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Performance evaluation of blended PVDF membranes for desalination of seawater RO brine using direct contact membrane distillation

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ABSTRACT

This paper assesses the feasibility of further desalination of seawater reverse osmosis (SWRO) brine by direct contact membrane distillation (DCMD) process using novel blended polyvinylidene fluoride (PVDF) membranes. Blends of PVDF homopolymer (HP; Solef® 6020, Solvay), as a core polymer, with PVDF copolymer (CP; Solef® 21510, Solvay) and N-methyl-2-pyrrolidone (NMP) as a solvent were used at two PVDF concentrations and various CP/HP ratios to prepare flat sheet membranes using the non-solvent induced phase separation (NIPS) method. The average porosity of membranes was found 42% and 46% when the PVDF concentration of the dope solution was 20 and 25 wt%, respectively. At lower values of CP/HP ratio, no clear trend of porosity changes was observed; however, the higher values of CP/HP ratio improve the porosity of the membranes. With distilled water as a feed, the permeate water flux of prepared membranes decreased from 2.9 to 1.6 kg/m^2.h when the PVDF concentration increased from 20 to 25 wt%, respectively. For the commercial PVDF membrane, the permeate water flux achieved was 17.5 kg/m^2.h at cross flow velocity of 0.25 m/s and was almost doubled when the cross flow velocity increased to 0.75 m/s. The water flux was almost reduced by half when SWRO brine was used as feed instead of pure water for both the prepared and commercial membranes. The flux performance efficiency of the MD system was evaluated and was found to be an appropriate indicator of the temperature polarization.

Keywords: Direct contact membrane distillation; PVDF membranes; PVDF blending; Seawater RO brine desalination; Temperature polarization

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1. Introduction

Membrane distillation (MD) is a thermally driven desalination process where a hydrophobic porous membrane is used as a barrier between a high vapor pressure feed solution and low vapor pressure permeate. The unique feature of MD is that it can be driven by a relatively low temperature heat source, which makes MD an excellent choice for use with solar thermal energy, as in case of off-grid remote locations, or in situations where low-grade thermal energy is available, as in case of multi-stage flash (MSF) and multi-effect distillation (MED) desalination plants [1,2]. The recent drive toward renewable energy resources and energy efficiency improvement of MSF plants through utilization of the exergetic content of MSF reject stream has created increasing demand for desalination processes that can utilize low-grade thermal energy, and MD fits this description nicely [3,4]. Moreover, the inherently lower susceptibility of MD to membrane fouling and scaling, in particular, allows it in principle to operate on concentrate streams of other membrane processes [5–7]. These features combined create a very attractive potential for using MD to increase both the overall recovery ratio and overall energy efficiency of existing and new MSF/MED desalination plants. The desalted water recovery ratio of MSF and MED desalination plants is basically low due to inherent operational limitations of the core components in the plants. Various options such as hybridization with other desalination processes have been suggested to increase the desalted water recovery ratio and thus improving the economic performance of the plants [8]. The MD process is capable of treating streams with high TDS content such as reverse osmosis (RO) concentrate discharge. For the inland brackish groundwater RO plants, where brine disposal is a major challenge, any improvement of the overall water recovery ratio of the plant translates into a minimization of RO brine quantities, thus lessening negative environmental impacts associated with the brine disposal [9,10].

The focus of the continued research on MD process is to improve the permeability (productivity) and durability of MD membranes. Both characteristics are closely related to the membrane material and structure. It has been shown that the membrane permeability is a function of overall porosity, pore size and morphology, membrane thickness and pore size distribution [11]. Basically, the porosity can be increased either by controlling the concentration of polymer in the dope solution [12] or by using pore forming additives such as polyvinylpyrrolidone (PVP), polyethersulfone (PES), polyethylene glycol (PEG) and ethylene glycol (EG) [13–17].

The durability of the membrane is related to its operational characteristics such as liquid entry pressure (LEP), fouling resistance and chemical, thermal and mechanical stability, which depend on a set of physical and chemical properties of the polymer, additives and solvent such as viscosity, polymer molecular weight, surface energy, and thermal conductivity. Fouling resistance of polymeric membranes is enhanced through the incorporation of silver and cobalt nanoparticles in the membrane matrix at the membrane preparation process [18–20]. High viscosity ensures good mechanical strength of the membrane. The viscosity of casting solutions can be improved by blending low with high molecular weight polymers in correct proportion or by increasing the polymer concentration [21–23]. Hydrophobic materials with low surface energy and low thermal conductivity, such as polypropylene (PP), polytetrafluoroethylene (PTFE), polyvinylidenefluoride (PVDF) etc., were used to fabricate MD membranes [13,24,25]. Recently, the PVDF polymers have been extensively used for preparing membranes suited for different MD process applications due to its favorable mechanical and physicochemical properties [11,23]. Many PVDF polymers with different properties such as molecular weight and degree of linearity are available in the market. It can be expected that membranes made from blends of different PVDF polymers will have different structural and performance properties. The focus of recent research efforts is toward improving the structural and performance characteristics of PVDF membranes through the selection of a polymer with proper molecular weight, blending of different polymers at a right blending ratio, blending with non-solvent additives and optimizing parameters of dope solution preparation and casting/spinning [26–28].

