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Direct contact membrane distillation for seawater desalination

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ABSTRACT

Membrane distillation (MD) is a non-isothermal membrane separation process. It is based on the phenomenon that pure water in its vapor state can be extracted from aqueous solutions, with vapor passing through a hydrophobic microporous membrane when a temperature difference is established across it. In this work, three commercially available hydrophobic microporous membranes were used for seawater desalination via direct contact MD. The effects of pertinent operating parameters on the permeation flux have been studied. A plate and frame module was used for seawater desalination. Long-term performance evaluation was carried out to evaluate the process as a stand-alone desalination alternative. The results indicated that polytetrafluoroethylene membrane had the best performance when a hot feed temperature of 80˚C with 800 ml/min flow rate was used. At optimum condition a 99.99% salt rejection was achieved.

Keywords: Seawater desalination; Direct contact membrane distillation (DCMD); Permeate flux; Hydrophobic membrane; Polarization

1. Introduction

The availability of potable water is a major problem in many regions of the world. Oceans contain about 97% of the world water, by volume, which is too salty for drinking, irrigation or industrial use. About 3% of the fresh water is available and suitable for mankind use. Therefore, growth of industries, agriculture and population through the world, and higher water demand led to increased shortage for fresh water resources [1–4].

Desalination is a process in which fresh water is extracted from saline solutions and is used to alleviate the water shortages [5,6]. Many methods have been used over the years for water desalination. These methods can be classified into various categories based on the driving force, such as thermal-, pressure- and electrical-potential driven processes. The thermally driven processes, e.g. multi-stage flash and multi-effect distillation, are the oldest and the most widely used on large scales, especially in the Persian Gulf region because of low cost for fossil-fuel based energy resources in this arid region. Reverse Osmosis (RO) is a relatively new membrane process with pressure difference driving force that is taking an increasing share of the world desalination capacity [4,5,7].

Membrane distillation (MD) is a non-isothermal membrane separation process. It is based on the phenomenon that pure water can be extracted from aqueous solutions by evaporation, with the vapour passing

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through a hydrophobic microporous membrane when a temperature difference is established across it. The temperature difference leads to a vapour pressure difference across the membrane. Due to hydrophobic nature of the membrane, only the vapor can pass across the membrane and the liquid solution could not pass [8,9]. It should be noted that in MD process the vapour pressure difference across the membrane is the driving force, which is quite different from the other membrane separation processes [8,10].

Based on the permeate side condition and configuration, MD systems can be classified in four modes [11]:

(a) Direct contact membrane distillation (DCMD) in which the membrane is in direct contact with two liquid streams.
(b) Vacuum membrane distillation (VMD) in which the permeate side is kept under vacuum and the generated vapour is drawn to a separate condenser.
(c) Sweeping gas membrane distillation (SGMD) in which a stripping gas is used as a carrier for the produced vapour and,
(d) Air-gap membrane distillation (AGMD) in which an air gap is interposed between the membrane and the condensation surface.

Qtaishat et al. [12] studied the fabrication of novel composite membranes that contain two host hydrophilic polymers, polyethersulfone and polyetherimide. The membranes fabricated by phase inversion technique. Several tests were conducted to characterize the membranes. DCMD apparatus was used in the desalination of 0.5 M sodium chloride solution. The performance of synthesized membranes was compared with a commercial polytetrafluoroethylene (PTFE) membrane. In another work, Dumeé et al. [13] developed a carbon nanotube-based composite membrane for DCMD desalination application. Their experimental results indicated that average salt rejection of 95% and lifespan of up to 39 h of continuos testing achieved. Osman et al. [14] applied DCMD process for water and chemicals recovery from RO and electrodialysis brines. In mentioned work, water recovery between 70 and 80% and salt rejection of 99.5% were obtained. Nghien et al. [15] studied the feasibility of treating high salinity aqueous solutions contain RO brine and a saturated $CaSO_4$ solution, using a DCMD apparatus equipped with a 0.22 μm pore size PTFE membrane. Results indicated that organic fouling and scaling significantly reduce the permeate flux. They indicated that a pre-treatment step to remove organic matters is essential to prevent membrane fouling. Moreover, other MD configurations are potentially used for desalination when considering various points of view [16–22].

