

The effect of unfavourable process conditions on the water desalination by membrane distillation

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ABSTRACT

The exploitation of household membrane installations by unqualified people may lead to errors in the installation operation. The impact of poor maintenance of such an installation and its role on water desalination by membrane distillation was presented. The polypropylene membranes Accurel PP S6/2 and Accurel PP V8/2 HF were used in the studies. The operation conditions of installations, which were supplied with poor quality water, for example, from small surface reservoirs in the arid zone, were analysed. The desalination of a lake water salted with NaCl and clay was performed for this purpose. The influence of a lack of periodical cleaning of installation, feeding the installation with high turbidity water and the maintaining conditions allowing for the intensive growth of micro-organisms on the membrane wettability was studied. A considerable decline of the permeate flux and a deterioration of quality of obtained freshwater was not found, although the membrane modules were operated continuously for 1 year. The examination of membranes samples using an electron microscope confirmed that the membrane fouling was relatively light despite a long period of exploitation and unfavourable conditions of installation work.

Keywords: Membrane distillation; Water desalination; Freshwater; Fouling

1. Introduction

The desert areas characterized by low rainfall (arid zone) are in general sparsely populated, and the households may be at considerable distance from each other. In practice, it eliminates the possibility of production of freshwater in large installations and the application of small, individual installations is the only option. If the brackish or saline water is available, the application of a compact membrane installation for water desalination is a reasonable solution. The utilization of membrane distillation (MD) for the production of freshwater has been considered as a basic application of this process [1–5]. A potential use of MD includes the possibility of drinking water production from highly saline water and its ability to operate at relatively low temperatures [6,7]. The economics of MD installation with a high capacity is

comparable with other water desalination techniques [7,8]. However, the industrial MD installations with the yield close to reverse osmosis (RO) plants have not yet emerged despite 50 years of intensive studies on the process.

The major reasons hindering the industrial application of the MD are facts that this process generates a lower flux than RO process and exhibits a lower thermal efficiency than a multistage flash [9]. The assessment of using MD may be advantageous in the case of small household installations for the production of drinking water, in places where the possibility of obtaining freshwater is of the highest importance, especially, for example, when a high salinity disables the application of RO for water desalination [8,10]. An idea of small MD installations has been already presented at the beginning of the process development [3], and such installations are currently developed by several industrial companies in a pilot scale [4,5,11,12]. The implementation has become possible due to the development of industrial MD modules.

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The most notable companies specializing in the MD modules in high-efficiency systems include: Memstill, Aquastill, Scarab AB, Memsys and Fraunhofer Institute for Solar Energy Systems [5,8,11–14].

During the MD process water is evaporated, which is required to supply a considerable amount of heat. The theoretical energy (without the heat losses) required to operate the direct contact MD system is 628 kWh/m^3 [7,8]. On the other hand, at real conditions it has been estimated that the consumption of energy amounts to over $1,200 \text{ kWh/m}^3$ for MD installations deprived of a system [4]. Even if the power is available it will be difficult to supply such amounts of energy from a typical household electric installation. In the remote areas, the use of the heat generated in solar systems for operation of MD process has been explored [5,11–14]. Using the spiral-wound MD modules integrated with solar collectors, Fraunhofer ISE has offered advanced installations that have been tested for several years in a pilot scale. These modules are also available in a variant equipped with a heat recovery mode [5]. Moreover, other companies such as Scarab AB and Aquaver offer small, solar-powered MD installations with spiral-wound or plate-and-frame modules [11,13]. Such installations enable to obtain a feed temperature in the range of 30°C – 60°C (relatively low), which limit the efficiency of MD process. However, the application of lower MD process temperatures for water desalination is advantageous because it allows to limit a membrane scaling, thereby, to increase the possibility of long-term exploitation of a membrane module [15].

During the MD process membrane pores contact only with the gas phase, and the maintenance of membrane nonwettability is one of the principal requirements for the realization of this process. This can be achieved by the application of membranes made of strongly hydrophobic polymers such as polytetrafluoroethylene or polypropylene (PP) [1–4]. Hence, the limitation of fouling/scaling is very important in the MD process since the formation of deposits on the membrane surface accelerates its wettability [11,16,17]. In order to ensure a long-term exploitation of a membrane module, a feed pretreatment and the application of several operational procedures is required [18,19].

In the case of household installations it can happen that the MD systems will be supplied with water deprived of any pretreatment, as no special attention is paid to its quality. Moreover, it should not be expected that the individual operators of the MD installation possess an adequate knowledge and skills required for staff employed for the operation of industrial membrane installations. This may lead to errors in the operation of the MD systems and as a result, the performance of membranes will be disrupted. In order to determine a resistance of membranes to hazards, which may arise of an inappropriate operation, the long-term studies of MD installation operation were performed at potentially unfavourable conditions. A special attention was particularly paid to the feeding of the installation with water of high turbidity carelessness to a growth of micro-organisms.

2. Experimental

In the simplest household installation, a solar collector (or other energy sources) may be used for direct heating of

the feed tank, in which a submerged MD membrane module is placed. Such a variant of MD installation was studied in this work, using an experimental set-up shown in Fig. 1. In this installation a role of energy source was performed by a magnetic stirrer equipped with a heating element (600 W, IKA, USA).

Two submerged modules made from PP membranes Accurel PP (Membrana GmbH, Germany) were placed in the glass feed tank (4 L). The nominal diameter of the membranes pores was $0.2 \mu\text{m}$ and the open porosity was 73% (on the basis of the supplier data). In the MD1 module, four Accurel PP S6/2 ($d_{\text{in}}/d_{\text{out}} = 1.8/2.6 \text{ mm}$) membranes with the length of 20 cm were assembled. The MD2 module was composed of a single membrane Accurel PP V8/2 HF ($d_{\text{in}}/d_{\text{out}} = 5.5/8.6 \text{ mm}$) with the length of 25 cm. Each of the modules was connected to an individual distillate tank, cooled in a water bath (18°C). The initial volume of distilled water in the distillate tanks amounted to 1.5 L. The peristaltic pumps were used to obtain the volumetric flow rate of distillate (inside the capillary membranes) equal to $6 \pm 0.2 \text{ mL/s}$ (linear velocity of 0.59 m/s – MD1 module and 0.79 m/s – MD2 module).

The MD installation was operated continuously (day and night) for almost 1 year (with technological breaks). The permeate flux and solute concentrations in the feed and distillates were measured usually once per day. The permeate flux was calculated on a basis of changes in the distillate volume over studied period of time (20–24 h). The feed tank was refilled with distilled water (to keep solutes constant concentration in the feed during batch process mode) or by process solutions (continuous operation) to a constant volume (4 L) once a day.