This research work was undertaken to assess the feasibility of further desalination of SWRO brine using direct contact membrane distillation (DCMD) process. The performance of lab-made blended PVDF membranes and one commercial MD membrane (Durapore, Merck Millipore) was evaluated. The effect of feed flow cross velocity on the membrane performance was established using distilled water and SWRO brine as feed solutions. A new approach for the evaluation of temperature polarization in the MD system is described as well.

2. Experimental methodology

2.1. Materials

The PVDF ultra-high molecular weight (Mw) homopolymer (HP), Solef® 6020, Mw 670–700 kDa, and the PVDF medium molecular weight copolymer (CP), Solef® 21510, Mw 290–310 kDa were provided by Solvay Specialty Polymers Italy S.p.A. Solvent N-methyl-2-pyrrolidone (NMP) was purchased from Sigma-Aldrich, Germany. The commercial PVDF membranes were obtained from Merck Millipore, Germany.

2.2. Membrane preparation

Six blends of the HP PVDF Solef® 6020 with the CP PVDF Solef® 21510 and NMP as a solvent were prepared in selected concentrations to fabricate flat sheet membrane samples using the non-solvent induced phase separation (NIPS) technique. Table 1 shows the composition of dope solutions of the prepared membrane samples (B1–B6). Prior to preparing the casting solution, the polymers in powder form were dried for 24 h at 60°C in a vacuum oven to disregard moisture contents. The solutions were prepared using a closed heating technique assisted with high-speed magnetic stirrer at a temperature of 85°C for 12 h. The dope solution was then left for 3 d to allow any bubbles to escape. The casting was done at room temperature (25°C) by pouring the dope solution onto a smooth glass plate (35 × 25 cm) of a motor-driven film applicator unit (Erichsen Unicoater 409, Germany). All blends were cast using casting knife with 400 μm casting depth. Immediately

Table 1
Composition of dope solutions of blended PVDF polymers with NMP as a solvent (casting depth 400 μm)

Blend S. No.	Total PVDF concentration of dope solution, wt%	Composition of dope solution, wt%			CP/HP, %
		Homopolymer (HP) (Solef® 6020)	Copolymer (CP) (Solef® 21510)	NMP	
B1	20	18	2	80	11
B2	20	16	4	80	25
B3	20	14	6	80	43
B4	25	20	5	75	25
B5	25	18	7	75	39
B6	25	15	10	75	67

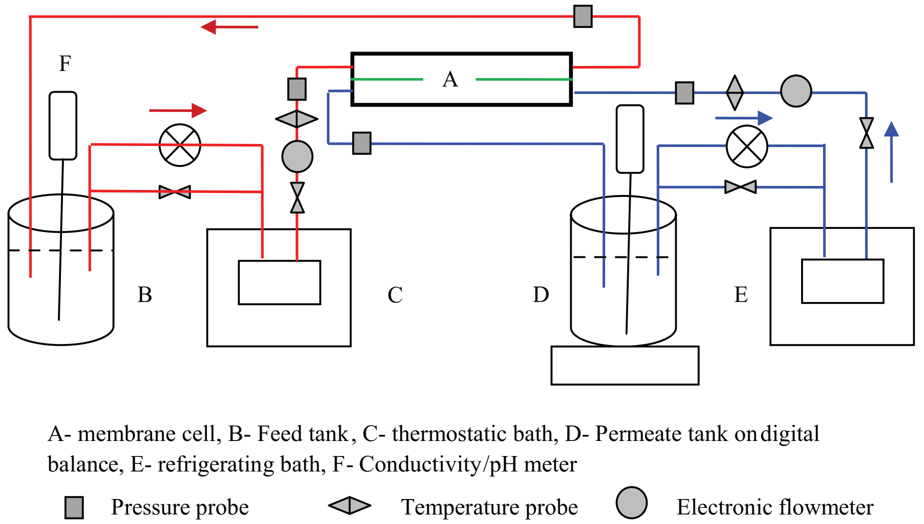

Fig. 1. Experimental setup used for DCMD tests.

after casting, the membrane was immersed in a cold water bath (5°C) with isopropanol added (water/isopropanol ratio 7:3) for 1–2 min, until the membrane was released from the casting glass plate. The membrane was then treated in washing bath for 15 min at 9°C. After washing, the membrane was annealed for 0.5 h at 70°C in water, and then it was washed in a water and glycerin bath for 15 min. The membranes were oven dried at 60°C for 1 h.