In this work, three hydrophobic membranes made of different materials were used for desalination of seawater via DCMD process. The performance evaluations were carried out by considering the effect of various operating parameters including feed temperature, feed flow rate and cold stream flow rate. Long-term runs were conducted to evaluate DCMD as stand-alone desalination process.

2. Materials and methods

Three flat sheet hydrophobic microporous membranes made of PTFE, polyvinylidene fluoride (PVDF) and polypropylene (PP) with a reported pore size of 0.22 μm were used for experiments. Fig. 1 shows the scanning electron microscopy (SEM) of the membranes. The specifications of the membranes are presented in Table 1.

Persian Gulf seawater which was provided from South Pars offshore (located in the south part of Iran) was used as feed. Table 2 shows the analysis of the feed.

A direct contact MD set-up with 0.0169 m^2 effective membrane area located in a plate and frame module mounted horizontally was designed and constructed. Fig. 2 shows a general scheme of the applied DCMD set-up flow diagram. In all of the experiments, the active layer of the membranes was faced up to the hot feed stream. Cross-current flow pattern was established in the module for both hot and cold streams using two diaphragm pumps (So~Pure, Korea). In order to establish a steady state condition for long-time experiments during 15 days, the permeate stream was recycled to the feed storage tank.

The conductivity of the permeate flow was measured with an EC-meter (model EC470-L, ISTEK, Korea). SEM (VEGA, TESCAN, Czech Republic) was used for studying the structure of the membranes. Further morphological observation was provided for PTFE membrane using atomic force microscopy (AFM) (DUALSCOP 95-200E, DEM, Denmark) image (Fig. 3) Hydrophobicity of the membranes was tested by a contact angle measuring system (KRUSS G-10, Germany).

The performance of membranes was evaluated based on two major parameters, permeate flux and salt rejection. Flux is defined as the mass or volume (kg or L) of the collected permeate per the membrane effective area (m^2) per operating time (h). The salt

