

Desalination of sea and geothermal water on commercial membranes using pervaporation

Izabela Gortat^{a,*}, Joanna Marszałek^a, Bodethala Narayanan Vedha Hari^{b,c},
Marek Brzeziński^c, Paweł Wawrzyniak^a

^aDepartment of Process and Environmental Engineering, Lodz University of Technology, Wolczanska 213, 93-005 Lodz, Poland, emails: izabela.gortat@dokt.p.lodz.pl (I. Gortat), joanna.marszalek@p.lodz.pl (J. Marszałek), pawel.wawrzyniak@p.lodz.pl (P. Wawrzyniak)

^bSchool of Chemical and Biotechnology, SASTRA Deemed University, Thanjavur-613401, Tamil Nadu, India, email: vedhahari@sabt.sastra.ac.in

^cCentre of Molecular and Macromolecular Studies, Polish Academy of Sciences, Sienkiewicza 112, 90-363 Łódź, Poland, email: marek.brzezinski@cbmm.lodz.pl

Received 1 October 2023; Accepted 18 December 2023

ABSTRACT

Freshwater scarcity is currently one of the most pressing global issues. Desalination processes offer a solution to address this challenge. In this work, pervaporation (PV) is proposed as a membrane technique with the potential to contribute to water desalination and complementing reverse osmosis in the future. Three commercial PV membranes were tested for desalination using the PV method. Four different types of water systems were used: model and real systems with salinity from the Baltic and Adriatic Seas and geothermal water from Central Poland. The efficiency and selectivity of the PV process were examined. The PERVAP 4510 membrane showed the best results, with a retention factor of >99% for two applications in model and real systems. In addition, the scaling phenomenon during the PV process was studied. Scanning electron microscopy images were used to visualize the membrane before and after 200 h of operation. The aging process of PERVAP membranes was demonstrated using the example of 2210, which showed a significant decrease in permeate production.

Keywords: Desalination; Pervaporation; Sea or geothermal water; Polymeric membranes; Fouling

1. Introduction

The scarcity of water is currently one of the most pressing global issues. Desalination, is the process of obtaining fresh water from sea and oceans, it a vital method, especially in countries affected by periodic or permanent water shortages [1]. Currently, over 20,000 desalination plants globally produce about 115 million m³/d of freshwater (data from February 2020) [2]. It is estimated that most water desalination installations are located in the Persian Gulf countries, Spain, and China [3–5].

Desalination techniques are divided into thermal methods and membrane techniques. In the middle of the last century, thermal methods, specifically, distillation-based approaches like, either multiple-effect or multi-stage distillation, were most predominant. However, due to increasing interest in environmental protection and desire to reduce greenhouse gas emissions resulting from fuel combustion for heating water, membrane techniques have gained greater popularity [2,6–8]. Therefore, currently, the most widely adopted method of desalinating water, in the world, is reverse osmosis (RO). The production of freshwater by RO

* Corresponding author.

presently accounts for over 70% of all water desalination installations [9–11].

However, there is an increasing limitation, that RO faces challenges when desalinating water with high salinity (>7 wt.%) [12]. In the RO process, as a result of the use of high salt concentrations in the feed solution, necessitates the application of progressively high pressure that surpasses the osmotic pressure of the feed. Consequently, from an energy perspective, the process becomes less economical, and the membrane distillation or pervaporation process can effectively solve the problem of high salt concentrations in the feed, becoming energy-competitive.

Ongoing efforts are focussed towards exploring new methods for seawater desalination. Pervaporation (PV) emerges as a potential alternative to RO under conditions of high feed salinity, while membrane distillation (MD) also play a important role in the desalination process. Above the certain salinity threshold, vapor pressure-based processes (MD or PV) become competitive with RO. A number of recent review articles in peer reviewed scientific journals have presented on the results of experimental desalination studies involving model NaCl solution or seawater [12].

Desalination of water using pervaporation (PV) involves separating an aquatic salt (brine) solution from salt on a non-porous polymeric membrane. The separation of the mixture occurs under reduced pressure on the low-pressure side of the membrane, unlike in the case of RO where high transmembrane pressure plays a significant role on the feed side. In this case, the component of the mixture - the solvent (water), due to its affinity to the membrane material, is preferentially transported to the other side of the membrane. During the passage of the mixture components, a phase change of the permeating component occurs, confirming the dissolution–diffusion model in the mass transfer. Further separation of the mixture occurs on the side of reduced pressure (several kPa) [13–18].

Membranes used in the PV process are mostly polymer-based. Depending on the type of process conducted, membranes can be classified as hydrophilic or hydrophobic [19–23]. In the case of desalination of water by pervaporation, hydrophilic membranes based on polyvinyl alcohol (PVA) are used in this experiment. Since membranes used exclusively for water desalination are not yet available commercially, hydrophilic membranes for alcohol dehydration can be used [24–26].

PERVAP membranes (from Sulzer Chemtech, Switzerland) have a three-layer asymmetric structure (from the bottom): a high-porosity support layer, a low-porosity assisting layer, and the thinnest non-porous active layer. The active layer is responsible for component separation and transport to the other side of the membrane. The absence of pores in the active layer of PV membranes makes the process more resistant to treating water-containing impurities and membrane scaling due to mineral deposition [12]. According to Wang et al. [18], pervaporation membranes can be made from many materials, including cellulose, polyvinyl alcohol, and silica. Tests conducted on individual materials show a high degree of separation (at a level of 99%), which produces water of high purity [18]. A thin polarization layer is created on a feed solution, which causes an unfavorable phenomenon during the separation process [24].

One of the PV applications may be the desalination of geothermal water to obtain utility water for agricultural and industrial purposes. The purification of geothermal water involves the removal of microorganisms, heavy metals, and salts [27,28]. Geothermal water in Poland is currently used in heating installations, for recreational purposes (thermal pools), and for various utility applications [29]. However, the use of geothermal water requires, in some cases, its purification, desalination, and treatment. The distribution of geothermal waters in Poland is shown in Fig. 1. Geothermal deposits encompass four main locations: the Eastern Province (A), the Polish Lowlands (B), the Subcarpathian (C), and the Carpathian Mountains (D).

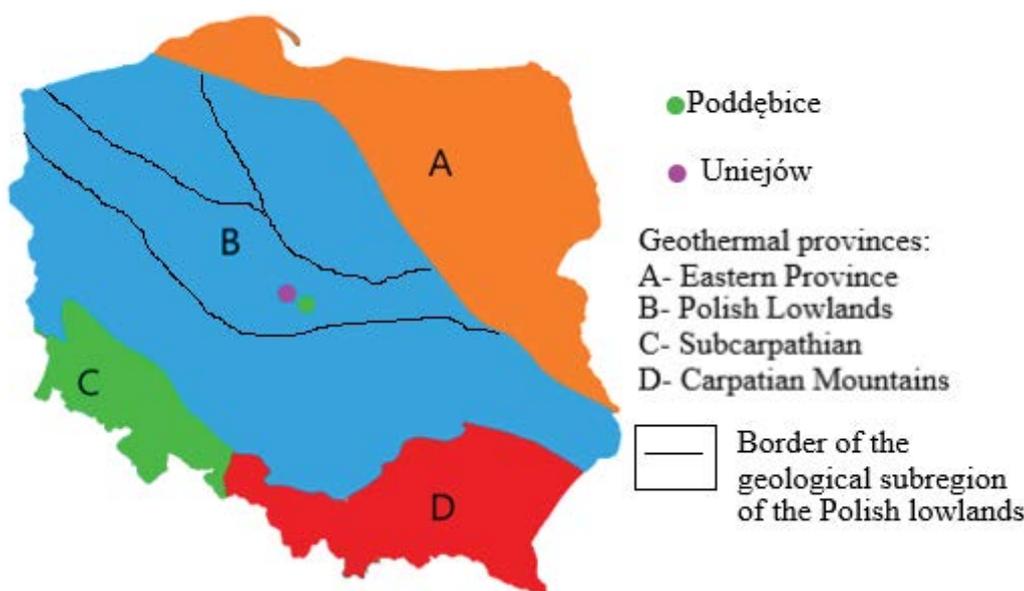


Fig. 1. Distribution of thermal waters in Poland (drawing based on a map presented by the Polish Geological Institute).