2.3. Experimental setup for DCMD experiments

The experimental setup used for carrying out the DCDM performance tests is shown schematically in Fig. 1. This is a bench-scale custom-made setup fabricated by DeltaE S.r.l., Rende, Italy. The setup consists of two flow loops for the feed water (hot side) and the permeate water (cold side), where as each loop has identical process components and controls, which include a gear pump, a thermostatic bath, and a tank. The feed water and the permeate recirculate into the feed and permeate tanks, respectively. The feed solution was pumped through a coil placed in the thermostatic bath prior to entering the membrane cell. A membrane segment with an effective area of 50 cm^2 was placed into the membrane cell. Distilled water was used as a condensing fluid for the permeate vapor. The temperature of the condensing fluid was controlled by a refrigerating circulator with a digital controller (PolyScience, Niles, IL, USA). An electronic balance (accuracy 0.1 g) was used to measure continuously the weight of the permeate condensing fluid tank. The pH and conductivity values of the fluids were observed using two pH and two conductivity meters. Digital flow meters and temperature and pressure sensors were used for observing the values of the process parameters. All measurement instrumentations were connected to data acquisition system and a computer, and the data was recorded every minute.

2.4. DCMD experiments

Four sets of experiments were conducted to evaluate membrane flux of the PVDF membranes fabricated at the laboratory and the commercial MD membranes. Table 2 shows the purpose of each set and the details of process parameters. Pure water, pretreated seawater and seawater RO brine were used as feed fluids. The pure water was produced by an RO lab system (Purelab Option SR-7, Elga Veolia, UK) and was used for the preparation of the solutions and also for coagulation bath. The pretreated seawater and seawater RO brine feeds were obtained from RO desalination plant located on Jeddah Red Sea coast, owned by Water and Environmental Services Company (WESCO). The volume of the feed water at the start of each experiment was kept at 2 l. The duration of each experiment was 3 h. At the end of each experiment,

Table 2
Details of DCMD experiments

Experiments	Purpose	Process parameters			
		T_f, °C	T_p, °C	Q_f, l/min	Q_p, l/min
Set #1	DCMD testing of lab-made PVDF membranes using pure water as a feed	70	20	1.7	1.9
Set #2	DCMD testing of selected lab-made PVDF membranes using SWRO brine as a feed	55	20	1.2	1.2
Set #3	Studying the effect of feed cross flow rates on the performance of commercial PVDF membranes using pure water as a feed	70 70 70	20 20 20	1 1.6 3	1.8 1.8 1.8
Set #4	Studying the effect of feed cross flow rates on the performance of commercial PVDF membranes using SWRO brine as a feed	56 56 56	20 20 20	1 2 3	1 1 1

Note: T_f = Feed temperature, T_p = permeate temperature, Q_f = feed cross flow rate, Q_p = permeate cross flow rate.

the setup was flushed, and the membrane was cleaned thoroughly with fresh water. Based on the geometry of cross-sectional area of feed (or permeate) channel of the membrane cell, the cross flow rate of feed (or permeate) of 1 l/min corresponds to a cross flow velocity of approximately 0.25 m/s.

The change in weight of the permeate tank represents the weight of condensed water vapor flux through the membrane, *W*, collected over the time of the experiment, *t*. Water flux, *J*, was calculated using the following mass flow rate equation:

$$J = \frac{W}{t \cdot A} \tag{1}$$

where *A* is the membrane sample area, m^2.

2.5. Membrane porosity

Three circular pieces were cut from each membrane sheet with a radius of 20 mm each and soaked in kerosene for 24 h. The weights of membrane pieces before and after soaking were recorded. The blended membrane overall porosity, ε, refers to the ratio of the volume of the pores in the membrane structure to the total volume of the membrane and can be calculated as follows:

$$\varepsilon = \frac{(W_W - W_d)/\rho_k}{\left((W_W - W_d)/\rho_k\right) + (W_d - \rho_p)} \tag{2}$$

where W_w is the weight of wet membrane (g); W_d is the weight of dry membrane; ρ_p is the density of polymer mixture (g/cm^3); and ρ_k is the density of kerosene (g/cm^3). The density of polymer mixture is calculated by the inverse rule of mixtures [29] as follows:

$$\frac{1}{\rho_p} = \frac{f_{hp}}{\rho_{hp}} + \frac{f_{cp}}{\rho_{cp}} \tag{3}$$

where f_{hp} and ρ_{hp} are the weight fraction and density of the HP, respectively, and f_{cp} and ρ_{cp} are the weight fraction and density of the CP, respectively.