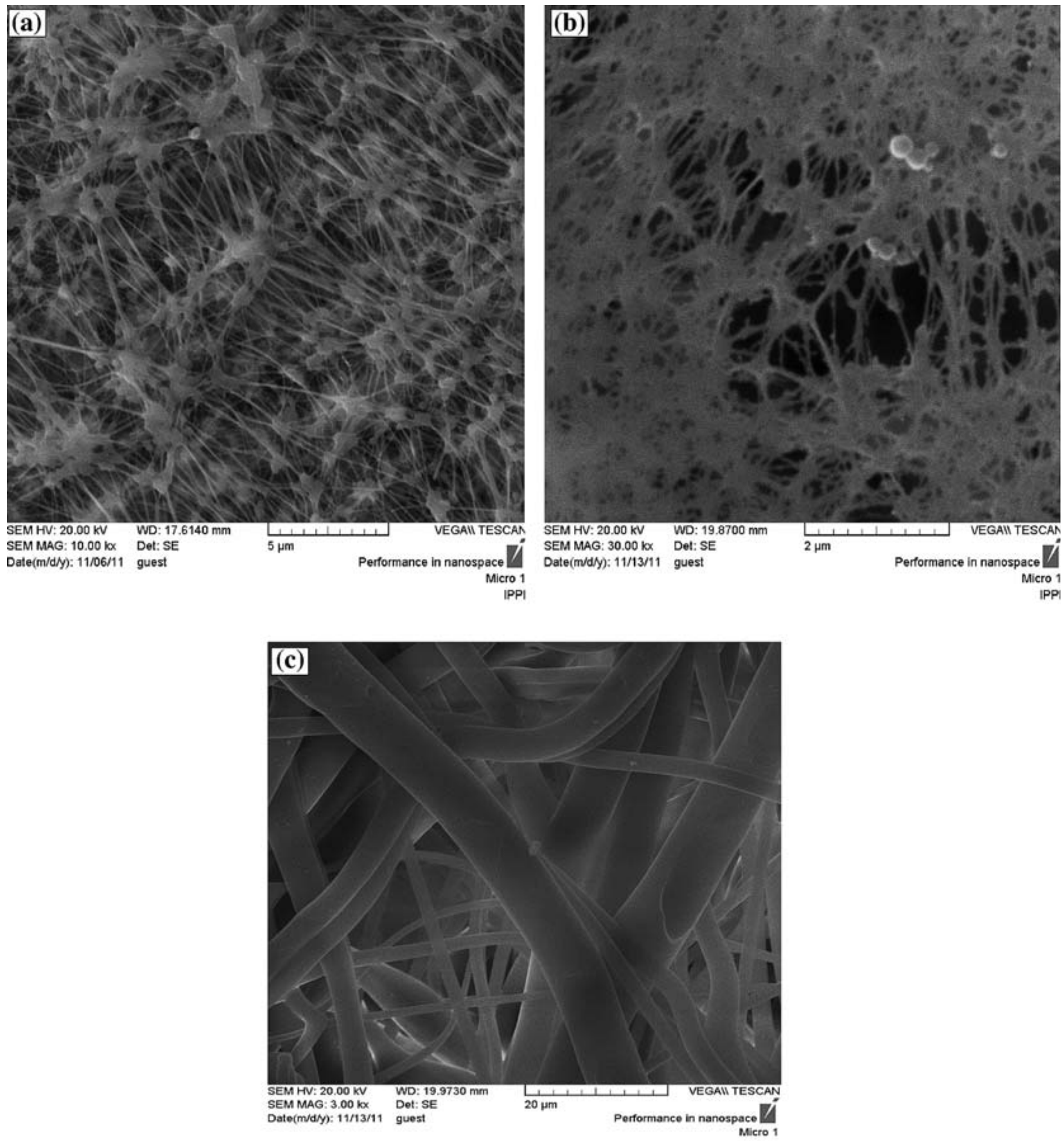

Fig. 1. The SEM images of (a) PTFE, (b) PVDF and (c) PP membranes with 0.22 μm pore size.

Table 1
The specifications of the membranes used in this study

Material	Pore size (μm)	Thickness (μm)	Porosity (%)	Manufacturer
PTFE	0.22	178	70	Millipore
PP	0.22	200	75	Membrane-solutions
PVDF	0.22	180	80	Sepro

rejection for each applied membrane was measured by use of the following expression:

$$R(\%) = 100 \times \left(1 - \frac{\text{permeate concentration (mg/L)}}{\text{feed concentration (mg/L)}}\right) \quad (1)$$

Table 2
The analysis of the Persian Gulf water used in this work

Item	Value	Unit
Na^+	14,985	ppm
Cl^-	27,272	ppm
SO_4^{2-}	3,667	ppm
Mg^{2+}	1,940	ppm
Ca^{2+}	1,231	ppm
K^+	581	ppm
SiO_2	0.30	ppm
Mn^{2+}	0.12	ppm
Fe^{2+}	0.054	ppm
NH_4^+	0.05	ppm
TSS	46.7	ppm
TDS	48,000	ppm
pH	8.7	–
Conductivity @ 20˚C	65,000	µS/cm

3. Results and discussion

3.1. Hydrophobic membranes performance

In the first step, to evaluate the performance and salt rejection of the membranes, a constant operating condition ($T_h = 80$˚C, $T_c = 20 \pm 5$˚C, $\dot{V}_h = 800$ mL/min and $\dot{V}_c = 400$ mL/min) was established. Fig. 4 shows the permeate flux, salt rejection and conductivity of the permeate streams for the three membranes after 10 h of continuous operation. It was observed that PTFE membrane showed the highest flux and rejection. PVDF achieved higher flux when compared with PP membrane, but PP membrane offered higher salt rejection (about 99%) than PVDF (about 96.57%).

