

Application of membrane distillation process for tap water purification

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Abstract. Membrane distillation process was used for purification of pre-treated natural water (tap water). The rejection of inorganic and organic compounds in this process was investigated. The obtained rejection of inorganic solutes was closed to 100%, but the volatile organic compounds (VOCs) diffused through the membrane together with water vapour. The content of trihalomethanes (THMs) in the obtained distillate was two-three fold higher than that in the feed, therefore, the rejection of the total organic compounds present in the tap water was reduced to a level of 98%. The intensive membranes scaling was observed during the water separation. The morphology and composition of the fouling layer was studied using scanning electron microscopy coupled with energy dispersion spectrometry. The influence of thermal water pre-treatment performed in a heat exchanger followed by filtration on the MD process effectiveness was evaluated. This procedure caused that significantly smaller amounts of CaCO_3 crystallites were deposited on the membrane surface, and a high permeate flux was maintained over a period of 160 h.

Keywords: membrane distillation; water treatment; hydrophobic membrane; desalination.

1. Introduction

A growing demand for water along with the progressing contamination of the conventional water resources creates several technological problems for industry and domestic water supplies. Chronic water pollution and growing economies are driving municipalities and companies to consider the desalination as a solution to their water supply problems (Viessman and Hammer 2005).

Over the past 20 years, the membrane processes, such as reverse osmosis (RO), ultrafiltration (UF) and nanofiltration (NF) have found a wide application in water treatment (Singh 2006). A fast development of new membrane processes, such as membrane distillation (MD), is now being observed (El-Bourawi, *et al.* 2006, Karakulski, *et al.* 2009, Singh 2006). The MD process enables the production of clean water from natural water (or wastewater), the quality of which impedes a direct application of the RO for this purpose (Karakulski, *et al.* 2009). Therefore, the MD process received worldwide attention from both academia and industry in the last decade (Abu Al-Rub, *et al.* 2002, Gryta 2005b, Lawson and Loyd 1997, Song, *et al.* 2007).

Membrane distillation is defined as an evaporation process of volatile compounds through the non-wetted porous membrane (El-Bourawi, *et al.* 2006, Gryta 2008a, Li and Sirkar 2004). Various modes of the MD process are known for several years: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD), vacuum membrane

distillation (VMD) and osmotic membrane distillation (OMD). These variants are differing in a way of permeate collection, the mass transfer mechanism through the membrane, and the reason for driving force formation (Gryta 2005a, Lawson and Lloyd 1997). DCMD variant is the most frequently studied and described mode of MD process (Alklaibi and Lior 2004, Gryta 2008a). In this case the surfaces of the membrane are in a direct contact with the two liquid phases, hot feed and cold distillate (Fig. 1). DCMD is a thermally driven process in which relatively low feed temperatures (below 363 K) are applied. This allows the utilization of solar heat or so-called waste heat, e.g. the condensate from turbines or heat exchangers (Abu Al-Rub, *et al.* 2002, El-Bourawi, *et al.* 2006, Li and Sirkar 2004).

Hydrophobic microporous membranes, with the pore size below 1 μm , are primarily used in MD process (Bonyadi and Chung 2007, El-Bourawi, *et al.* 2006, Karakulski, *et al.* 2002, Wang, *et al.* 2008). These membranes are prepared from polymers having a low value of the surface energy, such as polypropylene (PP), polytetrafluoroethylene (PTFE), or polyvinylidene fluoride (PVDF). The hydrophobic nature of the membrane prevents the aqueous solution from penetrating into the pores, thus creating a vapor-liquid interface is formed at each pore entrance. The evaporation of volatile components of the feed (mainly water) takes place at the hot side of the membrane, followed by the transport of the generated vapour through the dry membrane pores, and finally, the condensation of the vapour transported to the other side of the membrane (Gryta 2005a, Lawson and Lloyd 1997). The driving force for the mass transport is a gradient of vapour pressure, which results from the differences both in the temperatures and compositions of solutions in the layers adjacent to the membrane (Fig. 1).