3. Results

3.1. Physicochemical characteristics of pretreated seawater and SWRO brine

Seawater pretreatment at WESCO RO plant is realized by a hybrid pretreatment system consisting of a conventional dual media filtration (DMF) in conjunction with a dissolved air flotation (DAF). This system was proven to produce RO feed water with acceptable and stable quality. The SWRO brine samples were collected from the outlet of RO units. Both types of samples were analyzed for physicochemical properties (Table 3).

3.2. Effect of dope solution composition on porosity

Initially, the casted membranes were coagulated in a water bath without the addition of isopropanol. It has been noticed that the membranes possessed uneven surface, characterized by intercrossed valleys and hills type corrugations. The occurrence of this uneven surface could be related to the wide difference between the porosity and thickness of the skin layer of the membrane and the porosity and thickness of the membrane substructure. The high affinity of NMP for water results in an instantaneous demixing process, which produces a membrane with a highly porous substructure (with macrovoids) and a finely porous, thin skin layer. Due to porosity differences, the shrinkage of the skin layer will be larger than that of the membrane substructure layer. However, with the addition of isopropanol into the coagulation bath, the rate of demixing is decreased, and a dense and thick skin layer will be formed. Subsequently, the surface morphology of the membrane becomes smooth and even. Similar observations have been reported by Rashid et al. [30] who studied the effects of the addition of different types of non-solvents such as isopropanol, ethanol and methanol in the coagulation bath on the morphology of membranes.

The trends of change of membrane porosity in response to the changes of dope solution compositions are shown in Fig. 2. The porosity of the prepared membranes varied in a narrow range between 41% and 46% when the PVDF blend concentration increased from 20% to 25% as shown in Fig. 2.

Table 3
Physicochemical properties of pretreated seawater and SWRO brine

Property	Pretreated seawater	SWRO brine
pH	7.97	7.74
Conductivity, mS/cm	59.5	85
TDS, mg/l	36,720	55,390
Salinity, ppm	39.8	60
TOC, ppm	2.8	8.1
Fluoride, ppm	4.8	8.5
Chloride, ppm	21,676	32,843
Bromide, ppm	79	122
Sulfate, ppm	3,088	4,829
Sodium, ppm	12,237	18,799
Potassium, ppm	409	624
Magnesium, ppm	1,456	2,278
Calcium, ppm	550	692
Strontium, ppm	8.96	13.3

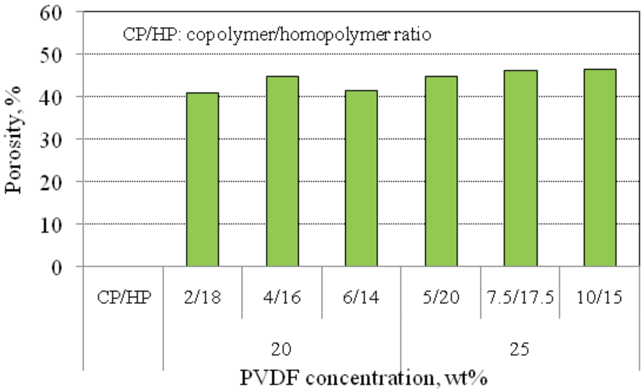

Fig. 2. Effect of total PVDF concentration and blending ratio on membrane porosity with NMP as a solvent.

There is no clear trend in porosity changes at the lower values of the CP/HP ratio. However, the higher values of CP/HP ratio improve the porosity of the membranes. The average porosity of membranes prepared with a PVDF blend concentration of 20% (B1–B3) is 42.4%, which is lower than the porosity of membranes prepared with a PVDF blend concentration of 25% (B4–B6, average porosity 45.9%). On the first judgment, this would be regarded as unexpected result. However, when by examining the CP/HP ratio at both levels of the PVDF blend concentration, it could be seen that the CP/HP ratio is higher at the 25 wt% level (Table 1), i.e., at the higher PVDF blend concentration the CP is present at a higher percentage relative to the HP. Due to this reason, the porosity of the membranes increased at the 25 wt% PVDF blend concentration. Membranes prepared by CPs, which are basically low molecular weight polymers, have high porosity compared with high molecular weight polymers [22].