These can be explained by characteristics (Table 1), morphology and hydrophobicity of the membranes. As it can be seen in Table 3, PTFE membrane had the highest contact angle with water droplet (132.2 ± 5˚), which means higher hydrophobicity (one of the major conditions which is required for MD membranes) when compared with the two other membranes. Compared to PVDF membrane, PP membrane showed higher contact angle and thickness that led to higher salt rejection. Moreover, the SEM images showed that PTFE and PP membranes have more uniform structure than those for PVDF membrane. The non-uniform structure and the presence of the large gaps in the PVDF membrane is a powerful potential for brine leakage from feed side into

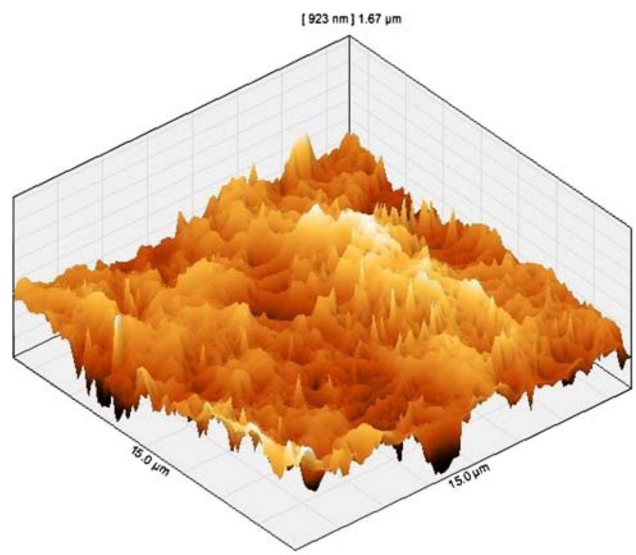

Fig. 3. A 3-D AFM image of PTFE membrane.

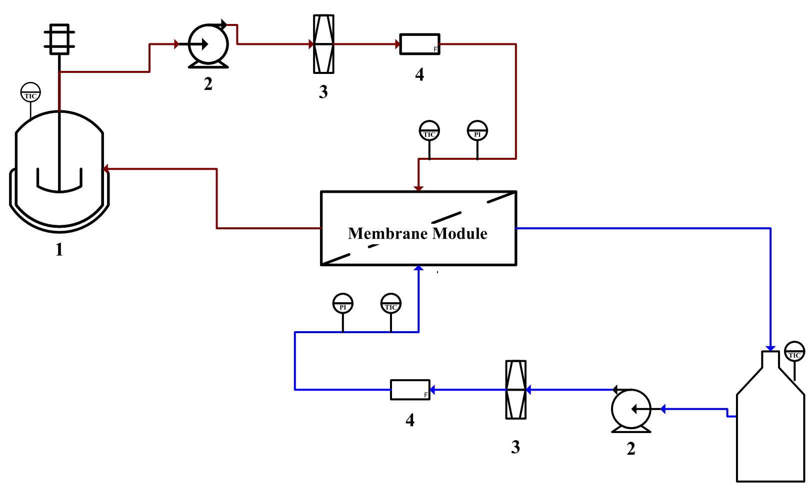

Fig. 2. A schematic diagram of the DCMD experimental set-up: (1) feed tank, (2) diaphragm pump, (3) regulator, (4) flow-meter and (5) permeate tank.