Region (C), and the Carpathian Mountains (eastern and western) (D). The water temperature in these areas ranges from 30°C to 130°C, and the depth of occurrence in sedimentary rocks ranges from 1 to 10 km. Depending on the types of dissolved compounds in geothermal waters their different types and names there are: sulfates, sulfides, brines, acidulous waters, siliceous waters, boron waters, and bromide waters [30]. In this area (Fig. 1), there is the geothermal well called PIG (Polish Geological Institute) "Poddebice". In the plant exploiting the deposit it is called GT-2 and that is also what it was called in the text: GT-2 is well located in Poddebice. Water from the well was determined to be a hydrocarbon-calcium profile with a total mineralization of 432 mg/dm³ and a temperature of 72°C. Just 20 km away from Poddebice, there is the geothermal well named according to PGI "Uniejów I". In the plant exploiting the deposit, it is called IGH-1, as it was also called in the text. The IGH-1 well in Uniejów is characterized by a mineralization level of 6.7–8.8 g/dm³ and a temperature of 68°C. The differences in mineral content within a distance of just 20 km may indicate the presence of a hydrochemical barrier, which causes significant changes in the physicochemical profiles of geothermal waters in different areas of the country [31,32].

1.1. Fouling and membrane aging phenomenon

Fouling is an unfavorable phenomenon that causes a decrease in the efficiency of the desalination process, up to its complete stoppage as observed in many experiments using membrane techniques [33–36]. In the case of reversible fouling, the selective properties of the membrane can be partially restored by backwashing. However, in the case of irreversible fouling, which causes contaminants to penetrate the interior of the membrane pores, recovery is not possible. Colloidal, organic, and mineral fouling (scaling) are distinguished. Scaling mainly occurs in processes for the purification of mineral mixtures, including water desalination, most commonly in nanofiltration (NF) and RO processes [35,37–40].

In the literature, the phenomenon of membrane aging is still a topic that has not been fully explored. Aging can involve mechanical, hydrodynamic, or chemical destabilization of individual membrane layers and the material from which it is made. This depends on the purpose of the material used, the interactions to which it is exposed, and its quantity [41–44].

There are many methods of accelerated aging testing, including the use of aging chambers imitating specific atmospheric conditions. The methods focus primarily on the impact of UV radiation and humidity on the durability and stability of the material. TGA analysis can also be used for the accelerated aging process, determining the change in material mass for specific temperature values, which makes it possible to determine thermal stability. The DSC method, in turn, allows you to determine the heat capacity of the material in a selected temperature range for samples of known composition. Changes in heat capacity for material samples allow for determining the polymer degradation process [45,46].

The main effect of aging is polymer degradation, which leads to disruption in the functioning of the membrane.

Separation properties and process efficiency can deteriorate. Degradation can also occur during material storage. Changes in temperature, humidity, and direct exposure to light are the most common degrading factors [41]. Membrane aging also affects their organoleptic evaluation. The new commercial membranes used in this work (Sulzer Chemtech) were characterized by a milky-white color and high elasticity (manufacturer's data). They are stored in laboratory conditions protected from light in the packaging provided by the manufacturer [24]. In this article, we used research on changes in membrane performance during storage. We tested the membrane in the pervaporative desalination process, assessing its efficiency and selectivity over time.

The research conducted in this work aimed to confirm the possibility of using the PV process for sea (from Baltic or Adriatic Sea), and geothermal (from wells IGH-1 and GT-2 deposits) water desalination and to identify the strengths and weaknesses of PV. In addition, we familiarized ourselves with commercial membranes on the market and examined their transport and separation properties. Attention was also paid to the fouling phenomenon occurring during the PV process and the aging of membranes along with the time of their storage.

2. Materials and methods

2.1. Membranes

The membranes used for the experiments were purchased from Sulzer Chemtech (Switzerland). These were non-porous PERVAP 4100, 4101, and 4510 membranes (as designated by the manufacturer). The active layer of the membrane is based on crosslinked PVA. The same selected membranes were used in the laboratory experiments, which were then cleaned and conditioned in deionized water. Membrane aging was observed based on desalination experiments conducted on the same PERVAP 2210 membrane. The former PERVAP 2210 now corresponds to the PERVAP 4510 membrane according to the manufacturer's data.

2.2. Model, real and geothermal feed

For the pervaporation desalination experiments, model seawater - NaCl water solution was used as an aqueous solution of sodium chloride purchased from Chempur (Poland). The model system (deionized water and NaCl) corresponded to the salt content for the Baltic Sea and the Adriatic Sea, which was 7‰ and 35‰, respectively. Real seawater used for the experiments was sourced from the Baltic Sea and the Adriatic Sea. Water from the Baltic Sea was collected in March 2021 near Kołobrzeg, while water from the Adriatic Sea was collected in September 2021. from the area around the Istrian peninsula in Croatia. The temperature of the water from the Baltic Sea was 8°C, and the water from the Adriatic Sea was 24°C (own research). The amount of water was approximately 20 dm³ for each of the seas mentioned.

For geothermal water, two aqueous salt solutions named hereinafter m-IGH-1 and m-GT-2, were created. The saltwater solution corresponding to the conductivity-tested real sample taken from the Uniejów IGH-1 intake is shown in Table 1.

The content of NaCl and KCl ions in the model water was determined based on the respective ion concentrations found in the real water samples from the Uniejów IGH-1 and Poddębice GT-2 wells. Geothermal water samples from Uniejów IGH-1 and Poddębice GT-2 were used as the feed solution too. For comparison, the Poddębice GT-2 had a low TDS (total dissolved solids) content of 432 mg/dm³. The NaCl content after conductometric measurements was found to be 230 mg/dm³, and KCl was 200 mg/dm³. The temperature of geothermal waters: IGH-1 was 68°C and GT-2 was 72°C.

The authors' goal was not to reproduce the full composition of sea and geothermal waters but to repeat the research on a simple feed system in order to study the desalination process using the pervaporation method.

2.3. Method and equipment for performing PV experiments

PV water desalination experiments were performed in the Department of Process and Environmental Engineering (TUL). Primary the PV process laboratory equipment was provided by Sulzer Chemtech (Switzerland). A diagram of the current station is shown in Fig. 2. The PV process was carried out at a constant pressure (3 kPa) on the low-pressure side of the membrane. The permeate was condensed in the collector using liquid nitrogen (freezing).