The kinetics of membrane formation by the phase inversion method is influenced, among other factors, by the viscosity of the dope solution. With the increase in the viscosity of the dope solution, the miscibility of the solution is reduced, and therefore, the solution thermodynamic stability is enhanced, which means that less porous membranes are obtained. Besides the temperature of the dope solution, the polymer concentration and the polymer molecular weight are identified as the key parameters that control the viscosity of the dope solution. For a single polymer dope solution systems, higher polymer concentrations and higher polymer molecular weights result in a higher viscosity of dope solution and hence a lower porosity values of the membranes [31]. Blending of polymers of different molecular weight can be regarded as a mean for viscosity control of dope solution and subsequently porosity control of the casted membrane. When the casting solution is prepared from a blend of polymers of different molecular weight, the viscosity will depend not only on the total concentration but also on the ratio of different components of the system. Initially, it has been observed that blending ultrahigh molecular weight PVDF HP with medium molecular weight PVDF CP reduces the viscosity of the dope solution and improves the mechanical properties of the membranes. The dope solutions prepared with single polymer Solef® 6020 of concentrations 20 and 25 wt% were too viscous for easy casting of membranes at room temperature. However, by blending Solef® 6020 with Solef® 21510, it became possible to cast membranes with a total polymeric concentration of 20 and 25 wt% at room temperature. Chen et al. [21] have found that the porosity of PVDF composite membrane consisting of high molecular weight PVDF (1,367 kDa) and low molecular weight PVDF (410 kDa) varied between 25% and 28% when the mixing ratio of high molecular weight PVDF to low molecular weight PVDF was varied between 4:6 and 8:2. However, high porosity values of 80% and 85% were reported for membranes prepared with PVDF bends, composing of medium and high molecular weight PVDF polymers [23]. When considering the previous research [21–23] and this work, it could be concluded that the interactions between polymer molecular weight, polymeric concentration of dope solution and blending ratio control the porosity of blended membranes. Hence, the selection of appropriate values of these parameters is an important step in preparing good blended membranes.

3.3. Effect of dope solution composition on permeate flux

Pure water was used as a feed for performing DCMD tests for all membrane samples (Fig. 3). Increasing the total polymeric concentration of dope solution has negative effects on porosity and subsequently on water flux. When the polymeric concentration of dope solution varied from 20 to 25 wt%, the water flux decreased from 2.9 to 1.6 $kg/m^2.h$, respectively.

At any given level of polymeric concentration, water flux values for various blends are comparable with insignificant variations, i.e., varying the CP/HP ratio did not bring about significant changes in water flux. This does not imply that the morphology of membranes and their mechanical properties will remain similar. Blending ratios and casting conditions play a determinant role in defining properties of produced membranes. Recently, Figoli et al. [23] have observed that membrane morphology, both surface and cross-sectional, and membrane properties such as thickness, porosity, and

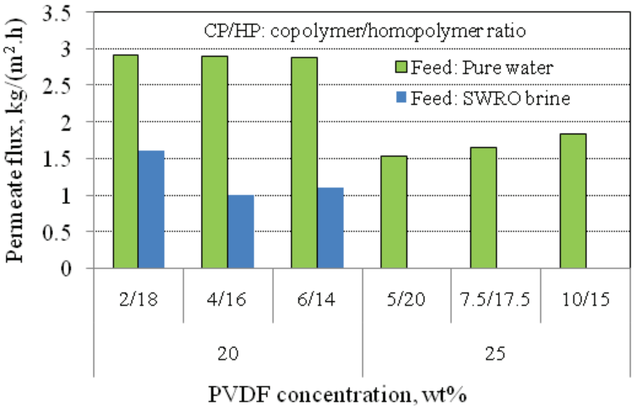

Fig. 3. Effect of total PVDF concentration and blending ratio on permeate flux.

pore size strongly depend not only on polymer properties but also on the composition of the polymeric dope and coagulants.

The permeate flux values achieved by the prepared membranes is low compared with the published results for many membranes prepared from a single PVDF polymer or PVDF blend with additives. Most of the published work on PVDF blending is related to the use of various types of additives such as hydrophilic polymers, weak non-solvents, weak cosolvents and inorganic salts in the fabrication of PVDF membranes. However, to the best of our knowledge, only two papers on blending of different types of PVDF polymers at various blending ratios have been published so far [21,23]. Generally, PVDF blends consisted of a low molecular weight polymer and a high molecular weight PVDF polymer. The underlying principle of blending is to produce a membrane, which combines the expected properties of membranes if they were prepared with the single polymers alone. As the work on PVDF blending is yet emerging, large deviations in results were noticed from work to another work. Table 4 compares the main structural properties of the membranes and their performance under MD process. By comparing the permeate flux values achieved by the prepared membranes with the values shown in Table 4, it could be seen that these values are falling in the range of the reported values.