The MD separation mechanism is based on vapour/liquid equilibrium of a liquid mixture. For solutions containing non-volatile solutes only water vapour is transferred through the membrane; hence, the obtained distillate comprises demineralized water (Alklaibi and Lior 2004, Karakulski and Gryta 2005, Song, *et al.* 2007). However, when the feed contains several volatile components, they are also transferred through the membranes to the distillate (El-Bourawi, *et al.* 2006, Gryta, *et al.* 2006). Based on this separation mechanism, the major application areas of membrane distillation include water treatment technology, seawater desalination, production of high purity water and the concentration of aqueous solutions (El-Bourawi, *et al.* 2006, Drioli, *et al.* 2004, Gryta, *et al.* 2006, Hsu, *et al.* 2002, Karakulski, *et al.* 2006, Martínez-Díez and Florido-Díaz 2001, Srisurichan, *et al.*

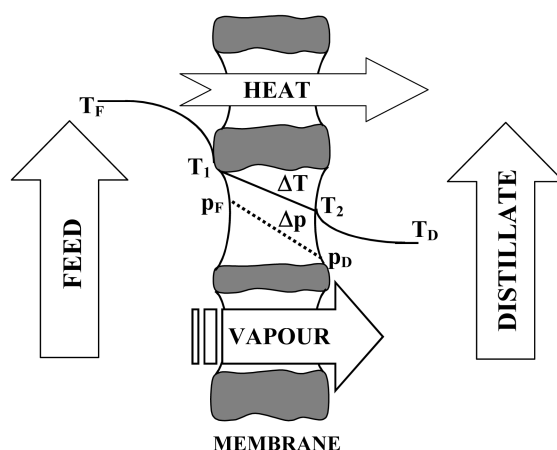


Fig. 1 Principles of the DCMD process. T - temperature, p - vapour partial pressure. Subscripts: F - feed and D - distillate

2005, Teoh, *et al.* 2008).

In comparison with other desalination processes, the main advantages of membrane distillation are: (1) 100% separation (in theory) of ions, macromolecules, colloids, cells etc., (2) lower operating pressures, (3) lower requirements concerning the mechanical properties of the membrane, and (4) less space requirement compared to conventional distillation processes (El-Bourawi, *et al.* 2006, Gryta, *et al.* 2006, Hsu, *et al.* 2002, Karakulski and Gryta 2005, Lawson and Lloyd 1997, Song, *et al.* 2007). However, besides these advantages, membrane distillation still faces difficulties for commercialization. The major difficulties are basically associated with a phenomenon of membrane wetting and the formation of the deposit on its surface (fouling and scaling) (Alklaibi and Lior 2004, Gryta, *et al.* 2001, Srisurichan, *et al.* 2005). These phenomena are responsible not only for a decline of the plant yield, but may also cause a membrane damage over a short period of time (Gryta, *et al.* 2006, Gryta 2008a, Tun, *et al.* 2005).

In the MD process one can distinguish the four possible degrees of membrane wetting: non-wetted, surface-wetted, partial-wetted (only a part of pores through the membrane wall was filled by liquid) and wetted. The wettability of the surface layer, although proceeding on a significant depth, still enables to maintain a gaseous gap between the feed and distillate within the membrane. This excludes a leakage of feed and permits to produce the distillate of a high purity. However, a deterioration of distillate quality will occur when a partial wettability of the membrane will take place (Gryta 2007).

The main techniques currently used to control fouling are the feed pre-treatment and membrane cleaning (El-Bourawi, *et al.* 2006, Gryta, *et al.* 2001, Karakulski, *et al.* 2002, Singh 2006). The integration of membrane processes enables a reduction in the scaling potential of the separated solutions (Drioli, *et al.* 2004, Gryta 2005, Karakulski, *et al.* 2009). The membrane scaling can be effectively controlled by the use of the appropriate MD process conditions. The CaCO_3 precipitation was limited by lowering the feed temperature and by increasing the feed flow rate (Gryta 2008b). Moreover, the HCO_3^- ions concentration may be reduced at the pre-treatment stage, e.g. by water softening process (Gryta 2008c) or by using the pressure driven membrane processes (Gryta 2005, Karakulski and Gryta 2005, Karakulski, *et al.* 2009). On the other hand, an excessively advanced pre-treatment system significantly increases the installation costs (Karakulski, *et al.* 2006). Therefore, the development of simple and inexpensive methods for module cleaning or fouling prevention is necessary in order to implement the membrane distillation on a commercial scale.