In the first stage of studies the effectiveness of applied MD modules was tested using the standard solution containing distilled water salted with 1 g/L of NaCl (ChemPur, Poland) as a feed. Assuming that household installations will be equipped with small and cheap plate solar collector (energy system of low effectiveness), the influence of feed temperature on the MD process efficiency was studied in the range from 23°C to 45°C . In order to determine a

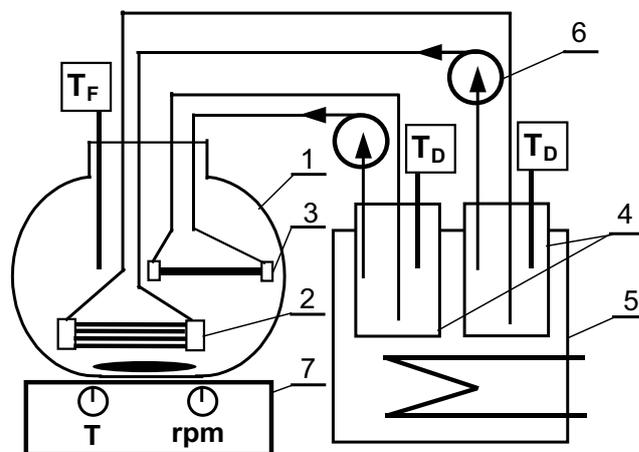


Fig. 1. The scheme of the experimental set-up. 1 – Feed tank, 2 – MD1 module, 3 – MD2 module, 4 – distillate tanks, 5 – cooling bath, 6 – pump, 7 – magnetic stirrer with heating and $T_{F,D}$ – thermometers.

decrease of modules yield along with the increase of solutes concentration in the feed, the salt content in the feed was gradually increased up to 300 g/L.

In warm water of small surface reservoirs, as a rule, a rich biological life is normally met. The feeding of MD installation with such a water without any pretreatment may facilitate membrane biofouling. In order to investigate the impact of micro-organisms growth on the process performance, the feed tank was filled with the water collected from lake and the membrane was immersed in this water for a 2 summer months (25°C–30°C), which caused an intensive growth of green algae on the membranes surface and tank walls (MD process was interrupted during this period). The formed biofilm was removed by threefold intensive rinsing of the tank with tap water. Subsequently, in order to determine an eventual change in the yield and a degree of separation, the MD experiments were repeated using feed containing 1–40 g NaCl/L.

The small water reservoirs are formed in places structured of impermeable substrate (e.g., clay). The natural mixing of water (waves, animals, etc.) makes that the clay readily forms the colloidal suspensions and such water characterizes with a high turbidity. Thus, the studies were also performed with the water to which 1–3 g dry clay/L were added, in order to check the effect of the presence of such suspension on the membrane fouling.

The observations of a wet layer of biofilm formed on the membrane surface were performed using a digital microscope VHX-5000 (Keyence International, Belgium) connected with high-resolution microscope lens VH-Z20R/Z20T or VH-100R/Z100T. The micro-organisms present in the biofilm were also observed using the optical microscope NICON ECLIPSE 50i (Japan) connected with LV-UEPI illuminator and DS-5M digital camera.

A membrane morphology and a composition of deposits were studied using scanning electron microscope (SEM) coupled with the energy dispersion spectrometry (EDS). The samples for a cross-sectional study were prepared by a fracturing of the capillary membranes in liquid nitrogen. All samples were sprayed with chromium to obtain the desired coating.

The concentration of anions and cations was measured using 850 Professional Ion Chromatograph with conductometric detector (Herisau Metrohm, Switzerland). The separation of anions was performed on a 1.7 × 3.5 mm Metrosep RP guard column operated in series with a 250 × 4.0 mm Metrohm A Supp5-250 analytical column. The eluent solution included 3.2 mM/L Na₂CO₃ + 1.0 mM/L NaHCO₃ (flow rate 0.7 mL/min). A C2 guard column operated in series with a 150 × 4.0 mm Metrosep C2-150 analytical column was used for the separation of cations. In this case, the eluent was a mixture of tartaric acid (4 mM/L) with 0.75 mM/L 2-picoline acid.

3. Results

3.1. The efficiency of MD modules

The driving force for mass transfer in MD is a difference in the vapour pressure; hence, the feed temperature has a considerable influence on the process efficiency (Fig. 2).

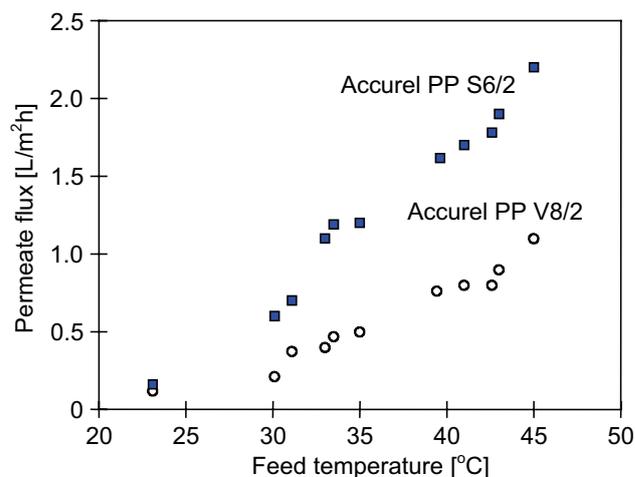


Fig. 2. The influence of feed temperature on the permeate flux. $T_p = 17^\circ\text{C} - 19^\circ\text{C}$.

In the studied case, an increase of temperature from 30°C to 45°C allowed to obtain a three- to fourfold increase of the permeate flux, for example, from 0.6 to 2.1 L/m² h (Accurel PP S6/2). The feed temperature in this range could be obtained by assembling a solar collector of an area of 1 m² when recalculated on 1 m² of assembled membranes [14]. The application of collector with a larger area would allow to increase the feed temperature and to obtain a considerably larger yield. On the other hand, this could also result in an intensive scaling [17]. Therefore, the use of low feed temperature and the increase of installation yield by applying a module with a larger area of membranes seem to be a better solution, particularly in a small household installation.

The formation of deposits on the membrane surface accelerates its wettability in the MD process, which can lead to a destruction of module [1,4,6,15]. A significant increase of module durability, even in the case of scaling, can be achieved by assembling the membranes with thicker walls, such as Accurel PP V8/2 [20]. These membranes have four times thicker walls (1.5–1.6 mm) in comparison with the membranes Accurel PP S6/2. However, the resistance of vapour transport increases along with the membrane thickness, and as a consequence, a yield obtained for thicker membranes was two times smaller (Fig. 2). In the case of small MD installation (of capacity, e.g., 20–50 L/d), an increase of the investment costs associated with a higher membrane area (Accurel PP V8/2 membranes) equalizing the higher walls thickness, can be compensated by obtaining longer installation durability.