3.4. Effect of feed water type on water flux

Tests with SWRO brine as a feed were carried out only for membranes prepared with a total polymer concentration of 20 wt%, i.e., blends B1, B2 and B3 (Fig. 3). With SWRO brine as a feed, the average water flux for the three membranes was found as 1.2 kg/m^2.h compared with a value of 2.9 kg/m^2.h when pure water was used as a feed (i.e., a reduction of 57%). The high salinity of feed solutions affects permeate flux more severely than low salinity does [32], and also the permeate flux decline with time is more obvious in the case of treating feeds of high salinity [33]. Martinez [32] attributed the reduction of the permeate flux to the decrease in water activities due to high salt concentration and the buildup of a saturated boundary layer on the membrane surface.

3.5. Effect of feed cross flow rate on water flux and MD system flux performance efficiency

Commercial PVDF membranes having a pore size of 0.22 μm (Durapore, Merck Millipore) were used to compare the performance of DCMD process when pure water and seawater RO brine are used as feed under varied transmembrane temperature gradients and cross flow rates. Figs. 4 and 5 show the pattern of permeate flux with time at three different feed cross flow rates and under constant feed and permeate temperatures and constant permeate cross flow rate when pure water and SWRO brine were used as feed, respectively. Both figures show that the patterns of permeate flux initially have lower values before steady state is established after elapse of a certain time, which was approximately between 40 and 60 min from the start of each test. In tests with pure water as feed, the steady state permeate flux values were found as 17.5, 26.1 and 38 kg/m^2.h for feed cross flow rates of 1, 1.6 and 3 l/min, respectively (Fig. 4). This means that by increasing the feed cross flow rate by three times the permeate flux approximately doubled (117%). The values of the steady state permeate flux were noticeably lower when the SWRO brine was used as a feed and were varied between 11.2 and 14 kg/m^2.h when the feed cross flow rate increased from 1 to 3 l/min, respectively (Fig. 5). Also, Fig. 5 indicates that the response of the permeate flux to the changes in feed cross flow rates is weak when saline

Table 4
Membrane properties and DCMD performance of PVDF blend membranes

PVDF polymers and concentration, wt%	Additives and concentration, wt%	Solvent type and concentration, wt%	Porosity, %	Pore size	MD process type	Permeate flux, kg.m^{-2}.h^{-1}	Ref.
Kynar 740/HSV900, 9%/6%	H_2O, 1.25%	DMAC, 83.75%	27.7	0.033	VMD pure water	0.692	[21]
Solef® 6012/Solef® 6020, 10%/5%	H_2O/PVP K-17, 6%/15%	NMP, 64%	84	0.28	VMD pure water	22	[23]
Solef® 6012/Solef® 6020, 10%/5%	H_2O/PVP K-17, 6%/15%	NMP, 64%	84	0.28	VMD seawater	19	[23]
Solef® 6012/Solef® 6015, 10%/5%	H_2O/PVP K-17, 6%/15%	NMP, 64%	79	0.34	VMD pure water	27	[23]
Solef® 6012/Solef® 6015, 10%/5%	H_2O/PVP K-17, 6%/15%	NMP, 64%	79	0.34	VMD seawater	22	[23]

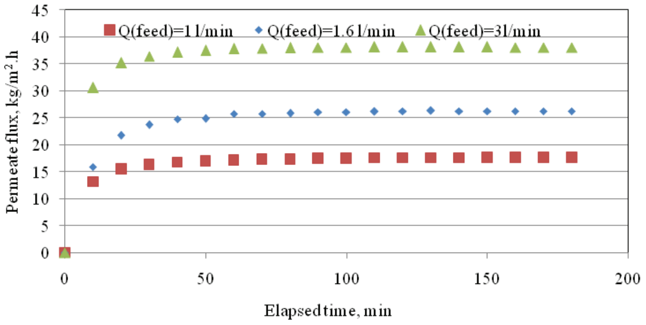

Fig. 4. Profiles of permeate flux at different feed cross flow rates (type of feed water: pure water).