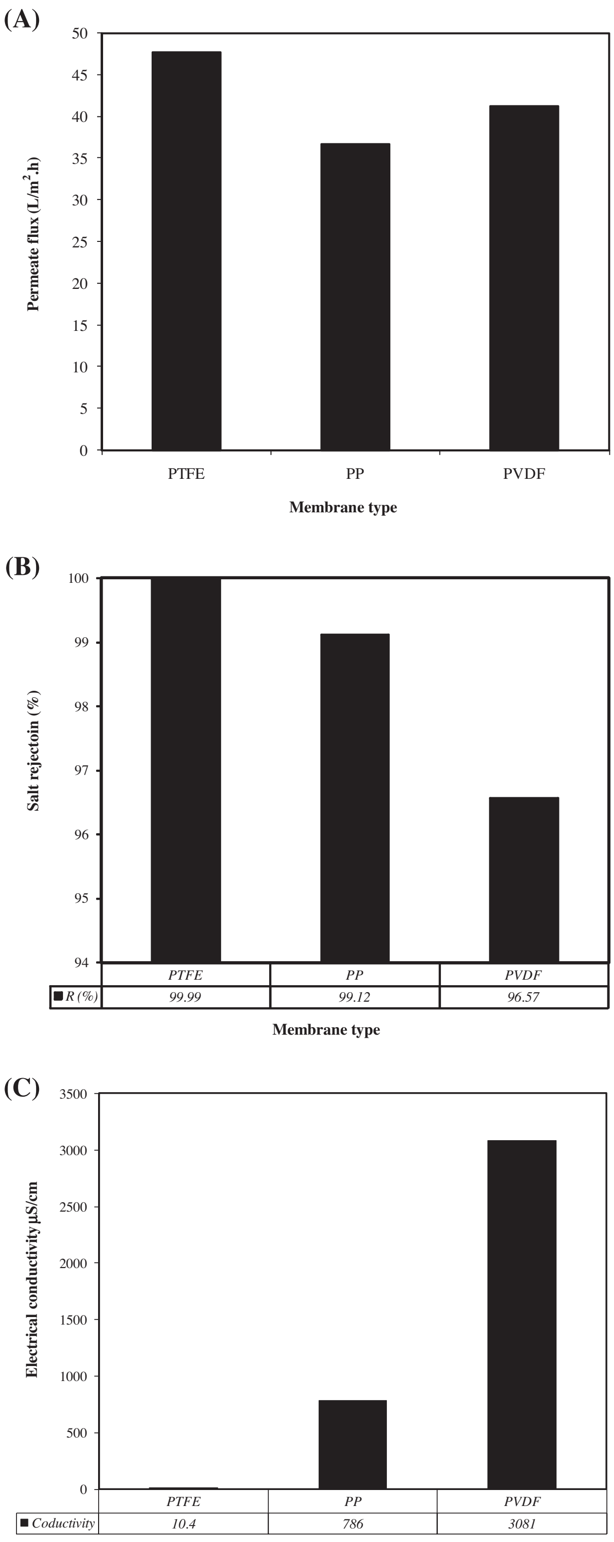

Fig. 4. Permeate flux (A), salt rejection (B) and conductivity (C) of the permeate stream for PTFE, PP and PVDF membranes.

Table 3
Contact angle values for the three membranes

PTFE	PP	PVDF
$132.2 \pm 5^{\circ}$	$113.5 \pm 5^{\circ}$	$98.7 \pm 5^{\circ}$

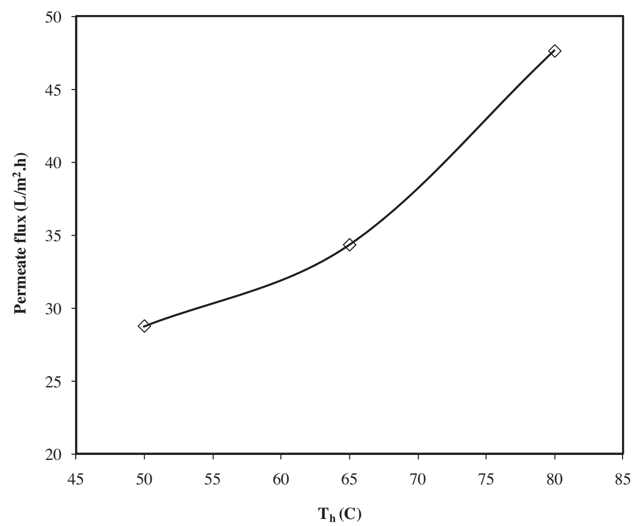

Fig. 5. The effect of feed temperature on the permeate flux. $\dot{V}_h = 800$ mL/min, $T_c = 20 \pm 5$°C, $\dot{V}_c = 400$ mL/min.

the permeate side. Therefore, PTFE membrane is considered for next experiments.