In regard to a temperature polarization, an assurance of good hydrodynamic conditions in the MD module often determines the process efficiency [17]. The results presented in Fig. 3 indicate that in the case of used submerged modules such conditions were already obtained for small agitation speeds (100 rpm) on the feed side, therefore the similar results were obtained at a higher mixing speed (700 rpm). This confirmed the conclusions from other works, that the influence of temperature polarization was definitely smaller for a low feed temperature (e.g., 40°C), thus, there was no need for the feed to flow turbulently over the membrane surface [21].

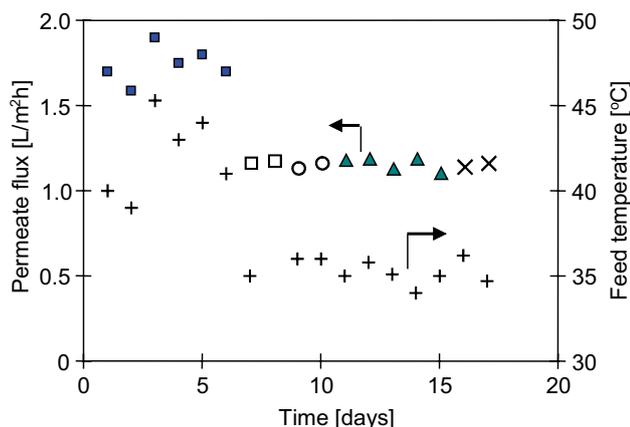


Fig. 3. The influence of feed mixing speed on the permeate flux and feed temperature (+) during the MD process. The studies were carried out at the same heating power of feed tank. Fluxes for speeds (rpm): ■ – 0, □ – 100, ○ – 400, ▲ – 600 and × – 700. Distillate temperature 18°C.

Hence, in small MD installations with submerged modules, it is possible to resign from forced mixing of feed (recycling pump) and to utilize the flow of water caused only by the natural convection generated inside the feed tank. Such a solution can limit the intensity of heat exchange with the MD module, which can lead to small changes in the permeate flux. However, from the point of view of a residential user, it can be a better solution in comparison with the necessity of assembling an additional pump.

The highest permeate flux was obtained in the case (Fig. 3), when the feed was not mixed because the water temperature was higher in a bottom part of the tank in the vicinity of the surface of heating element (where the modules were assembled). In regard to a larger stability of the installation operation, the mixing of feed was used in this work, which enabled a more accurate study of the influence of applied process parameters on its capacity and stability.

In regions with poor rainfall, the only source of water is usually brackish water [22]. The influence of salt concentration in the feed on the process yield was presented in Fig. 4. An increase in the feed concentration up to 300 g/L caused the yield decrease by 40% in the case of S6/2 membranes and by 30% for V8/2 membranes. A smaller decline of yield for V8/2 membranes resulted of a fact that the resistance of vapour diffusion through a fourfold thicker wall had a definitely larger influence on the process yield in comparison with a reduction of the driving force of MD process caused by the increase of salt concentration. The obtained results confirmed that desalination of water by MD process could be performed even for the concentrated solutions of salt, which was regarded as the main advantage of this process [2,6,20].

A slight increase of the conductivity of obtained distillates (up to 37 $\mu\text{S}/\text{cm}$) was observed along with the increase in the feed concentration (Fig. 4). This indicated that some of the pores in the membranes were already wetted, which enabled the penetration of salt from the feed into a distillate. The studies of desalination of concentrated salt solutions were performed at the operation time of modules amounted to 1,200 h. In the previous work, it was demonstrated that

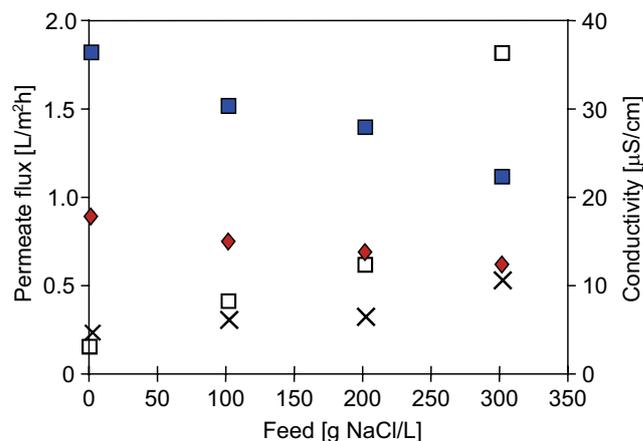


Fig. 4. The influence of feed concentration on the permeate flux and conductivity of distillates. Feed temperature 43°C. Flux: ■ – S6/2, ◆ – V8/2. Conductivity: □ – S6/2, × – V8/2.

the applied Accurel PP membranes stabilized during the initial 50–100 h of operation and a small number of the pores were wetted [23]. It has to be emphasized that the production of distillate with conductivity of 37 $\mu\text{S}/\text{cm}$ at the feed concentration of 300 g NaCl/L still proves salts retention about 100%. The distillate conductivity for the membrane Accurel PP V8/2 increased only to 10 $\mu\text{S}/\text{cm}$, which confirms the previous conclusions concerning a definitely larger resistance to wettability for the membranes with thicker wall [20,23].

The basic difficulty in the realization of MD process is the maintenance of the membrane nonwettability over a long period of modules exploitation. The unfavourable changes of properties of the hydrophobic membranes used in the process may proceed very slowly; hence, it is necessary to perform a long-term study in order to determine an actual possibility of process realization. Hence, the continuous studies of water desalination were performed for over 2 months (with weekend breaks). The obtained results of these studies were presented in Fig. 5. The MD installation was supplied with water collected from the lake, the composition of which is presented in Table 1. A constant level of the feed was maintained in a tank during the process by adding periodically either water or NaCl solution.

During the initial 9 d of studies (Fig. 5), the feed temperature amounted to 42°C, which allowed to obtain the permeate flux 1.7 L/m² h (MD1 – S6/2) and 0.9 L/m² h (MD2 – V8/2). The process temperature was decreased to 33°C during the consecutive days, in order to limit scaling. However, the yield for the module MD1 and MD2 decreased to 1.2 and 0.5 L/m² h, respectively, as a result of temperature decrease.