In this work, the membrane distillation process was used for purification (demineralization) of tap water. The separation efficiency with both inorganic and organic compounds was investigated. The influence of the thermal softening on the performance of the MD process was evaluated. The effect of heterogeneous crystallization performed inside the heat exchanger on the flux stability was also presented.

2. Experimental

2.1. DCMD investigations

The studies of membrane distillation were carried out using a laboratory installation presented in Fig. 2. Hydrophobic capillary polypropylene membranes (Accurel PP S6/2, Membrana, Germany), with outside/inside diameter equal to $d_{\text{out}}/d_{\text{in}} = 2.6 \text{ mm}/1.8 \text{ mm}$, were used for these studies. The capillary membranes have the pore size with the maximum and nominal diameter of $0.55 \text{ }\mu\text{m}$ and

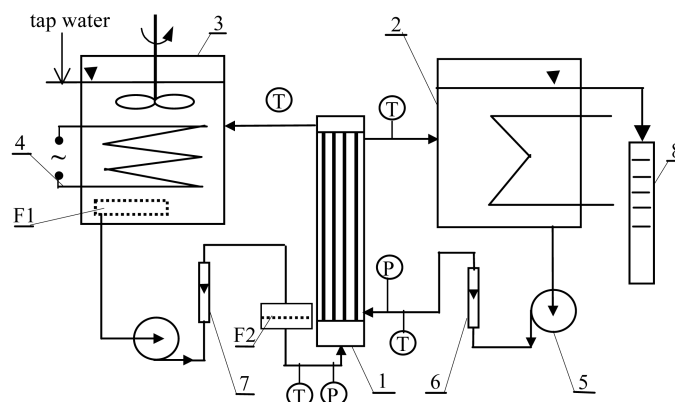


Fig. 2 Schedule of experimental DCMD laboratory installation. 1 - membrane module, 2 - cooled distillate tank, 3 - feed tank with mixer and feed dosing system, 4 - electrical heater, 5 - pump, 6, 7 - flowmeter, 8 - measurement cylinder, F1, F2 - net filter, T - thermometer, P - manometer

0.22 μm , respectively, and the porosity of 73% (manufacturer's data). The capillary modules used in this work resemble the construction of shell and tube heat exchanger. The MK1 module was equipped with the 18 membranes with 0.54 m length (working area 0.055 m^2) assembled in a housing with the inner diameter equal to 0.017 m. The MK2 module had a single capillary membrane (1.05 m length) mounted in the housing with the inner diameter equal to 0.012 m (working area 0.0059 m^2).

The feed and distillate streams flowed co-currently from the bottom to the upper part of MD module. The feed flows inside the capillary bore, whereas the distillate flows on the housing (shell) side. The inlet temperatures of the streams of feed and distillate were kept at a constant level of 353 K and 293 K, respectively. The flow rate of the feed alongside the membrane surface was 1.2 m/s (MK1) and 1 m/s (MK2), whereas that of the distillate amounted to 0.3 (MK1) and 0.05 m/s (MK2). The same hydraulic pressure (0.53 kPa – MK1 and 0.16 kPa – MK2) of both streams (feed and distillate) was applied at the module inlet.

A net F1 filter (150 μm , area of 80 cm^2) was assembled inside the feed tank, and an additional F2 filter (100 μm , area of 10 cm^2) was located near the module inlet. The volume of feed tank was 10 dm^3 when MK1 module was used, whereas 1.5 dm^3 when MK2 module was investigated.

2.2. Analytical methods

The concentration of individual anions and cations concentrations were measured using an ion chromatography method with conductivity detector (850 Professional IC, Herisau Metrohm - Switzerland). The separation of anions was achieved on 1.7×3.5 mm Metrosep RP guard column in series with a 250×4.0 mm Metrohm A Supp5-250 analytical column. A Metrosep C2-150 separation column (150×4.0 mm) was used for determination of the standard cations.

The morphology and composition of the deposit layer formed on the membrane surface was studied using a scanning electron microscopy (SEM) coupled with energy dispersion spectrometry (EDS). Membrane samples for examination by SEM were collected from the MD modules, which were previously rinsed with distilled water.

The electrical conductivity and total dissolved solids (TDS) of the used waters was measured with a 6P Ultrameter (Myron L Company). The content of inorganic carbon (IC) and total organic carbon

(TOC) both in the feed and permeate was determined using a TOC-Analyzer multi N/C (Analytic Jena).