Table 1
Composition of Uniejów IGH-1 and Poddębice GT-2 geothermal water solutions used as feed for pervaporation processes

Salt/feed	Concentration (g/dm ³)	
	IGH-1	GT-2
NaCl	6.01	0.23
KCl	1.90	0.2
Total	7.91	0.43

The process was conducted until the equilibrium state was reached (2.5 h), that is, until the mass of the collected permeate stabilized during the process. After thawing the permeate, its mass was determined, and the flux was calculated with reference to the membrane surface area and the process duration. The pervaporation process was carried out at three different temperatures ($T = 40^\circ\text{C}$, 60°C , and 80°C) and three different feed flow rates ($Q_F = 40$, 60 , and 80 dm³/h). In this way, the most favorable conditions for desalination feed in the PV process were determined. The temperature range analyzed in the process was the temperature range of geothermal waters.

The efficiency and selectivity of the commercial membranes used were determined. The efficiency of the membrane process was referred to as productivity, which represents the amount of obtained desalinated solution (permeate) per unit membrane area during the duration of the membrane process. The permeate flux J_p is expressed by Eq. (1).

$$J_p = \frac{m_p}{A \cdot t} \cdot \frac{\text{kg}}{\text{m}^2 \cdot \text{h}} \quad (1)$$

After the PV process was completed, the selectivity of the membranes was determined by measuring the retention factor, R , which represented the salt reduction during the process in relation to the salt concentration in the feed solution. The salt concentration was measured using the CPC-511 conductometer from Elmetron (Poland), and the retention factor was calculated using Eq. (2).

$$R = \left(\frac{C_F - C_p}{C_F} \right) \times 100\% \quad (2)$$

Knowing the efficiency and selectivity of the membrane process, its performance can be compared to other membrane processes used for water desalination.

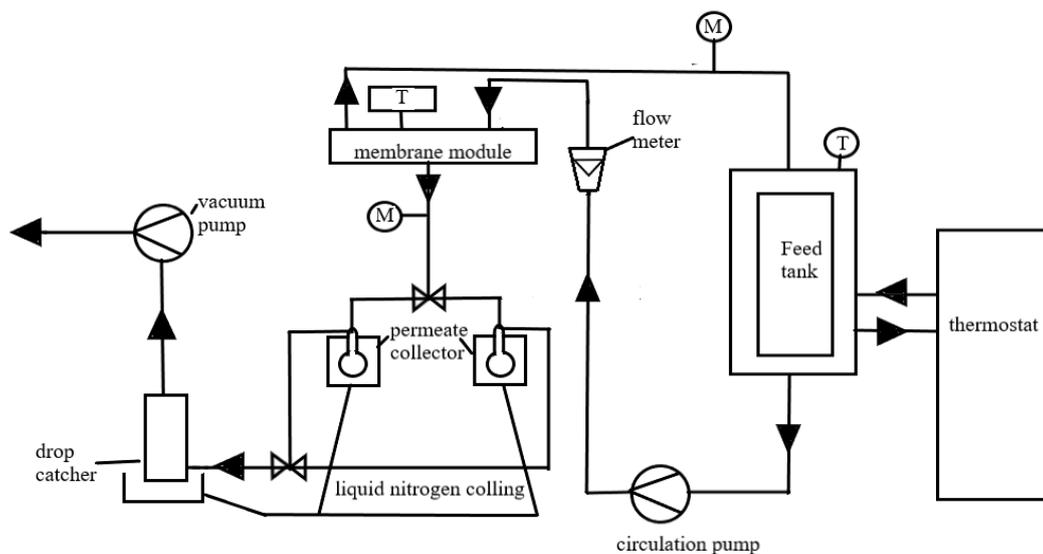


Fig. 2. Diagram of the modified laboratory apparatus for the pervaporation process.

2.4. Methodology of scanning electron microscopy measurement and membrane aging experiments

Scanning electron microscopy (SEM) photos were taken in the Centre of Molecular and Macromolecular Studies (PAN). An SEM microscope (JEOL, JSM-6360, Japan) was used.

In this article, we used research on changes in membrane performance during storage. The aging experiments were conducted at a 4-y interval. The membrane aging studies consisted of performing separation tests of a model feed (saline water) using the PV technique on the same PERVAP 2210 membrane and comparing the results of performance and separation in the 2017 and 2021 y.

3. Results and discussion

3.1. Desalination seawater in the pervaporation process

Determining the most favorable operating conditions for pervaporation is essential. The pervaporation process on commercial Sulzer membranes was successful. According to the literature, PERVAP membranes belong to polymer composite membranes, on which desalination processes using

the PV method are conducted. The experiments conducted in this study on three different PERVAP membranes, 4100, 4101, and 4510, have shown that only the PERVAP 4510 membrane can be used in the desalination process due to the much higher permeate flux. For the remaining membranes, the amount of obtained permeate was too small for further analysis. The usefulness of the PV membrane for desalination was determined based on the amount of obtained permeate. Tests were conducted on two models and real feed systems. The results are presented in Figs. 3 and 4.

The flux for seawater was low and ranged between 1.5–2 kg/(m²·h). As the feed flow rate and temperature increased, the permeate flux also increased as shown in Fig. 4. Therefore, for PV membranes, it is more advantageous to conduct the process at higher temperatures and feed flow rates [24]. It is also possible to note an approximately 10% increase in efficiency (expressed by J_p) for samples from the Adriatic Sea compared to samples from the Baltic Sea.

The experiments showed that the PERVAP 4510 membrane had an extremely high retention factor (above 99%) for NaCl salt (Fig. 5), which qualifies the obtained permeate as ultrapure water. The amount of permeate flux obtained at higher temperatures (around 80°C) was about 2 kg/

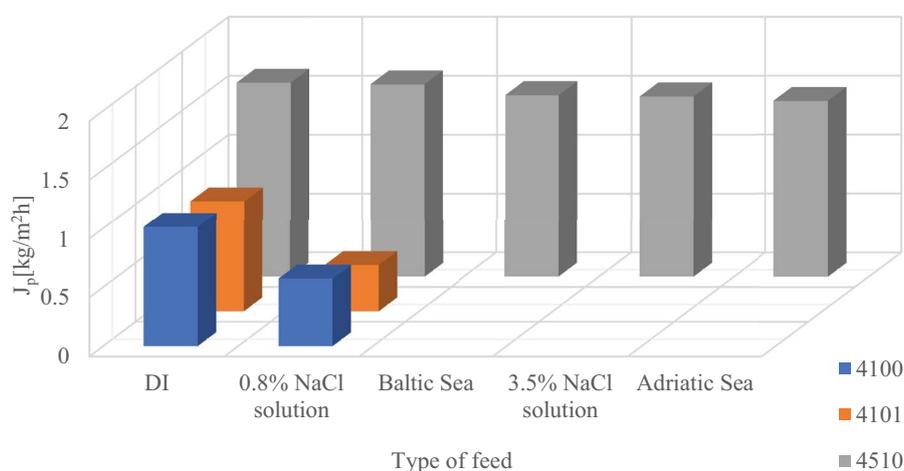


Fig. 3. Average permeate flux (J_p) analysis ($T = 40^\circ\text{C}$, $Q_F = 40 \text{ dm}^3/\text{h}$) of PERVAP 4100, 4101, 4510 membranes in the pervaporation process, on model systems: “DI” (deionized water) as well as “0.8% NaCl solution” (corresponding to the Baltic Sea) and “3.5% NaCl solution” (corresponding to the Adriatic Sea) and real seawaters: “Baltic Sea” and “Adriatic Sea”.