After 10 d of the studies the fresh portions of salt were added to the feed tank, gradually increasing the salinity of feeding solution from 1 to 45 g NaCl/L. This increase of the feed salinity caused the yield of MD1 module reduction from 1.2 to 0.94 L/m² h, whereas that of MD2 module from 0.5 to 0.43 L/m² h (Fig. 5). After completing this stage of studies (Fig. 5 – 42 d), the brine was removed from the tank and the installation was again supplied with water containing 1 g NaCl/L. As a result, the obtained yield increased to a value

Table 1
The composition of feed water and MD retentate (after 9 d of the process duration)

Ions (mg/L)	Water	Retentate
Cl ⁻	46.8	70.9
NO ₃ ⁻	1.1	1.6
SO ₄ ²⁻	86.7	136.1
Na ⁺	23.9	35.1
K ⁺	5.5	7.4
Ca ²⁺	64.3	92.4
Mg ²⁺	16.6	24.2

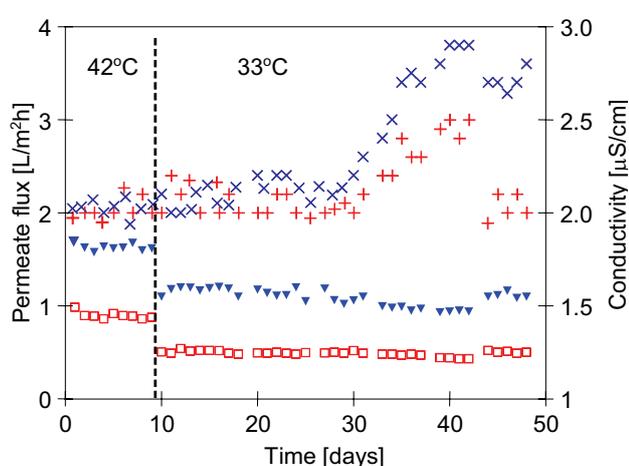


Fig. 5. The changes of the permeate flux and the distillate conductivity during a continuous water desalination by MD process. Feed temperature 42°C or 33°C. Flux: ▼ – S6/2, □ – V8/2. Conductivity: × – S6/2, + – V8/2.

of 1.1 L/m² h for MD1 module and to 0.5 L/m² h for the module MD2. This indicated that during 2 months of studies, the yield of MD2 module did not change, whereas that of MD1 module (S6/2) slightly decreased. Most probably, this resulted of a small increase of the degree of S6/2 membrane wettability, which was pointed out by a slight increase of the conductivity of the distillate from 2 to 2.8 µS/cm. Moreover, it should be noted that the results obtained during 2 months of continuous studies confirmed a good and stable performance of both used modules, which corresponded to a previously demonstrated suitability of the membranes Accurel PP for water desalination [3,20].

The results presented in Table 1 indicate that the concentration of particular ions in the feed was considerably increased due to a periodical addition of process water to the feed tank. This created a danger of formation of oversaturation followed by the precipitation of deposits such as CaCO₃ and CaSO₄ [6,17]. Thus, it is important, that the users remember about a frequent removal of the retentate from MD installation. Omitting this step is not the only error one can make during MD process exploitation, and the negative effects caused by other errors were determined in the subsequent stages of those studies.

3.2. High turbidity feed supply

The feeding of membrane modules with high turbidity water is not beneficial, moreover, in case of spiral-wound modules become unacceptable [18]. Thus, the water turbidity is reduced in the industrial installations using, for example, sedimentation, coagulation and sand filters [24]. In the case of small household installations a stage of preparation of feed water may comprise only of a bucket to which the water is collected from a reservoir. Even if the water is originally clean, when collected it may become contaminated with the materials from the bottom of the lake, such as sand and clay. Clay mixed with water forms a colloidal suspension, which is difficult to separate and may form the deposits on the membrane surface. Due to this, in the studies, it was verified how the presence of clay suspension influenced on the performance of the membrane modules.

In order to compare the changes of module yields of the MD installation the feed containing only 1 g NaCl/L was supplied for the first 4 d. In the consecutive days of studies, a portion of clay (1 g/L) was added three times into this solution, and each time a different performance of the system (Fig. 6) was observed.

After the addition of the first portion of clay, the module yield decreased from 1.15 to 1.0 L/m² h (MD1) and from 0.55 to 0.51 L/m² h (MD2) – Fig. 6. The yield of MD1 module slightly increased from 1 to 1.05 L/m² h during 3 consecutive days, whereas that of MD2 module was practically constant. This indicated that a thickness of a deposit layer formed on the membrane surface did not grow along with the MD process duration. In order to find out whether an increase of turbidity causes an increase of fouling intensity, the second portion of clay was added after 9 d of study, which resulted in a systematic decline of the permeate flux, but only since the 13th day of studies (Fig. 6). At the end of this experimental series, the modules yield amounted to 0.93 L/m² h (MD1) and 0.44 L/m² h (MD2). The addition of the third portion of clay did not cause a further flux decline. This resulted most probably of a well-known fact that the thickness of a deposit layer on the membrane surface stabilized at given conditions of

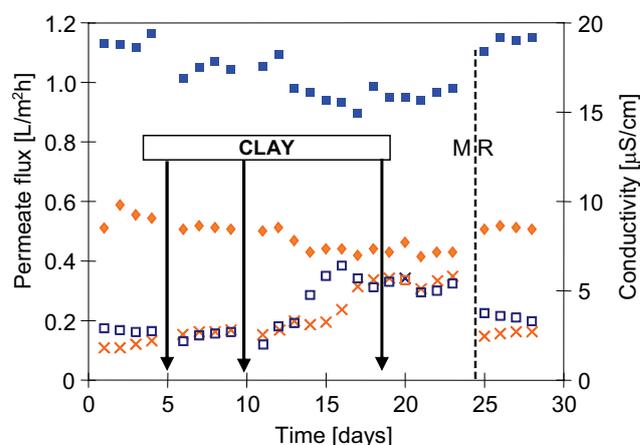


Fig. 6. The changes of permeate flux and distillate conductivity during MD process of feed water containing clay suspension. Flux: ■ – S6/2, ◆ – V8/2. Conductivity: □ – S6/2, × – V8/2. MR – membranes rinsing.

the feed flow [25]. As a consequence, the feeding of modules with water containing a large content of clay suspension (3 g/L) caused the module yield to decrease only by less than 10%, which was found to be a significant advantage of the MD process over the filtration processes, such as micro- and ultrafiltration, where the module yield was rapidly decreased due to the formation of a filtration cake [18,25].