The concentrations of trihalomethanes (THMs) in the samples of permeate and feed was determined by a gas chromatography (GC-14, Shimadzu) equipped with an electron capture detector (ECD) using a head-space technique. The fused silica capillary column (BP624, moderately polar) was 25 m in length with a 0.53 mm diameter. The injection port was kept at a temperature of 453 K. The initial column temperature of 373 K was raised to 453 K with a temperature ramp of 15 K/min and was maintained at this temperature for 3.5 min. The temperature of the ECD was kept at 503 K. Nitrogen (NG 450, Peak Scientific) was used as the carrier gas at a flow rate of 12 ml/min. The identification of THMs was performed by a comparison of the retention times of unknown peaks with those of the standards under the same analytical conditions. A quantitative analysis was carried out by an external standard method.

3. Results

3.1. Efficiency of separation

The conventional drinking water treatment processes, including chlorination, were used for production of investigated tap water. The electrical conductivity of this water was in the range of 650-700 $\mu\text{S/cm}$, what correspond to the value of 430-450 ppm TDS. The tap water had the following average ionic composition (ppm): Na^+ – 29, Mg^{2+} – 18, Ca^{2+} – 65, K^+ – 6, Br^- – 0.13, SO_4^{2-} – 102, NO_3^- – 1.2 and Cl^- – 55. The content of inorganic carbon amounted to 21 mg C/dm^3 . The presence of organic compounds was confirmed by TOC analysis (7-8 mg C/dm^3). The gas chromatography analysis indicated that 3.5 $\mu\text{g/dm}^3$ of CHCl_3 and 0.6 $\mu\text{g/dm}^3$ of CHClBr_2 was present in the tap water. Trihalomethanes are formed during the disinfections step of drinking water if free chlorine was used as a disinfectant (Viessman and Hammer 2005).

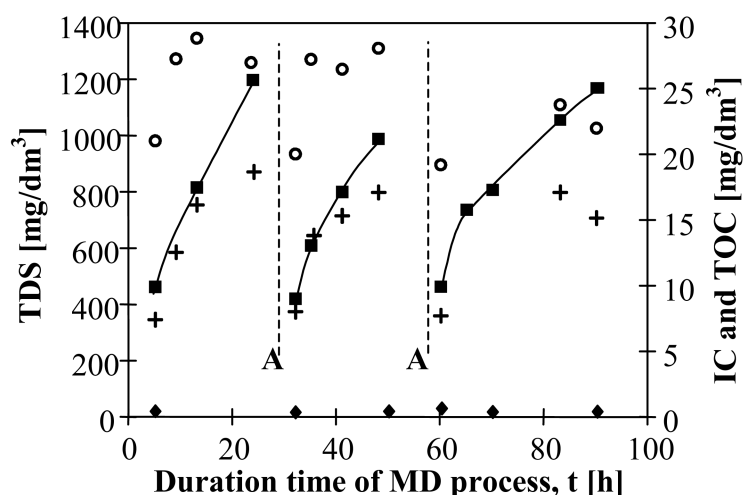


Fig. 3 Changes TDS, IC and TOC values during the MD process of tap water. Feed: ■ - TDS, ○ - TOC, + - IC. Distillate: ◆ - TOC. Point A - the feed was replaced by new portion of fresh tap water

During the operation of MD installation a part of water evaporated, therefore, the new portions of the tap water were continuously dosing to the feed tank in order to maintain a constant liquid level (Fig. 2). A gradual increase in the solute concentration was observed in the recycled feed due to water vapour permeation through the membranes (Fig. 3). After 29 h and after 58 h of MD process duration, when the volume of the permeate achieved 75% of the total volume of the dosed tap water, the liquid from the feed tank was removed and the feed tank was refilled with a portion of fresh tap water. The use a higher coefficient of water recovery may cause the CaSO_4 precipitation (Gryta 2009).