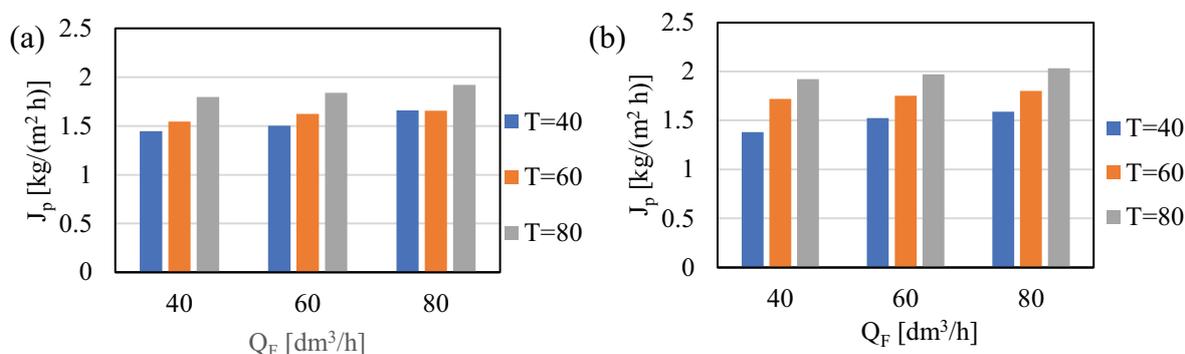


Fig. 4. Average permeate flux, (J_p) for (a) the Baltic Sea and (b) the Adriatic Sea, depending on the feed flow rate (Q_F) and the process temperature (T) for the PERVAP 4510 membrane.

($\text{m}^2\cdot\text{h}$) (Fig. 3). This is a good conclusion: the hydrophilic PERVAP 4510 membrane, used according to the manufacturer's recommendations for alcohol dehydration, can also be successfully used for seawater desalination.

3.2. Desalination geothermal water in the pervaporation process

The pervaporative desalination process was conducted on two types of geothermal waters (Uniejów IGH-1 and Poddębice GT-2). The work examined an aqueous solution of NaCl and KCl as a model system for selected geothermal waters (m-IGH-1). The results of the PV desalination experiments for the Uniejów IGH-1 intake are presented in Fig. 6. From the figure it can be concluded that the permeate flux comes to $6 \text{ kg}/(\text{m}^2\cdot\text{h})$ and the most favorable operating conditions for the geothermal real water PV process are temperatures $\geq 60^\circ\text{C}$ and feed flow rates $\geq 60 \text{ dm}^3/\text{h}$. Therefore, further PV experiments were conducted under these conditions.

For comparison, an efficient and selectivity analysis in the PV process was performed on the m-GT-2 (model Poddębice) and real system (Poddębice GT-2) (Fig. 7) for temperatures 60°C and 80°C and feed flow rates 60 and $80 \text{ dm}^3/\text{h}$. An extremely low permeate flux was obtained (max. $0.4 \text{ kg}/(\text{m}^2\cdot\text{h})$) but a high retention factor (99%).

As indicated by the conducted research, the degree of desalination of water from the Uniejów IGH-1 intake exceeds 99%, making the obtained water suitable for consumption. According to the Regulation of the Minister of Health regarding the quality of water intended for human consumption, "Water is suitable for use if it is free from pathogenic microorganisms and parasites in quantities that pose a potential threat to human health, any substances in concentrations that pose a potential threat to human health, and does not exhibit aggressive corrosive properties" [46]. The permissible chloride content ranging from $5.0\text{--}1,000 \text{ mg}/\text{dm}^3$ is determined by the PN-EN ISO 10304-1:2009+AC:2012 standard.

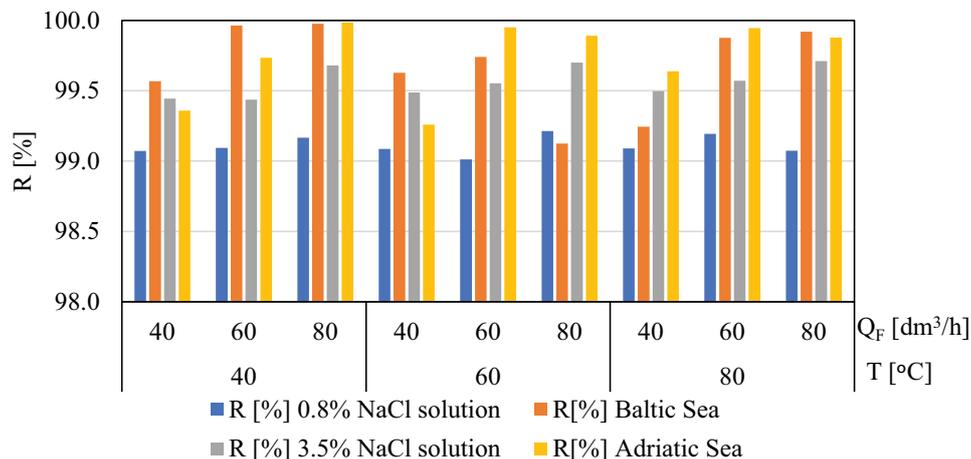


Fig. 5. Retention factor (R) analysis in the pervaporation process on PERVAP 4510 membrane for different process temperatures and feed flow rates on model systems: "0.8% NaCl solution" (corresponding to the Baltic Sea), "3.5% NaCl solution" (corresponding to the Adriatic Sea) and real seawater: "Baltic Sea" and "Adriatic Sea".

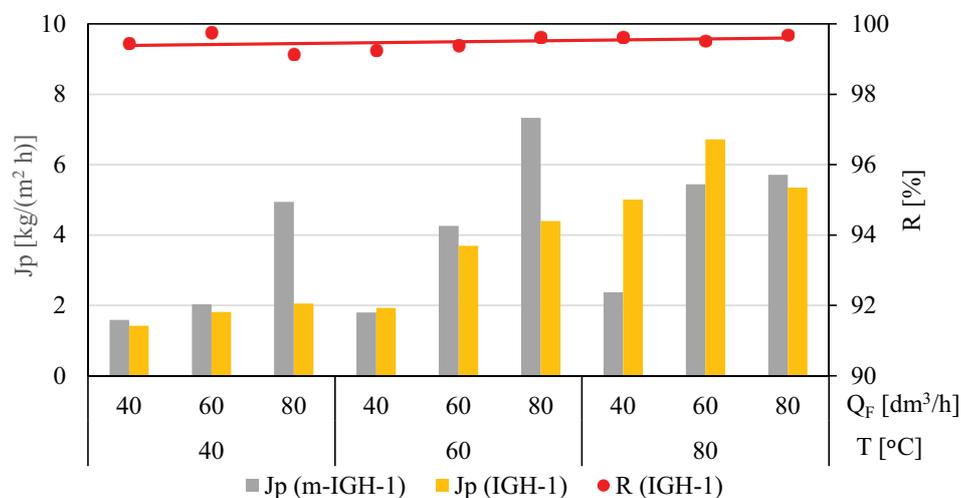


Fig. 6. Average permeate flux (J_p) and retention factor (R) analysis in the pervaporation process on PERVAP 4510 membrane for different process temperatures (T) and feed flow rates (Q_F) for the model: "m-IGH-1" and real system from Uniejów "IGH-1".