As the feed tank was drained it was found that the membrane surface was covered by a nonuniform layer of brown deposit (clay colour). The majority of deposit was removed from the membranes by rinsing them with tap water, which indicated that such deposit was loosely bonded with the membrane surface. As a result, an increase of the yield to 1.15 L/m² h (MD1) and 0.52 L/m² h (MD2), was observed after the MD process restart (Fig. 6, last 4 d), which was close to the level observed before the treatment of water with clay suspension. This indicated that the application of feed with a high turbidity did not cause a damage of the submerged modules over examined period of time and the membrane wettability was not considerably increased. This was also confirmed by a fact that the final distillate conductivity (about 3 μS/cm) only slightly increased in relation to one obtained during the first days of the studies.

SEM examinations of membrane samples collected from MD2 module (after rinsing with distilled water) confirmed that despite a considerable amount of clay suspended in water only small amounts of deposits were permanently bonded with the membrane surface (Fig. 7). The formation of crystallites characteristic for CaCO₃ or CaSO₄ on the membrane surface was not observed, although such crystallites were observed in large amounts in previous studies during the desalination of water with a similar composition using the feed temperature in the range 60°C–80°C [17]. This confirms that the application of a low-temperature process (30°C–40°C) is an effective method of scaling limitation [26].

A composition of deposits cumulated on the surface of examined membrane samples shown in Fig. 7(b) is presented in Table 2. The SEM–EDS examinations revealed that the observed deposits were mainly composed of Si,

Table 2

The composition (% wt.) of deposits accumulated on the membrane surface (Fig. 7(b))

Elements	Sample		
	A	B	C
C	29.76	40.62	57.74
O	23.37	9.22	0.56
Al	4.63	1.65	0.01
Si	7.26	3.11	0.35
Fe	2.07	3.47	1.27
K	2.05	0.59	0
Na	1.52	2.53	0.36
Ca	0.15	0.31	0.05
Mg	0.13	0.34	0.02
Cl	1.74	3.54	0.85

Al, Fe and O. These elements generally form oxides, which are hardly soluble in water [27]. Their accumulation on the membrane surface during, for example, 2–3 years of module exploitation can significantly decrease the yield of MD installation. Hence, it is recommended that the feed water used to supply the home installation has the turbidity as low as possible. This can be achieved by cheap and simple methods of feeding the installation not directly from water sources, but indirectly from, for example, a barrel, which can act as a storage tank and simultaneously as a settling tank.

3.3. Biofouling

The conditions of MD installation operation usually do not favour the micro-organisms growth, as it has been demonstrated in the previous works, thus, the influence of biofouling on the process is limited [26]. However, an excessive growth of micro-organisms can take place during installation downtime. It can be expected, that home installations will

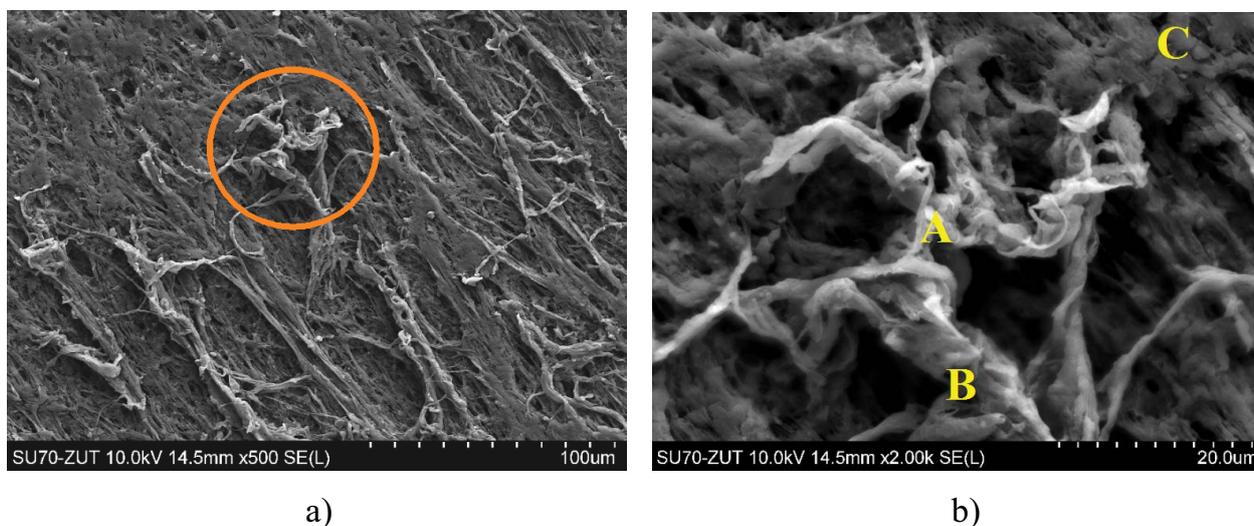
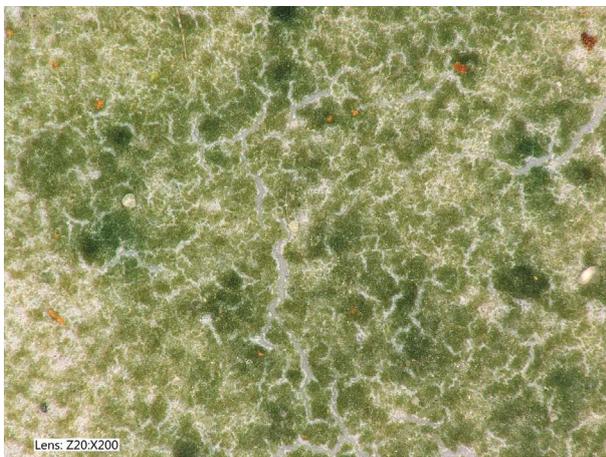


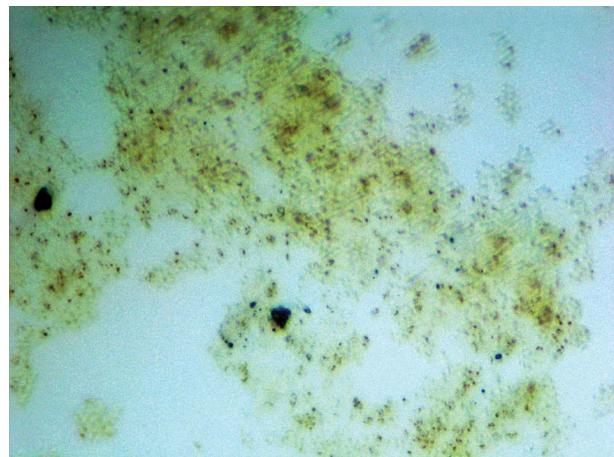
Fig. 7. (a) SEM images of membrane surface (MD2 module) after MD studies with clay suspension, (b) area marked by circle in Fig. 7(a).

not be properly prepared for longer downtimes, for example, by rinsing and filling with a storage solution. If a remaining process water (feed) containing algae and bacteria is kept for several weeks in a nonoperated MD installation, it may lead to the strong growth of a biofilm on the membrane surface. In this work, it was checked how such an effect could influence on the effectiveness of MD module operation. For this purpose, the feed tank was filled with water and after 2 weeks of MD installation operation it was shut down for 2 months. The ambient temperature during this time was changed in the range 22°C–30°C. After 2 months it was found that the tank walls and the membrane surface were covered by a green layer of algae (Fig. 8(a)). The presence of rod-shaped bacteria was also noted in the collected deposit (Fig. 9).