The results shown in Figs. 3 and 4 indicate that an increase in the feed concentration had a negligible effect on the quality of produced distillate. The electrical conductivity of distilled water, initially filling the distillate tank, was equal to $2.2 \mu\text{S}/\text{cm}$. However, the produced MD distillate was cleaner than the used distilled water, and the value of electrical conductivity was systemically decreased to $1.5 \mu\text{S}/\text{cm}$ (Fig. 4). Despite the increasing value of the feed concentration (Fig. 3), the IC content in the distillate was close to the analytic zero. It confirms the fact that regardless of the time of the process duration, the MD membranes demonstrated a high retention of inorganic solutes (Alklaibi and Lior 2004, Gryta 2007). Only a slight amount of TOC (below $0.5 \text{ mg C}/\text{dm}^3$) was detected in the distillate, which can be associated with the transport of the volatile compounds through the MD membranes. It was found that volatile organic compounds (VOCs) diffuse through the pores of hydrophobic membranes, similarly to water vapour, hence, they are not rejected in the MD process (Lawson and Lloyd 1997, Karakulski and Gryta 2005).

The diffusion of VOCs through the porous membrane in MD process was confirmed by the investigations of THMs concentration in the feed and produced distillate (Fig. 5). Because the molecules of CHCl_3 and CHClBr_2 have higher relative volatility than water, their transport through the membrane will be faster. As a consequence, the THMs concentration in the obtained distillate was higher than that in the feed. Moreover, the results shown in Fig. 5 demonstrate that the feed and distillate exhibit a stable level of TOC concentration. Probably, the VOCs diffused from liquid to the air and the equilibrium concentration was achieved in the operated system.

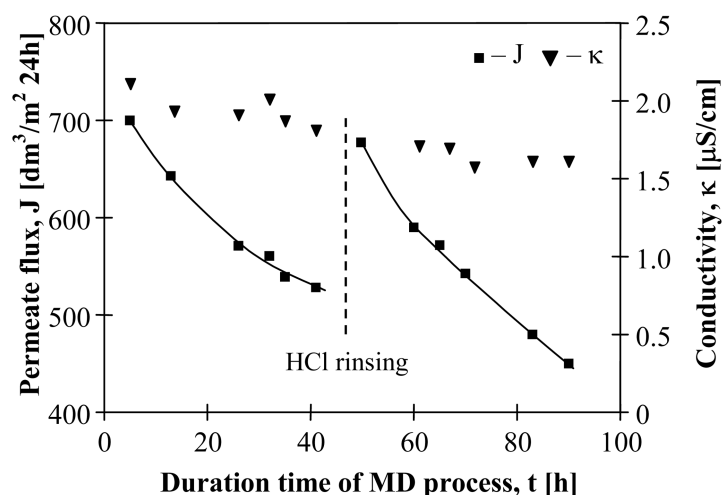


Fig. 4 Changes the permeate flux and electrical conductivity of the distillate obtained during the MD process of tap water. Module MK1

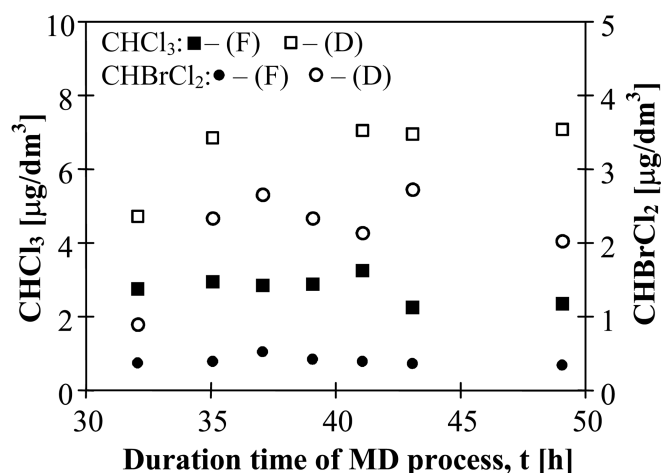


Fig. 5 Changes the THMs concentrations in the feed (F) and distillate (D) during the MD process of tap water

3.2. Membrane scaling

A sharp decline of the permeate flux was observed during MD process of tap water (Fig. 4). An increase of solute concentration in the feed (Fig. 3) caused a reduction of water vapour partial pressure. However, as was reported in the previous studies, the precipitation of CaCO_3 on the membrane surface was the major reason of the observed flux decline during the purification of tap water by MD process (Gryta 2008c, Karakulski, *et al.* 2002). Despite of dosing a new portion of tap water it was found that the increase of inorganic carbon content (mainly HCO_3^- ions) was stabilized at a level of 15-16 ppm (Fig. 3). This was associated with a continuous decomposition of the bicarbonates proceeding during the MD process operation. The initial flux was restored after module rinsing by HCl solution, what also indicated on the CaCO_3 precipitation.