3.2. The effect of feed temperature

As MD is a non-isothermal separation process, feed temperature (T_h) was considered as the first operating variable in the range 50–80°C. Fig. 5 shows the effect of T_h on the permeate flux. The results show that the higher the feed temperature, the higher permeate flux achieved. It can be explained by the well-known Antoine equation which expresses the relationship between the liquid temperature (T_h) and the corresponding equilibrium vapour pressure (the driving force for MD process). In other words, higher feed temperature leads to higher vapour pressure which provides further permeate flux. This result was in accordance with previous studies [11–22]. Therefore, 80°C feed temperature was considered for the next experiments.

3.3. The effect of feed flow rate

Like other membrane processes, MD process is sensitive to fouling, in which precipitation of the less

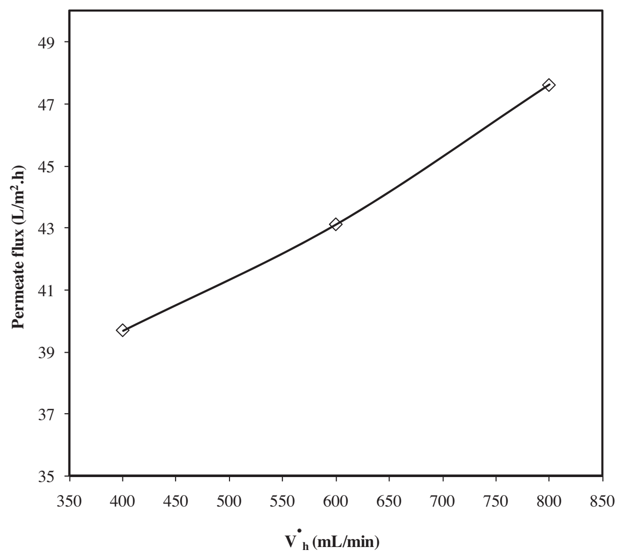

Fig. 6. The effect of feed flow rate on the permeate flux. $T_h = 80$°C, $T_c = 20 \pm 5$°C, $\dot{V}_c = 400$ mL/min.

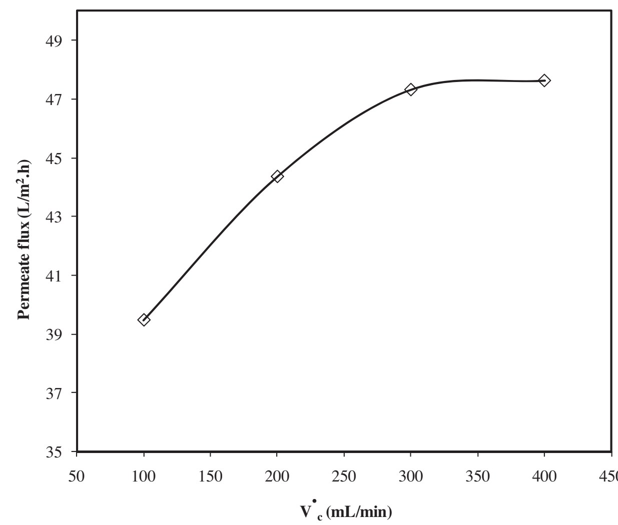

Fig. 7. The effect of cold stream flow rate on the permeate flux. $T_h = 80$°C, $T_c = 20 \pm 5$°C, $\dot{V}_h = 800$ mL/min.

soluble constituents in the operating condition on the membrane surface causes a reduction in the permeate flux. Moreover, as vapourization takes place in the membrane-feed interface, both concentration and temperature polarizations exist [23]. One way to overcome these unfavourable effects is to increase the turbulency in the feed channel at the hot side of the membrane module.