The application of intensive stirring of the feed (700 rpm) resulted in a significant removal of the fraction of micro-organisms from the membrane surface, and only some green spots of the biofilm were visible (Fig. 8(b)), probably composed of the residues of algae. Subsequently, the feed tank and modules were rinsed two times with a tap water, and the MD process was restarted. It was found that a shut-down of the installation accompanied with the growth of micro-organisms for 2 months led only to a small decline of the module yield (Fig. 10), if the modules were intensive rinsed. The permeate flux obtained for the MD1 module decreased from initial 1.05 to initial 0.85 L/m² h, and it was stabilized at a level of 0.72 L/m² h after 2 d of the process performance. In the case of MD2 module, the yield decreased



a)



b)

Fig. 8. The MD membrane surface covered by a green biofilm layer after 2 months of shutdown, magnification $\times 200$ (a), the MD membrane surface after rinsing the module, magnification $\times 1,000$ (b).

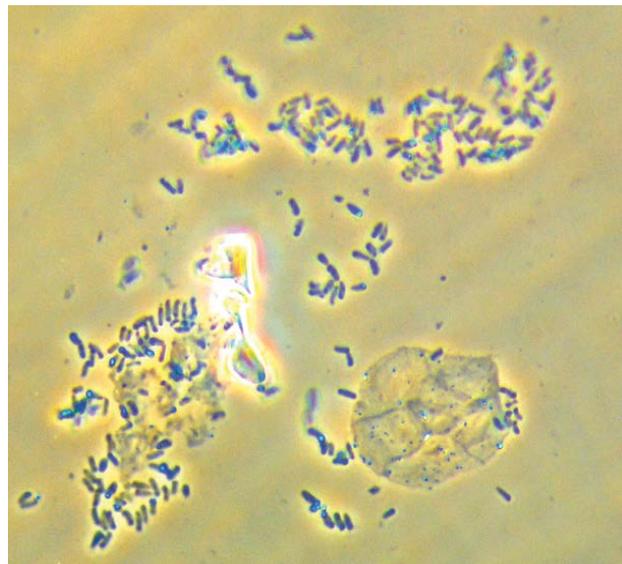
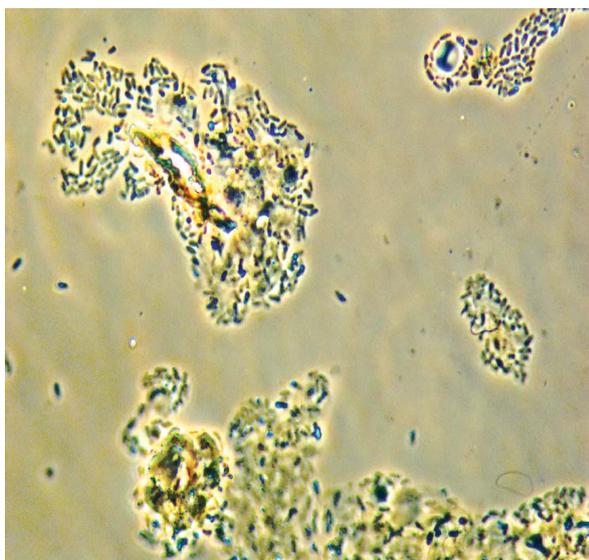


Fig. 9. Images of bacteria present in the biofilm formed on the membranes surface.

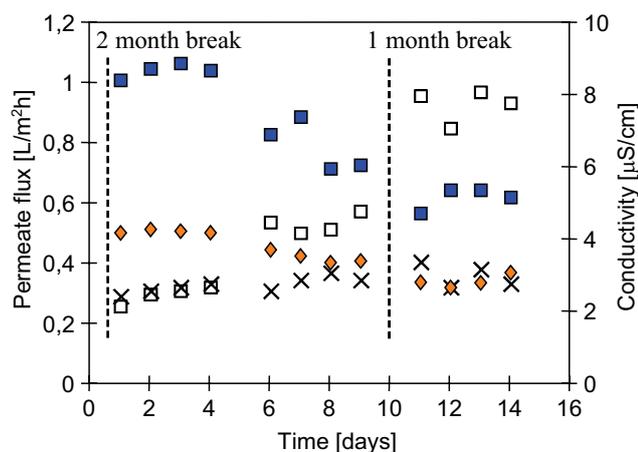


Fig. 10. The changes of permeate flux and electrical conductivity after 2 and 1-month shutdown period accompanied with deposition of micro-organisms on the membrane surface. Flux: ■ – S6/2, ◆ – V8/2. Conductivity: □ – S6/2, × – V8/2.

from 0.51 to 0.41 L/m² h. An increase of particular distillates conductivity from 2.7 to 4.8 µS/cm (MD1) and from 2.8 to 3 µS/cm (MD2) indicated that algae not only blocked the evaporation surface, but also caused the wettability of a part of membranes pores.

After stabilization of MD1 and MD2 modules yield (Fig. 10, point – 10 d), the MD installation was shut down for the next month. This enabled the proceeding of the growth of micro-organisms, which covered the membrane surface by a green film, similarly as in the previous case. This caused a further decline in the installation yield (Fig. 10, data after 11 d). The permeate flux for the MD1 module decreased from 0.72 to 0.63 L/m² h, and for MD2 module the decline was from 0.41 to 0.35 L/m² h. Totally, the yield of MD1 module decreased by 40%, whereas the yield of MD2 module by about 31% within a 3-month period of the micro-organisms growth on the membrane surface. Moreover, the distillate conductivity for the membrane Accurel PP S6/2 (MD1) increased from 2.7 to 8 µS/cm, whereas for the membrane Accurel PP V8/2 (MD2) changed only from 2.8 to 3.1 µS/cm. These results confirmed the conclusions from the previous works, that is, the membranes with thicker walls were more resistant to biofouling during the MD process [28]. The membranes used in the studies exhibited a good resistance to wetting during the treatment of water in a bioreactor covered with bacteria biofilm [29]. Hence, it can be concluded that the algae growth caused and/or accelerated the wettability of membranes.