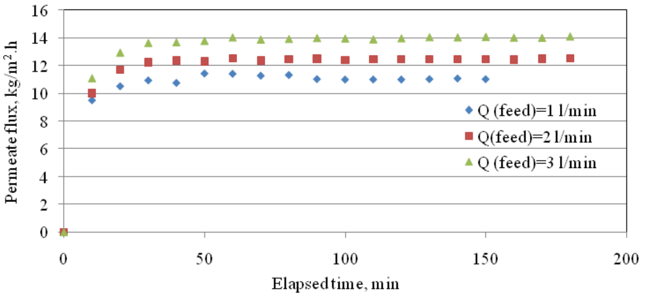

Fig. 5. Profiles of permeate flux at different cross flow rates (type of feed water: SWRO brine).

feed is used since the increase of permeate flux when feed cross flow rate increased by three times was just 25% more than its baseline value.

The flux performance efficiency of the MD system is related to the magnitude of temperature polarization (TP) prevailed in the system at the given operation conditions. Due to the characteristic mechanism of heat and mass transfer from the hot feed side to the cold permeate side across the MD membrane; the temperature at the membrane-liquid interface is not equal to the temperature in the bulk of the liquid. On the feed side the temperature in the bulk of the liquid is higher than the temperature at the membrane surface, while on the cold side the temperature in the bulk of the liquid is lower than the temperature at the membrane surface. The temperature variation in the zone near the membrane surface is called temperature polarization and is responsible for diminishing the efficiency of the MD process since it reduces the overall driving force for vapor transfer from the feed side to the permeate side. The temperature polarization coefficient was adopted to quantify the temperature polarization effect. This coefficient is defined as the ratio of the transmembrane temperature gradient, which effectively induces vapor transfer, to the difference between the temperatures of the feed and permeate bulk streams [34], i.e.:

$$E = \frac{\Delta T_m}{\Delta T_b} = \frac{T_{fm} - T_{pm}}{T_{fb} - T_{pb}} \tag{4}$$

where T_{fm} and T_{pm} are the temperatures at the membrane surface on the feed side and permeate side, respectively, and T_{fb} and T_{pb} are the feed and permeate bulk temperatures, respectively. Different models based on the heat balance principle were suggested to calculate the TPC [35]. Complex equations were derived to calculate T_{fm} and T_{pm} because the actual temperatures at the membrane surface on feed and permeate sides of the membrane cannot be measured by practical means [36]. An alternative approach to evaluate TPC was suggested using the ratio of the actual driving force inducing the vapor transfer to the overall driving force that would be potentially available under ideal conditions [37,38].

In this work, the ratio of the measured vapor flux to the potential vapor flux has been suggested as a measure of the performance efficiency of the MD system as well as an indicator of the TPC of the MD system. Similar approach was adopted by Bouguecha et al. [39] to calculate the permeability coefficient of an MD system. Obviously, the measured vapor flux indicates the effective temperature difference across the membrane, i.e., the actual values of T_{fm} and T_{pm}. The vapor flux would be at its maximum value if the temperatures at the membrane surface on the feed side and permeate side approached the corresponded feed and permeate bulk temperatures, i.e., when $T_{fm} = T_{fb}$ and $T_{pm} = T_{pb}$. In this case, the vapor flux will be limited only by the membrane mass transfer coefficient. Based on the approach described above, the TP could be assessed using the MD flux performance efficiency defined as follows:

$$E_p = \frac{Q_e}{Q_{\max}} \tag{5}$$

where Q_e is the measured vapor flux (kg.m^{-2}.h^{-1}), and $Q_{\max}$ is the maximum vapor flux (kg.m^{-2}.h^{-1}).

The vapor transfer across the porous MD membrane is induced by the saturated vapor pressure drop between the hot side and the cold side of the membrane and can be estimated using a linear equation as follows [40]:

$$Q_{\max} = C(P_{fb} - P_{pb}) \tag{6}$$

where C is the MD coefficient, and P_{fb} and P_{pb} are the saturation vapor pressure of pure water at the membrane surface on the feed and permeate side, respectively.

The saturated vapor pressure can be determined using the Antoine equation for pure water [34]:

$$P_w = \exp\left(23.1964 - \frac{3816.44}{T - 46.13}\right) \tag{7}$$

where T is the temperature at the membrane surface (K). For saline feed, the calculated value of the saturated vapor pressure should be adjusted to account for the molar fractions of water and the solute as follows [34]:

$$P_f = \chi_w (1 - 0.5\,\chi_s - 10\chi_s^2) P_w \tag{8}$$

where χ_w and χ_s are the molar fractions of water and the solute in the solution, respectively. Phattaranawik et al. [37] have found that the MD coefficient, C, is not affected by the cross flow rates and process temperatures and could be regarded constant for the given MD membrane, and they have reported a value of 3.459 × 10^{-7} kg m^{-2} s^{-1} Pa^{-1} for the MD coefficient for a PVDF membrane manufactured by Millipore having pore size of 0.022 μm. This value was adopted for the evaluation of TP in the MD membrane cell since the membrane used is similar.