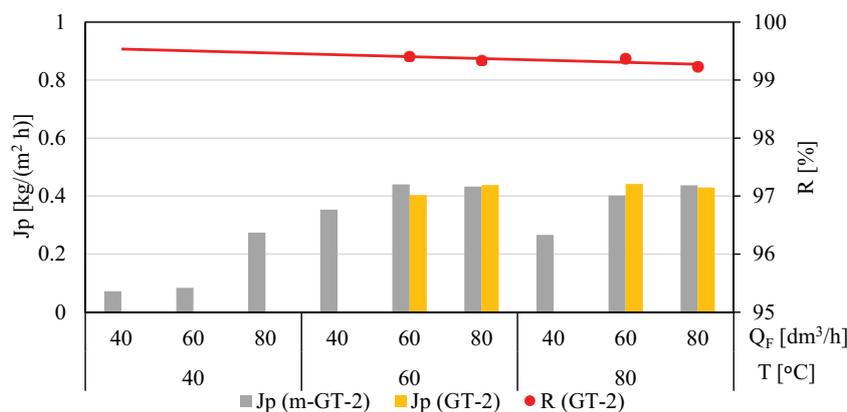


Fig. 7. Average flux (J_p) and retention factor (R) analysis in the pervaporation process on PERVAP 4510 membrane for different process temperatures (T) and feed flow rates (Q_F) for the m-GT-2 (model system) and Poddębice GT-2 (real system).

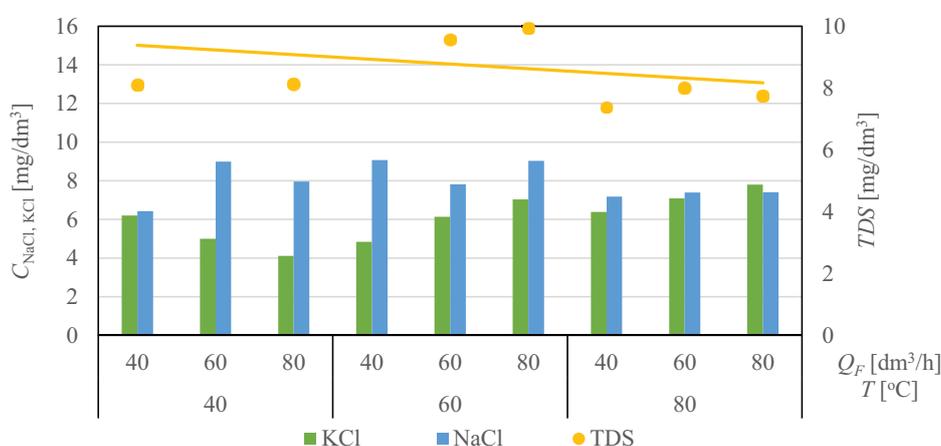


Fig. 8. Concentration of NaCl, KCl, (c), and TDS in permeate after the pervaporation process for the Uniejów IGH-1 samples.

In order to determine the amount of TDS in water from the Uniejów IGH-1 intake selectivity studies were carried out, taking into account the content of various ions in geothermal water. The results are presented in Fig. 8. In addition to potassium and sodium salts, the geothermal water from the Uniejów IGH-1 intake also contains other ions and minerals, which is consistent with the characteristic profile of the described geothermal water (data derived from the Uniejów geothermal source).

3.3. Scaling phenomenon

In the case of seawater, the deposition of organic compounds and mineral salts, known as scaling, is observed on the membrane surface. This creates a rigid, thick layer, which impedes its operation. Reversible fouling (scaling) can be removed by backwashing or by using hydroxides/acids to neutralize the deposit. After such treatments, the membrane is ready for reuse. The fouling phenomenon causes a reduction in the permeate flux and/or a decrease in selectivity.

The SEM photo in Fig. 9a shows a new PERVAP 4510 membrane with a smooth surface of the active layer. Cracks in the layer may indicate that the active layer of the

membrane is breaking during photo preparation. Below the smooth active layer, a jagged support layer can be observed. As the filtration (PV) process proceeds, scaling occurs, meaning a layer of salt crystals forms on the surface. The photo in Fig. 9b shows a thick layer of mineral salts on the membrane surface. It should be suspected that the mineral salts deposited on the surface cause peeling of the very thin (approx. $2 \mu\text{m}$) active layer of the membrane, which causes its destruction. The photo in Fig. 9c is a close-up of the salt crystals and other mineral contaminants after 200 h of PV operation. Additionally, it can be observed organoleptically that the stiffness of the membrane undergoes significant changes. New membranes are characterized by high elasticity and flexibility, while the membrane after the desalination process shows high stiffness. Furthermore, the thickness of the membrane increases due to the accumulation of salt and swelling of individual layers. The layer of contaminants on the membrane surface consists of salts contained in sea and geothermal waters [47–49].

3.4. Change in membrane performance during storage

Change in membrane performance during storage was observed based on desalination experiments conducted on

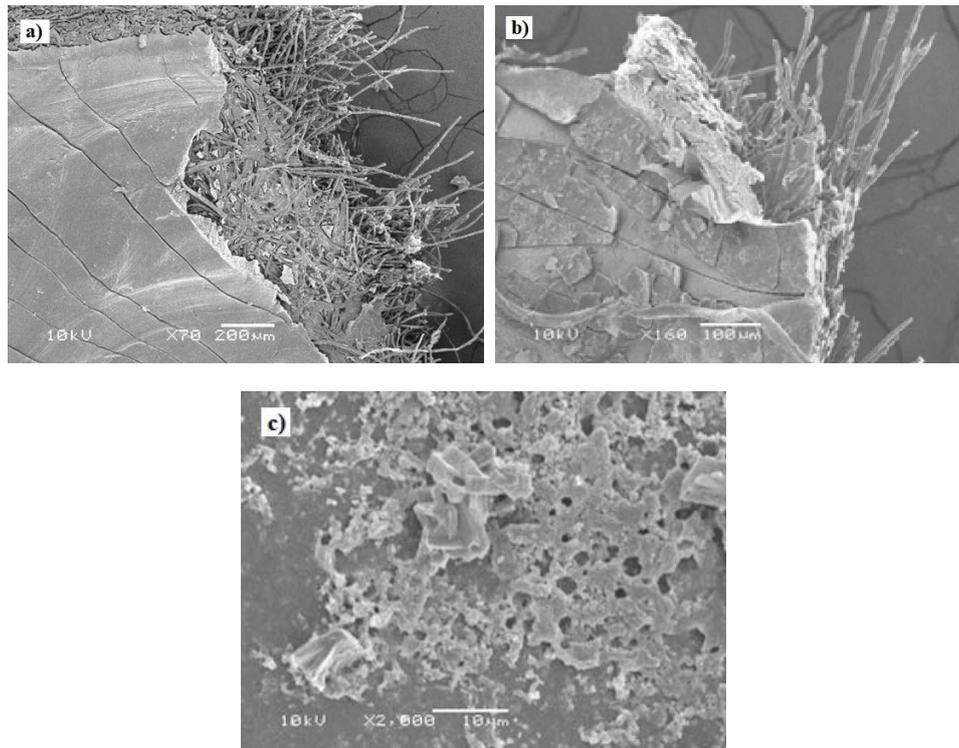


Fig. 9. Scanning electron microscopy images of the PERVAP 4510 membrane: (a) before the pervaporation process, (b) after 200 h pervaporation desalination process, and (c) visible salt crystals after the pervaporation process.