The wettability of pores in the membranes results in a leakage of the feed, which can lead to an excessive concentration of salts in the produced distillate. Thus, in the last stage of the studies the effect of process conditions on the rate of salt rejection by the examined membranes was checked. The studies started with the desalination of water containing 5 g NaCl/L and a systematic increase of the distillate conductivity was found, which in the case of MD1 module increased to over 50 µS/cm, and from 2.4 to 4 µS/cm for the MD2 module (Fig. 11). In the MD process, the water vapour

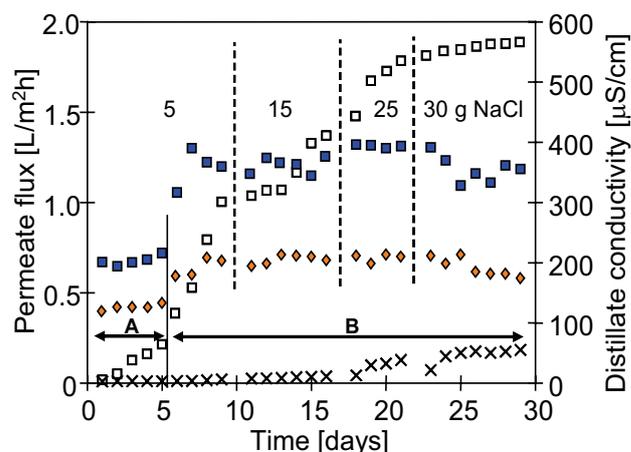


Fig. 11. The changes of permeate flux and distillate conductivity during MD process. Feed: NaCl solution of concentration: 5, 15, 25 and 30 g/L (dashed lines). Feed temperature: A – 33°C and B – 42°C. Flux: ■ – S6/2, ◆ – V8/2. Conductivity: □ – S6/2, × – V8/2.

flows through the membrane, thus, when the rate of membrane wettability is not changed, the permeate flux increases or the electrical conductivity of distillate decreases. On the other hand, an elevation of the feed temperature from 33°C to 42°C was shown not to cause such an effect. Moreover, in the case of MD1 module operated at the elevated temperature, the conductivity of distillate quickly increased (up to 300 µS/cm). This confirmed that, a deposition of micro-organisms on the membrane surface facilitated a further wettability of the pores during the consecutive days of MD process performed at elevated temperature.

The SEM examinations of membrane (collected from MD1 module) cross-sections performed after accomplishing the studies of water desalination revealed that a biological deposit was also formed inside the membrane wall (Fig. 12), which unfortunately facilitated the wettability. An increase of conductivity stopped after about 20 d of the process, despite the increase of the salt concentration in the feed. It indicated that only the pores which were located in a direct vicinity of biological deposits became wetted. In the case of MD2 module, the conductivity stabilized at a level of 51 µS/cm and it was 560 µS/cm for the MD1 module. It showed that even for more wetted membranes (i.e., Accurel PP S6/2), the obtained conductivity was still within the range acceptable for potable water (below 1,000 µS/cm).

The discussed results indicated that an intensive growth of micro-organisms could lead to a serious damage of MD modules. For this reason, the preventive actions against biofouling development should be applied even in household installations. During the studies of water desalination (Fig. 12), it was observed that after already few days the applied solution of NaCl (5 g/L) enabled the cleaning of the membrane surface and the membrane became white again. Thus, a periodical addition of a salt into the feed can be a simple method of protection of household installations. Moreover, the users can prepare such salt solutions simply using natural evaporation of the retentate discharged from the MD installation.

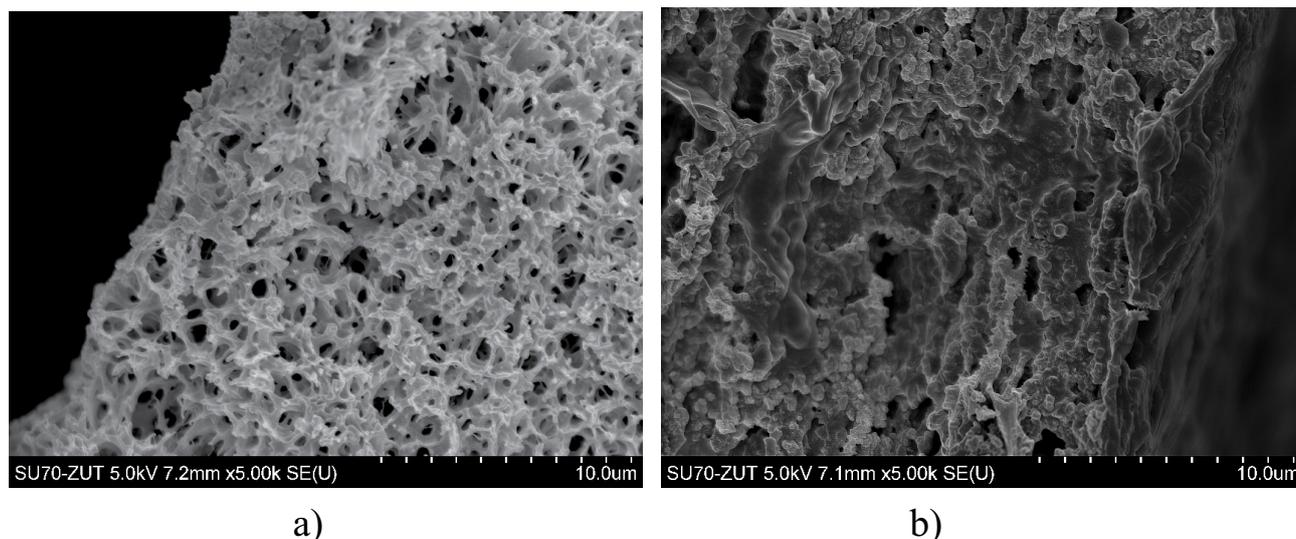


Fig. 12. SEM images of membrane cross-section collected from MD1 module. (a) New membrane and (b) deposit inside the pores.

4. Conclusions

The long-term studies of MD demonstrated that the tested PP membranes Accurel PP did not become significantly wetted despite the unfavourable process conditions, such as a high turbidity of the feed and biofouling and their satisfactory operation was revealed. The observed performance of these membranes indicated on their applicability in small MD installations dedicated for residential potable water production systems.