The formation of crystallites on the membrane surface was confirmed by SEM observations. The structure of deposit formed during the treatment of tap water by MD process was shown in Fig. 6. The SEM-EDS analysis revealed that apart a large amount of Ca, this deposit also contained Mg, Si, S, Fe, Ni, Al and Na.

The deposit covered a part of the membrane surfaces, which reduced the membrane permeability and changed the temperature polarisation (Gryta 2007). The values of heat transfer coefficients in both liquid phases and the membrane have a dominant influence on the values of T_1 and T_2 temperature of surfaces adjacent to the membrane (Fig.1). The deposit layer creates an additional thermal resistance, thus decreasing the heat transfer coefficient from the feed bulk to the evaporation and condensation surfaces, and the temperature polarisation increased. As a result, the driving force for mass transfer was reduced and a significant decline of the permeate flux was observed (Gryta 2008a).

The adherence of the deposit to the membrane surface is a critical factor for MD performance, as well as for other membrane processes (Gryta 2008a, Gryta 2009). It was found, that the deposit of CaCO_3 on the membrane surface can easily be removed by rinsing the module with a 3 wt. % solution of HCl, what allowed to restore the initial permeate flux (Fig. 4). After acid rinsing the images of membrane surfaces were similar to that observed for a new membrane (Fig. 7). However,

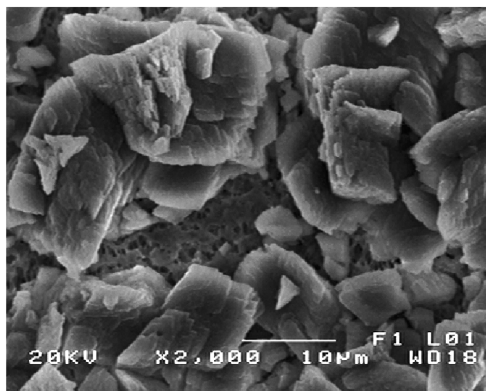


Fig. 6 SEM image of CaCO_3 deposit on the surface of the Accurel PP S6/2 membrane. Feed: tap water. Module MK1

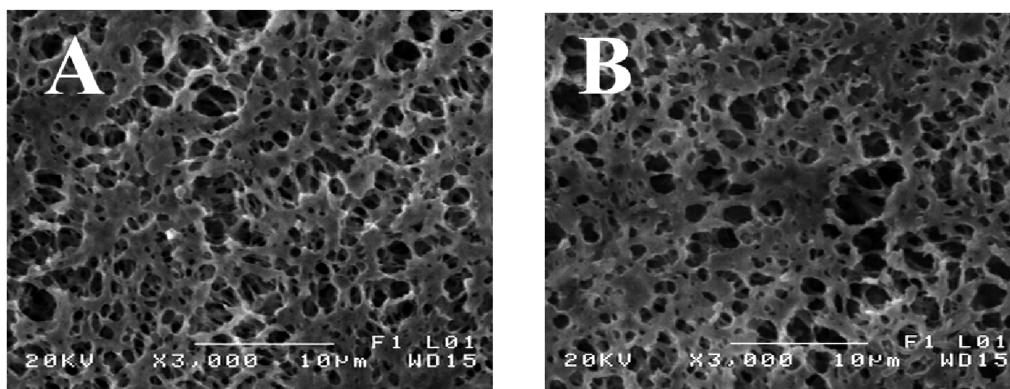


Fig. 7 SEM images the internal surface of Accurel S6/2 membrane. A) new, B) after rinsing by HCl solutions

the repetitions of module cleaning procedure by this method resulted in a gradual decline of the maximum permeate flux (Gryta 2008a). The SEM investigation of the membrane cross-sections revealed that the deposit covered not only the membrane surfaces but also penetrated into the pore interior (Fig. 8). The SEM-EDS line analysis of a change of the calcium content located into the membrane wall demonstrated that the deposit occurred up to the depth of 15-30 μm . Although, a rinsing acid solution dissolves the crystals, the wettability of the pores filled by deposit was accompanied to this operation. Therefore, the elimination of the scaling phenomenon is very important for MD process. The application of chemical water softening and the net filters (surface crystallization) allows to limit the amounts of precipitates deposited on the membrane surface during water desalination by MD process (Gryta 2008c).