Based on the approach described above, the MD flux performance efficiency values were calculated for varying feed cross flow rates for both distilled water and SWRO brine as feeds and are presented in Fig. 6. The pattern of change in the values of flux performance efficiency indicates that the feed cross flow rate is affecting both the hydrodynamic and thermodynamic conditions of the boundary layer, which in turn effectuate temperature polarization in the system. As a result, the performance efficiency improves with the increase in the feed cross flow rates. The calculated values of the flux performance efficiency for the distilled water were found as low as 0.36 when the feed cross flow rate was 0.6 l/min and approached 0.92 when the feed cross flow rate was 3 l/min. Elevated feed cross flow velocity increases the turbulence in the bulk of the stream, thus decreasing the thickness of the laminar boundary layer on the membrane surface. The reduced thickness of the boundary layer reduces the temperature difference between the bulk of feed and membrane surface, which results in increasing the temperature gradient across the membrane. The interaction between flow turbulence and temperature polarization was also observed by Phattaranawik et al. [37] who found that the temperature polarization coefficients for laminar flow varied between 0.50 and 0.60 and for turbulent flow varied between 0.94 and 0.95.

The values of flux performance efficiency for the SWRO brine are found lower than the pure water especially at higher feed cross flow rates (Fig. 6). In case of saline feeds, the negative effects of temperature polarization are accumulated by the negative effects of concentration polarization as well. In fact, the boundary layer near the membrane surface has a higher salt concentration than the bulk of feed due to evaporation of water. The high salinity effects on density and viscosity, and subsequently on the Reynolds number value, as well as on the vapor pressure value, which render toward lower value, all augment negative effects of temperature polarization. The effects of high salinity on DCMD permeate flux was reported in several studies [34,41]. A decline of permeate flux of up to 40% was found when a concentrated salt solution (167 g NaCl/l) was used as a feed instead of distilled water [42]. The decline of permeate flux of 20% was observed in the case of desalting brines from thermal desalination plants having salinities above 70 g/l [36].

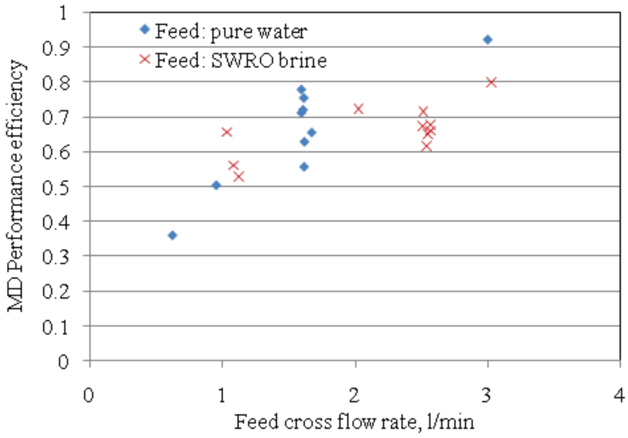

Fig. 6. Effect of feed cross flow rate on temperature polarization as expressed by the MD performance efficiency.

4. Conclusions

The feasibility of further desalination of SWRO brine through DCMD process using lab-made blended PVDF membrane as well as commercial membranes was assessed in this work. The lab-made flat sheet membranes were prepared by blending PVDF HP with PVDF CP at two different total polymeric concentrations of dope solution whereas for each selected polymeric concentration the ratio of the CP to the HP was also varied. The DCMD performance testing of the prepared membranes established the effects of polymeric concentration and blending and also the effects of cross flow rate for both pure water and SWRO brine.

The main conclusions of this work can be summarized as follows:

- Dope solutions having a higher concentration of HP PVDF alone are too viscous for easy membrane casting but when the HP PVDF was blended with the CP PVDF the dope solution becomes less viscous and the porosity of the membrane improves.
- At any given polymeric concentration of the dope solution, the variation of the CP/HP ratios causes only slight variation in water flux of blended membranes.
- Feeds with high salinity such as SWRO brine affect water flux severely. At any given set of operating conditions, the water flux when pure water was used as a feed is about twice higher than the water flux when seawater RO brine was used as a feed.
- Cross flow rate effects on water flux are more obvious when the salinity of feeds is low. However, at higher salinities, the increases in cross flow rate cause moderate variations in water flux.
- The flux performance efficiency defined by the ratio of the measured vapor flux to the potential vapor flux could be used as an indicator of the temperature polarization of the MD system.

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