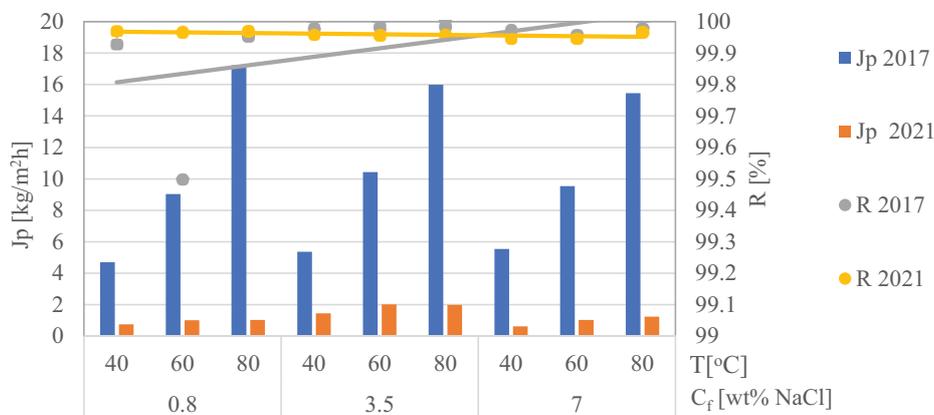


Fig. 10. Efficiency (J_p) and selectivity (R), of the desalination process for PERVAP 2210 membrane for feed flow rate ($Q_f = 40 \text{ dm}^3/\text{h}$) in different years of pervaporation tests, 2017 and 2021.

the same PERVAP 2210 membrane. PV desalination experiments were conducted at a 4-y interval. Initially, for newly purchased membranes from the manufacturer (2017), the obtained permeate fluxes in the analyzed measurement range (0%–7% mass NaCl in the feed) ranged from 4.5 to 16.0 kg/(m²·h). This was a satisfactory result compared to other literature data [18].

Desalination experiments were repeated after 4-y (in 2021). During this time, the membranes were stored in the laboratory without access to light, and packed in the manufacturer's packaging. Both observations of changes in membrane performance were made on a model system

(distilled water and an appropriate amount of dissolved salt), so there is no possibility of contamination of the membrane with biological substances from aqueous solutions. The experiments were carried out on the same laboratory equipment, which excludes equipment errors. Both processes were carried out under the same process conditions, that is, 40 dm³/h. The results are presented in Fig. 10.

The results of the desalination process, after 4 y, were surprising because the permeate flux decreased from 3 to 9 times and fluctuated between 0.62–1.64 kg/(m²·h). Hydrodynamic studies conducted after 4 y showed membrane aging of PERVAP 2210 due to polymer degradation,

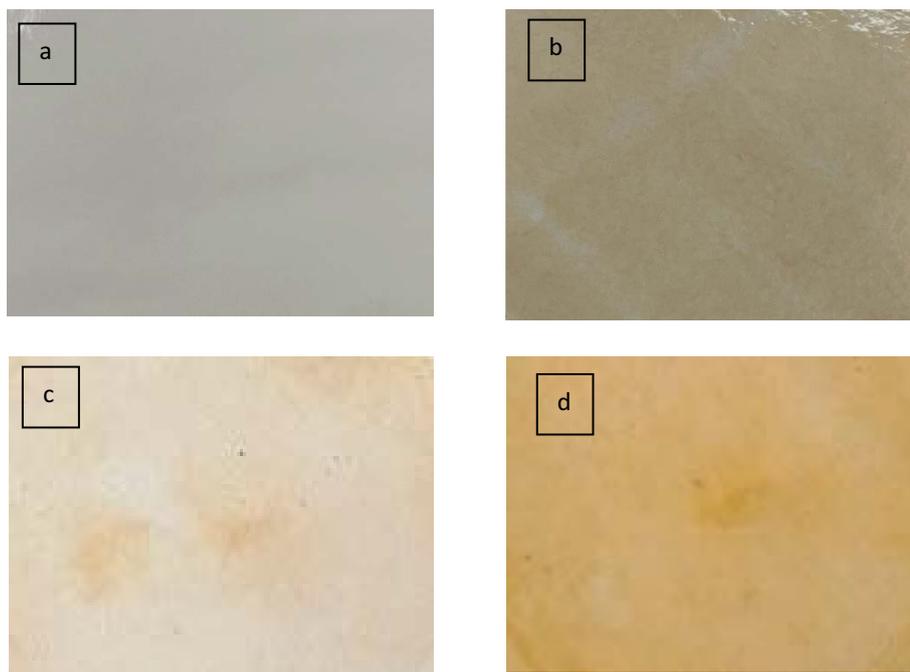


Fig 11. Photos of membranes before (a,b) and after pervaporation process (c,d) for PERVAP 4510 (a,c); and PERVAP 2210 membranes (b,d).

which is confirmed by numerous literature reports [41]. We believe that changes in membrane performance after long-term storage can be called aging of PV membranes and are related to changes in the structure of the polymer that has undergone aging.

It should be emphasized that the degree of salt retention on the membrane did not change and after 4 y it was approximately 99.8%. Since the former 2210 membrane now corresponds to the 4510 membrane according to the manufacturer's data, further aging studies will be carried out on commercial PERVAP 4510 membranes. Preliminary tests have already been performed. For the PERVAP 4510 membrane, a constant permeate production rate was observed during 200 h of operation. The preliminary performance and efficiency results of PV desalination of seawater and geothermal water shown in this manuscript indicate good stability of the commercial membrane.

Additionally, it can be organoleptically determined that the PERVAP 2210 membrane has changed after the PV process. A visible change in the color of the membrane from milky white to brown was observed too. Delamination of individual membrane layers was visible at the edges. Color changes of PERVAP 4510 and 2210 membranes after PV processes are shown in Fig. 11.

The photos show differences in the color of both membranes both before and after the PV process. The PERVAP 2210 membrane now is marked by a yellowish color. It was white right after purchasing it from the manufacturer. This should be emphasized because the new PERVAP 4510 membrane is white-gray in color and, according to the company, these membranes are equivalent. After the PV process, both membranes turned yellowish, suggesting the deposition of a salt layer on the membrane surface.

4. Conclusions

By using reduced pressure, the pervaporation process becomes attractive for a wider range of applications. In this work, PV was used to desalinate model, sea, and geothermal water. Desalination of seawater using commercial Sulzer membranes with an active layer of PVA yields promising results. The PERVAP 4510 membrane was selected for experiments among the purchased hydrophilic membranes for alcohol dehydration available from Sulzer. Satisfactory amounts of permeate in the form of ultrapure water were obtained at high selectivity values. A very high retention factor obtained makes it possible to use desalinated water in many industries.

