani et al. [14] investigated the separation of lithium from salt lake brine by a nanofiltration system and low-pressure reverse osmosis. They examined the separation of lithium in the presence of sodium. Sun et al. [11] examined the separation ratio of lithium and magnesium from brine using a nanofiltration membrane with setup operating conditions. Novel mode for hybrid capacitive deionization equipped with a cathode made of lithium selective material and anode consisting of activated carbon coated with anion-exchange membrane was introduced by Siekierka et al. [29]. They gained 73% of lithium capturing by optimizing the process mode. While Arroyo et al. [30] presented that desalination brines can be introduced to specific ion-exchange resins for lithium recovery. Tomaszewska [31] presented a new approach for the management of concentrates obtained during geothermal water desalination. Based on the conducted research, Tomaszewska [31] indicated that the concentrate in question may be a useful product in cosmetology, for inhalation and for rinsing the nose and mouth to loosen and remove mucus and relieve inflammation as well as for bathing and therapeutic purposes. Wiśniewska et al. investigated the possibility of obtaining lithium from geothermal water using natural and synthetic zeolites applying poly(acrylic acid). They proved that the maximum recovery of lithium cations from geothermal water (at the natural pH of 5.5) was obtained in the system containing natural clinoptilolite and an anionic polymer. Moreover, they concluded that the efficiency of lithium-ion sorption depends on the solution pH and polymer presence, and geothermal water can be a potential source of lithium ions [32].

4. Summary and conclusions

This work aimed to present the results of the assay oriented towards examining the efficiency of copper, boron, and lithium removal from highly mineralized water on a laboratory scale with the use of a one-stage RO module and SW30 membrane. The tests were conducted based on two highly mineralized water from northern Poland. Naturally, these waters exhibit elevated concentrations of main ions, and consequently the elevated value of mineralization, which was more than 41 and 35 g/L.

For W1 permeate, the reverse osmosis process using SW30 membrane resulted in 39% rejection of lithium from water with a high concentration of sodium, while for sodium only 5% rejection was gained. Notwithstanding, in W1 concentrate the concentration of sodium increased about 1.7 times while the content of lithium just slightly increases compared to raw W1 water. For W2 water also rich in sodium, the opposite tendency was observed. For W2 permeate, the RO process allows gaining only 8% of lithium removal with simultaneous 21% of sodium removal (retention coefficient). In W2 concentrate was gained a slight increase in lithium concentration in the absence of an increase in sodium concentration.

For both W1 and W2 permeates were received quite low boron removal ratios (the retention coefficient for boron in W1 permeate was 30% and in W2 permeate 6%). The increase of boron content in both concentrates was negligible.

The retention coefficient of copper in W1 permeate was 89% whereas for W2 permeate 69%. In both concentrates, the copper content slightly increase.

Despite the quite promising removal ratios gained for copper and lithium, the value of reduction of mineralization, boron, and some of the major ions was insufficient and their concentration values exceeded the parametric value introduced in the Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption and in The Polish Regulation of the Minister of Health of 7 December 2017 on the quality of water intended for human consumption. Both permeates do not meet the WHO, EU, and Polish Regulations for drinking water and cannot be directly used as drinking water sources, due to high boron and mineralization (concentrations of some major ions) concentration values. In the concentrates for these three parameters, negligible increases in concentrations were observed from the tests for both waters. According to the boron concentration in concentrates, only in the case of W1 concentrate, the permissible value of boron in drinking treatment was exceeded. Further research of the concentration of barium, antimony, arsenic, chromium, cadmium, nickel, lead, mercury, and aluminium in the concentrates gained will determine the possibility of their reuse in other applications and then external treatment, which is not limited by the concentration of individual components.

Considering the obtained test results and the conducted literature review on the removal of copper, boron, and lithium from geothermal, highly mineralized, and wastewaters, it can be concluded that further studies should be carried out to improve the efficiency of removal of these components, for example, the use of a multistage desalination process or secondary treatment. The research work carried out proved that the treatment of high-mineralized water with increased content of microelements, with the use of a one-step reverse osmosis system, is not an effective enough solution. However, the properly set-up membrane processes in water treatment can provide more or less selective removal of the target elements, especially when the separation of mono- and multi-valent ions is needed.

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