The permeate flux constitutes only 2-3 vol.% of the feed stream flowing through the module in MD process. In order to achieve a higher degree of water recovery, the feed was recycled to the module during the MD process. Heating of the feed causes a decomposition of bicarbonates present in the water and the supersaturation state is achieved inside the heat exchanger. Therefore, a combination of the thermal water softening with crystallization during heating of the feed seems to be a good solution. Performed investigations revealed that a significant amount of CaCO_3 was deposited

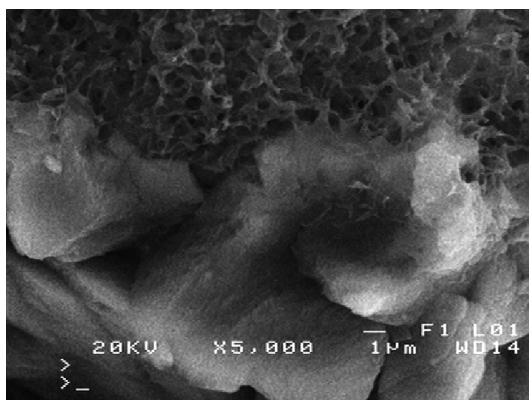


Fig. 8 SEM image of the cross section of membranes covered by the deposit formed during the MD of tap water. Module MK1

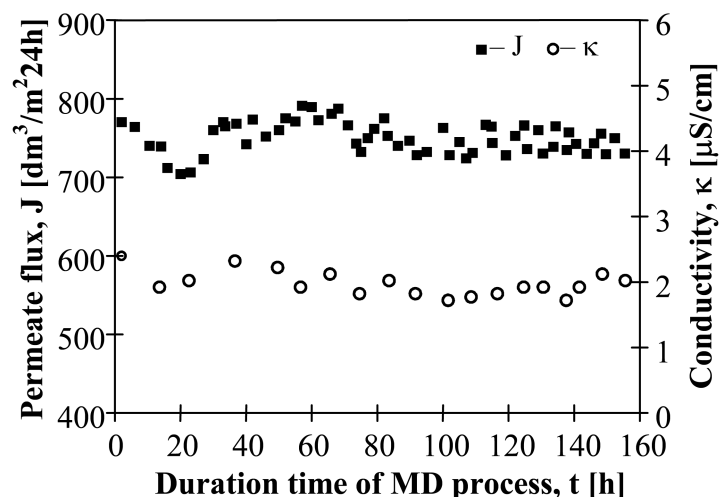


Fig. 9 Changes of the permeate flux and electrical conductivity of the obtained distillate during the long-term MD investigations. Feed: tap water. Module MK2

on the walls of the feed tank, filter surfaces and heating pipes. The total surfaces of these elements were 4-fold higher than that of the membrane in MK1 module, and the residue time of the feed in the feed tank was 3 min. However, in this case a decrease of CaCO_3 saturation rate during the feed heating was not enough effective, and the crystallites were also deposited on the membrane surfaces inside the MK1 module (Figs. 6 and 8). Probably, the residue time and surface of heterogeneous crystallization were too small.

In order to improve the conditions of CaCO_3 crystallization in the MD installation, a new feed tank and MK2 module were used. In this case the residue time was longer than 10 min, and the membrane area was 15-fold smaller than the surface of the filters and the walls in the feed tank. The obtained results of the long-term MD process investigations were presented in Fig. 9. During the consecutive 160 h of MK2 module operation the permeate flux was constant, and the obtained distillate was pure water with the electrical conductivity below 2 $\mu\text{S}/\text{cm}$. The SEM observation

confirmed that the majority of the membrane surface was free of deposit, and the CaCO_3 crystallized only in the vicinity of the module inlet (Fig. 10). For this reason the decrease in the permeate fluxes for the MK2 module was significantly smaller than that observed for the MK1 module (Fig. 4).