Desalination of water from the Baltic and Adriatic Seas was proposed and analyzed as one of the PV applications. Low efficiency but high selectivity of the process was achieved despite differences in the initial salinity of both seas. Therefore, the literature information about the possibility of using PV membranes for the desalination of water with a high degree of salinity is confirmed. Another application of the pervaporation process may be the desalination of geothermal waters. Here, slightly higher flux values for the Uniejów IGH-1 intake.

Analyzed PERVAP membranes can be used for about 200 h of continuous operation without additional cleaning. After this time, the process parameters of the membrane decrease - an additional fouling (scaling) layer is formed, manifested in the form of salt crystals forming on the active membrane layer. The fouling phenomenon can be partially eliminated by rinsing, thereby extending the membrane's lifespan.

It is also important to note the aging phenomenon of polymer membranes, over a sample period of 4 y, as

significant differences are shown in the change in process efficiency, not in its selectivity. Selectivity remains constant over time and is at a very high level. In our case, the aging process involves the degradation of the polymer due to the action of oxygen and temperature changes during material storage.

Currently, there are no commercially available pervaporation membranes with sufficient efficiency for the industrial desalination process. The authors are researching innovative membranes produced by the dry phase inversion method. The PV results are promising for their application in seawater desalination.

Symbols

A	—	Membrane area, m ²
Poddębice GT-2	—	Geothermal water from the Poddębice intake
Uniejów IGH-1	—	Geothermal water from the Uniejów intake
J	—	Permeate flux, kg/(m ² ·h)
m	—	Permeate mass, kg
m-IGH-1	—	Model composition (NaCl and deionized water) corresponding to geothermal water from the Uniejów intake
m-GT-2	—	Model composition (NaCl and deionized water) corresponding to geothermal water from the Poddębice intake
t	—	Process time, h
R	—	Retention factor, %
c	—	Salt (NaCl) concentration in the sample, mg/dm ³
Q	—	Flow rate, dm ³ /h
T	—	Temperature, °C
TDS	—	Total dissolved solids concentration, mg/dm ³
C	—	Salt concentration, mg/dm ³
P	—	Transmembrane pressure, Pa

Indexes

F	—	Feed
p	—	Permeate

References

- [1] F. Charlson, S. Ali, J. Augustinavicius, T. Benmarhnia, S. Birch, S. Clayton, K. Fielding, L. Jones, D. Juma, L. Snider, V. Ugo, L. Zeitz, D. Jayawardana, A. La Nauze, A. Massazza, Global priorities for climate change and mental health research, *Environ. Int.*, 158 (2022) 106984, doi: 10.1016/j.envint.2021.106984.
- [2] J. Eke, A. Yusuf, A. Giwa, A. Sodiq, The global status of desalination: an assessment of current desalination technologies, plants and capacity, *Desalination*, 495 (2020) 114633, doi: 10.1016/j.desal.2020.114633.
- [3] A. Koziolec, Wykorzystanie energii odnawialnej w procesie odsalania wody na przykładzie Rady Współpracy Państw Zatoki Perskiej: możliwości i wyzwania, *Pr. Nauk. Uniw. Ekon. We Wrocławiu*, 527 (2018) 160–170.
- [4] A. Zapata-Sierra, M. Cascajares, A. Alcayde, F. Manzano-Agugliaro, Worldwide research trends on desalination, *Desalination*, 519 (2021) 115305, doi: 10.1016/j.desal.2021.115305.
- [5] A. Gómez-Gotor, B. Del Río-Gamero, I. Prieto Prado, A. Casañas, The history of desalination in the Canary Islands, *Desalination*, 428 (2018) 86–107.
- [6] N.A. Ahmad, P.S. Goh, L.T. Yogarathinam, A.K. Zulhairun, A.F. Ismail, Current advances in membrane technologies for produced water desalination, *Desalination*, 493 (2020) 114643, doi: 10.1016/j.desal.2020.114643.
- [7] S. Aly, H. Manzoor, S. Simson, A. Abotaleb, J. Lawler, A.N. Mabrouk, Pilot testing of a novel multi effect distillation (MED) technology for seawater desalination, *Desalination*, 519 (2021) 115221, doi: 10.1016/j.desal.2021.115221.
- [8] C. Fritzmann, J. Löwenberg, T. Wintgens, T. Melin, State-of-the-art of reverse osmosis desalination, *Desalination*, 216 (2007) 1–76.
- [9] S.F. Anis, R. Hashaikeh, N. Hilal, Reverse osmosis pretreatment technologies and future trends: a comprehensive review, *Desalination*, 452 (2019) 159–195.
- [10] L.F. Greenlee, D.F. Lawler, B.D. Freeman, B. Marrot, P. Moulin, Reverse osmosis desalination: Water sources, technology, and today's challenges, *Water Res.*, 43 (2009) 2317–2348.
- [11] X. Zhang, J. Jiang, F. Yuan, W. Song, J. Li, D. Xing, L. Zhao, W. Dong, X. Pan, X. Gao, Estimation of water footprint in seawater desalination with reverse osmosis process, *Environ. Res.*, 204 (2022) 112374, doi: 10.1016/j.envres.2021.112374.
- [12] Y. Li, E.R. Thomas, M.H. Molina, S. Mann, W. Shane Walker, M.L. Lind, F. Perreault, Desalination by membrane pervaporation: a review, *Desalination*, 547 (2023) 116223, doi: 10.1016/j.desal.2022.116223.
- [13] X. Cheng, F. Pan, M. Wang, W. Li, Y. Song, G. Liu, H. Yang, B. Gao, H. Wu, Z. Jiang, Hybrid membranes for pervaporation separations, *J. Membr. Sci.*, 541 (2017) 329–346.
- [14] A. Darmawan, L. Munzakka, L. Karlina, R.E. Saputra, S. Sriatun, Y. Astuti, A.S. Wahyuni, Pervaporation membrane for desalination derived from tetraethylorthosilicate-methyltriethoxysilane, *J. Sol-Gel Sci. Technol.*, 101 (2022) 505–518.
- [15] G. Liu, W. Jin, Pervaporation membrane materials: recent trends and perspectives, *J. Membr. Sci.*, 636 (2021) 119557, doi: 10.1016/j.memsci.2021.119557.
- [16] Y. Song, F. Pan, Y. Li, K. Quan, Z. Jiang, Mass transport mechanisms within pervaporation membranes, *Front. Chem. Sci. Eng.*, 13 (2019) 458–474.
- [17] L.M. Vane, Review of pervaporation and vapor permeation process factors affecting the removal of water from industrial solvents, *J. Chem. Technol. Biotechnol.*, 95 (2020) 495–512.
- [18] Q. Wang, N. Li, B. Bolto, M. Hoang, Z. Xie, Desalination by pervaporation: a review, *Desalination*, 387 (2016) 46–60.
- [19] X. He, T. Wang, J. Huang, J. Chen, J. Li, Fabrication and characterization of superhydrophobic PDMS composite membranes for efficient ethanol recovery via pervaporation, *Sep. Purif. Technol.*, 241 (2020) 116675, doi: 10.1016/j.seppur.2020.116675.
- [20] M.S. Jyothi, K. Raghava Reddy, K. Soontarapa, S. Naveen, A.V. Raghur, R.V. Kulkarni, D.P. Suhas, N.P. Shetti, M.N. Nadagouda, T.M. Aminabhavi, Membranes for dehydration of alcohols via pervaporation, *J. Environ. Manage.*, 242 (2019) 415–429.
- [21] B. Liang, K. Pan, L. Li, E.P. Giannelis, B. Cao, High performance hydrophilic pervaporation composite membranes for water desalination, *Desalination*, 347 (2014) 199–206.
- [22] B. Liang, Q. Li, B. Cao, P. Li, Water permeance, permeability and desalination properties of the sulfonic acid functionalized composite pervaporation membranes, *Desalination*, 433 (2018) 132–140.
- [23] J. Meng, P. Li, B. Cao, High-flux direct-contact pervaporation membranes for desalination, *ACS Appl. Mater. Interfaces*, 11 (2019) 28461–28468.
- [24] W. Yave, The improved pervaporation PERVAP membranes, *Filtr. Sep.*, 54 (2017) 14–15.
- [25] W. Yave, A. Car, S.S. Funari, S.P. Nunes, K.-V. Peinemann, CO₂-philic polymer membrane with extremely high separation performance, *Macromolecules*, 43 (2010) 326–333.
- [26] J. Marszałek, M. Tylman, P. Rdzanek, W. Kaminski, The influence of hydrodynamic conditions on the recovery of acetone, butanol and ethanol in pervaporation membrane modules, *Chem. Process Eng.*, (2018) 155–163.