The use of low temperatures (33°C–42°C) of the feed allowed for obtaining 10–20 L/d of freshwater production in the small MD installation equipped with the module of the effective membrane area of 1 m². Moreover, the low membrane scaling was found to occur in such conditions.

The feeding of MD installation with the high turbidity water containing a clay suspension did not cause a destruction of the MD modules. However, taking into consideration 2–3 years long period of the system exploitation, it was recommended to use simple methods for the turbidity elimination such as a sedimentation in small feed water storage tanks.

Biofouling, especially the growth of algae, was found to accelerate wettability of membranes pores. For this reason, an excessive multiplication of micro-organisms in the MD installation should be prevented. A periodical rinsing of the installation with 5–10 g/L NaCl solution was found to be sufficient method of the biofouling control. The installation should be also fed with the salt solution in case of long breaks in its operation.

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References

- [1] A. Alkudhiri, N. Darwish, N. Hilal, Membrane distillation: a comprehensive review, *Desalination*, 287 (2012) 2–18.

- [2] E. Drioli, A. Ali, F. Macedonio, Membrane distillation: recent developments and perspectives, *Desalination*, 356 (2015) 56–84.
- [3] K. Schneider, W. Hölz, R. Wollbeck, S. Ripperger, Membranes and modules for transmembrane distillation, *J. Membr. Sci.*, 39 (1988) 25–42.
- [4] P. Wang, T.S. Chung, Recent advances in membrane distillation processes: membrane development, configuration design and application exploring, *J. Membr. Sci.*, 474 (2015) 39–56.
- [5] D. Winter, J. Koschikowski, M. Wieghaus, Desalination using membrane distillation: experimental studies on full scale spiral wound modules, *J. Membr. Sci.*, 375 (2011) 104–112.
- [6] H.C. Duong, P. Cooper, B. Nelemans, T.Y. Cath, L.D. Nghiem, Optimising thermal efficiency of direct contact membrane distillation by brine recycling for small-scale seawater desalination, *Desalination*, 374 (2015) 1–9.
- [7] R. Sarbatly, C.K. Chiam, Evaluation of geothermal energy in desalination by vacuum membrane distillation, *Appl. Energy*, 112 (2013) 737–746.
- [8] U.K. Kesime, N. Milne, H. Aral, C.Y. Cheng, M. Duke, Economic analysis of desalination technologies in the context of carbon pricing, and opportunities for membrane distillation, *Desalination*, 323 (2013) 66–74.
- [9] Y. Zhang, Y. Peng, S. Ji, Z. Li, P. Chen, Review of thermal efficiency and heat recycling in membrane distillation processes, *Desalination*, 367 (2015) 223–239.
- [10] I.A. Mohamed, E.K. Summers, H.A. Arafat, J.H. Lienhard V, Effects of membrane properties on water production cost in small scale membrane distillation systems, *Desalination*, 306 (2012) 60–71.
- [11] E. Guillén-Burrieza, J. Blanco, G. Zaragoza, D.C. Alarcón, P. Palenzuela, M. Ibarra, W. Gernjak, Experimental analysis of an air gap membrane distillation solar desalination pilot system, *J. Membr. Sci.*, 379 (2011) 386–396.
- [12] R. Schwantes, A. Cipollina, F. Gross, J. Koschikowski, D. Pfeifle, M. Rolletschek, V. Subiela, Membrane distillation: solar and waste heat driven demonstration plants for desalination, *Desalination*, 323 (2013) 93–106.
- [13] E. Mendez, Membrane distillation delivers greener clean water, *Filtr. Sep.*, 49 (2012) 26–28.
- [14] M.R. Qtaishat, F. Banat, Desalination by solar powered membrane distillation systems, *Desalination*, 308 (2013) 186–197.
- [15] J. Ge, Y. Peng, Z. Li, P. Chen, S. Wang, Membrane fouling and wetting in a DCMD process for RO brine concentration, *Desalination*, 344 (2014) 97–107.
- [16] L. Francis, N. Ghaffour, A.S. Alsaadi, S.P. Nunes, G.L. Amy, Performance evaluation of the DCMD desalination process

- under bench scale and large scale module operating conditions, *J. Membr. Sci.*, 455 (2014) 103–112.
- [17] G. Naidu, S. Jeong, S. Vigneswaran, Influence of feed/permeate velocity on scaling development in a direct contact membrane distillation, *Sep. Purif. Technol.*, 125 (2014) 291–300.
- [18] D. Dolar, K. Košutic, T. Strmecky, Hybrid processes for treatment of landfill leachate: coagulation/UF/ NF-RO and adsorption/UF/NF-RO, *Sep. Purif. Technol.*, 168 (2016) 39–48.
- [19] L.D. Tijing, Y.C. Woo, J.S. Choi, S. Lee, S.H. Kim, K.H. Shon, Fouling and its control in membrane distillation – a review, *J. Membr. Sci.*, 475 (2015) 215–244.
- [20] M. Gryta, M. Palczyński, Desalination of geothermal water by membrane distillation, *Membr. Water Treat.*, 2 (2011) 147–158.
- [21] A. Ali, P. Aimar, E. Drioli, Effect of module design and flow patterns on performance of membrane distillation process, *Chem. Eng. J.*, 277 (2015) 368–377.
- [22] G. Naidu, S. Jeong, Y. Choi, E. Jang, T.M. Hwang, S. Vigneswaran, Application of vacuum membrane distillation for small scale drinking water production, *Desalination*, 354 (2014) 53–61.
- [23] M. Gryta, Wettability of polypropylene capillary membranes during the membrane distillation process, *Chem. Pap.*, 66 (2012) 92–98.
- [24] N. Voutchkov, Considerations for selection of seawater filtration pretreatment system, *Desalination*, 261 (2010) 354–364.
- [25] K.J. Hwang, S.J. Lin, Filtration flux–shear stress–cake mass relationships in microalgae rotating-disk dynamic microfiltration, *Chem. Eng. J.*, 244 (2014) 429–437.
- [26] Q.M. Nguyen, S. Lee, Fouling analysis and control in a DCMD process for SWRO brine, *Desalination*, 367 (2015) 21–27.
- [27] M. Gryta, Effect of iron oxides scaling on the MD process performance, *Desalination*, 216 (2007) 88–102.
- [28] M. Gryta, The application of membrane distillation for broth separation in membrane bioreactors, *J. Membr. Sci. Res.*, 2 (2016) 193–200.
- [29] M. Krivorota, A. Kushmarob, Y. Orena, J. Gilrona, Factors affecting biofilm formation and biofouling in membrane distillation of seawater, *J. Membr. Sci.*, 376 (2011) 15–24.