During the investigations carried out with MK2 module, it was found that a significant amount of deposit was precipitated on the surfaces of filters and walls of feed tank. The SEM observations indicated that the deposit has the structure similar to that presented in Fig. 11. However, the scale was also deposited inside the feed tank during the MD investigations with MK1 module, and the permeate flux decline was faster in this case. This confirmed that used process conditions determined the effects of thermal softening process coupled with heterogeneous crystallization. Moreover, it was found that the presence of the formed crystallites also accelerated the rate of calcium carbonate (CaCO_3) deposition. The calcium content in the concentrating feed was significantly lower when the surface of feed tank was covered by deposit (Fig. 12, after 6 h of MD process) in comparison to the results obtained for MD investigation carried-out in the installation with clean feed tank surface (after MD installation rinsing with HCl solution).

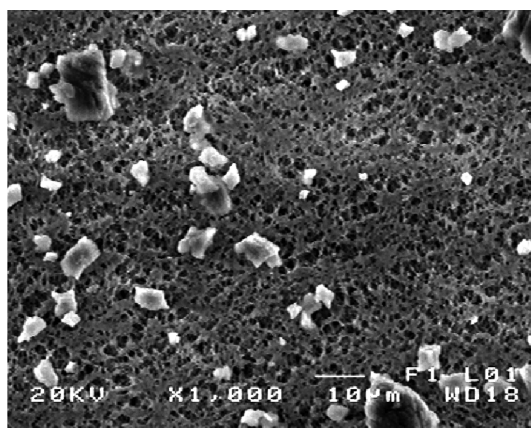


Fig. 10 SEM images of calcium carbonate scale deposited on the membrane surface in the vicinity of the MK2 module inlet

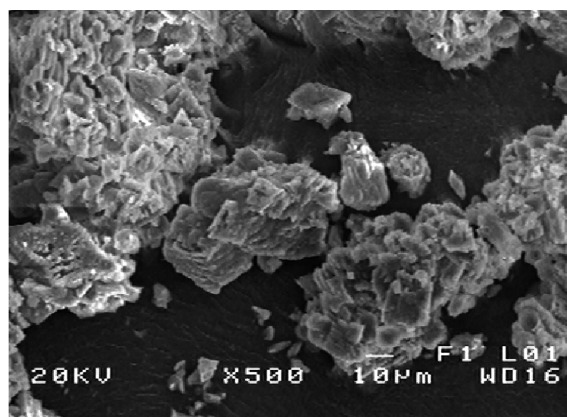


Fig. 11 SEM images of calcium carbonate scale deposited inside the net filter

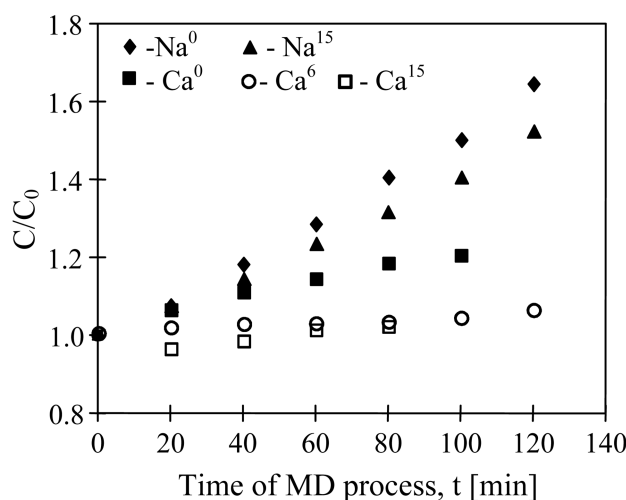


Fig. 12 Changes of ions content in the feed during MD process. Subscripts: 0 - MD installation without deposit (after rinsing with HCl solution); 6 and 15 - MD installation after 6 and 15 hours separation of tap water, respectively

4. Conclusions

The quality of obtained MD distillate was stable and practically independent on the feed concentration. The produced distillate has the electrical conductivity in the range 1.5-2.0 $\mu\text{S}/\text{cm}$ and the content of total organic carbon was below 0.5 ppm. The volatile organic compounds diffuse from the feed to distillate (similarly to water vapour), therefore, they cannot be completely removed in the MD process.

The experimental results indicate that the thermal pre-treatment of feed (connected with CaCO_3 crystallization) allowed to enhance the stability of the MD process run in a significant degree. The amount of HCO_3^- ions was reduced during the feed heating, what increases the supersaturation state. A heterogeneous crystallization performed inside a feed tank decreased the saturation ratio, and as a result, the amount of deposit formed on the membrane surface was also reduced.

Acknowledgements

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