- [27] B. Tomaszewska, Pilotowa instalacja odsalania wód geotermalnych w Polsce, p. 10.
- [28] B. Tomaszewska, Pozyskanie wód przeznaczonych do spożycia oraz cieczy i substancji balneologicznych w procesie uzdatniania wód geotermalnych, Kraków: Wydawnictwo IGSMiE PAN, 2018.
- [29] M. Ptak, A. Choiński, M. Sojka, S. Zhu, Changes in the water resources of selected lakes in Poland in the period 1916–2020 as information to increase their availability, *Sustainability*, 13 (2021) 7298, doi: 10.3390/su13137298.
- [30] W. Górecki, A. Sowizdżał, M. Hajto, A. Wachowicz-Pyzik, Atlases of geothermal waters and energy resources in Poland, *Environ. Earth Sci.*, 74 (2015) 7487–7495.
- [31] T. Maćkowski, A. Sowizdżał, A. Wachowicz-Pyzik, Seismic methods in geothermal water resource exploration: case study from Łódź Trough, Central Part of Poland, *Geofluids*, 2019 (2019) 3052806, doi: 10.1155/2019/3052806.
- [32] A. Sowizdżał, W. Górecki, M. Hajto, Geological conditions of geothermal resources occurrence in Poland, *Geol. Q.*, (2020), doi: 10.7306/GQ.1526.
- [33] Y. Baek, C. Kim, D.K. Seo, T. Kim, J.S. Lee, Y.H. Kim, K.H. Ahn, S.S. Bae, S.C. Lee, J. Lim, K. Lee, J. Yoon, High performance and antifouling vertically aligned carbon nanotube membrane for water purification, *J. Membr. Sci.*, 460 (2014) 171–177.
- [34] L. Fortunato, A.H. Alshahri, A.S.F. Farinha, I. Zakzouk, S. Jeong, T. Leiknes, Fouling investigation of a full-scale seawater reverse osmosis desalination (SWRO) plant on the Red Sea: membrane autopsy and pretreatment efficiency, *Desalination*, 496 (2020) 114536, doi: 10.1016/j.desal.2020.114536.
- [35] W. Gao, H. Liang, J. Ma, M. Han, Z.-l. Chen, Z.-s. Han, G.-b. Li, Membrane fouling control in ultrafiltration technology for drinking water production: a review, *Desalination*, 272 (2011) 1–8.
- [36] S. Yang, S. Abdalkareem Jasim, D. Bokov, S. Chupradit, A.T. Nakhjiri, A.S. El-Shafay, Membrane distillation technology for molecular separation: a review on the fouling, wetting and transport phenomena, *J. Mol. Liq.*, 349 (2021) 118115, doi: 10.1016/j.molliq.2021.118115.
- [37] W. Guo, H.-H. Ngo, J. Li, A mini-review on membrane fouling, *Bioresour. Technol.*, 122 (2012) 27–34.
- [38] Y.-G. Lee, S. Kim, J. Shin, H. Rho, Y. Lee, Y.M. Kim, Y. Park, S.-E. Oh, J. Cho, K. Chon, Fouling behavior of marine organic matter in reverse osmosis membranes of a real-scale seawater desalination plant in South Korea, *Desalination*, 485 (2020) 114305, doi: 10.1016/j.desal.2019.114305.
- [39] Y.C. Woo, J.J. Lee, L.D. Tijing, H.K. Shon, M. Yao, H.-S. Kim, Characteristics of membrane fouling by consecutive chemical cleaning in pressurized ultrafiltration as pre-treatment of seawater desalination, *Desalination*, 369 (2015) 51–61.
- [40] D. Zhao, J. Song, J. Xu, S. Yu, J. Liu, Y. Zhu, Z. Gu, G. Liu, Behaviours and mechanisms of nanofiltration membrane fouling by anionic polyacrylamide with different molecular weights in brackish wastewater desalination, *Desalination*, 468 (2019) 114058, doi: 10.1016/j.desal.2019.06.024.
- [41] Y. Lin, T.B. Kouznetsova, S.L. Craig, Mechanically gated degradable polymers, *J. Am. Chem. Soc.*, 142 (2020) 2105–2109.
- [42] M. Rutkowska, A. Heimowska, Degradation of naturally occurring polymeric materials in sea water environment, *Polimery*, 53 (2008) 854–864.
- [43] R. Scaffaro, A. Maio, F. Suter, E. Gulino, M. Morreale, Degradation and recycling of films based on biodegradable polymers: a short review, *Polymers*, 11 (2019) 651, doi: 10.3390/polym11040651.
- [44] B. Yang, Y. Yang, Z. Huo, Y. Yu, Advances in research on aging properties of polyvinyl chloride and polyvinylidene fluoride membranes, *Constr. Build. Mater.*, 367 (2023) 130292, doi: 10.1016/j.conbuildmat.2023.130292.
- [45] F. Khalid, A.S. Roy, A. Parveen, R. Castro-Muñoz, Fabrication of the cross-linked PVA/TiO₂/C nanocomposite membrane for alkaline direct methanol fuel cells, *Mater. Sci. Eng., B*, 299 (2024) 116929, doi: 10.1016/j.mseb.2023.116929.
- [46] C.-C. Yang, Synthesis and characterization of the cross-linked PVA/TiO₂ composite polymer membrane for alkaline DMFC, *J. Membr. Sci.*, 288 (2007) 51–60.
- [47] woda morska, Encyklopedia PWN: źródło wiarygodnej i rzetelnej wiedzy (Accessed: Nov. 19, 2023). Available at: <https://encyklopedia.pwn.pl/haslo/woda-morska;3997253.html>
- [48] D.O. Shaltami, Chemical composition of seawater.
- [49] F.J. Millero, R. Feistel, D.G. Wright, T.J. McDougall, The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale, *Deep Sea Res. Part I*, 55 (2008) 50–72.
- [46] 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 (in Polish)*.