Therefore, the feed flow rate in the hot side ($\dot{V}_h$) is considered as an important operating variable in the range 400–800 mL/min. The results have been shown in Fig. 6. The results showed that the increase in the feed flow rate led to an increase the permeate flux which are in agreement with previous studies [24]. Moreover, the effect of feed flow rate on the permeate flux was observed to be less than the effect of feed temperature. Feed flow rate of 800 mL/min was selected as the best flow rate for the next experiments.

3.4. The effect of cold stream flow rate

In DCMD, feed and product sides of the membrane are faced with the hot and cold stream process liquids, respectively. Therefore, the cold stream flow rate in the permeate side ($\dot{V}_c$) could be considered as another operating variable. The flow rate in the range 100–400 mL/min was selected as the cold stream flow rate. The results are presented in Fig. 7. As it can be seen, increase in the cold stream flow rate led to increase the permeate flux. However, this effect was less than those achieved by hot stream flow rate. Increase in the cold stream flow rate has two different effects on the permeate flux. The first, increase in the cold stream flow rate maintains the driving force for condensation at a high level because it reduces the temperature polarization at the permeate side. The second, increase in the cold stream flow rate increases the turbulence and Reynolds number at the cold stream side which increases the heat transfer between the hot feed stream and the cold stream. Considering that the membranes are very thin polymeric film with a thickness of 100–200 μm, they have a very low thermal resistance. Therefore increase in the cold stream flow rate, reduces the temperature gradient in the membrane which consequently reduces the permeate flux. The results confirms this conclusion because increase in flow from 300 to 400 mL/min had negligible effect on the permeate flux.

3.5. Long-term performance

To evaluate the DCMD as a stand-alone desalination process, long-term performance during 15 days was evaluated. Data were logged every 12 h. Two sets of experiments were carried out. In the first experiment, the seawater was filtered with a 5 μm non-woven polypropylene depth filter and the filtrate was used as the feed for the MD process. In the second experiment, after 10 days operation with the prescribed feed (the filtrated seawater) the feed solution was acidified by a 37% hydrochloric acid in the level of 1% wt. and this acidified solution was used as the feed hereafter. The results which have been shown in Fig. 8 showed that the permeate flux reduces slightly within the first 150 h of operation which is because of slightly pore blockage by solid particles presented in

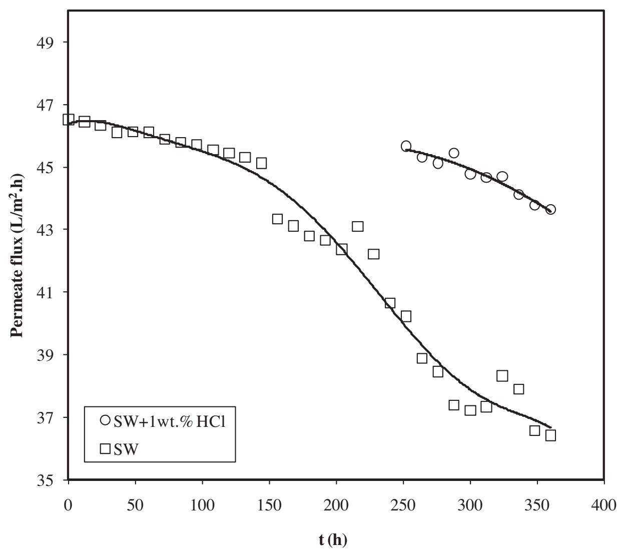

Fig. 8. The performance of DCMD during long-time run. $T_h = 80°C$, $T_c = 20 \pm 5°C$, $\dot{V}_h = 800\,mL/min$, $\dot{V}_c = 400\,mL/min$.

the feed solution. After almost 240 h a sharper decrease in the permeate flux was observed which is the result of scale formation on the membrane surface.

Addition of hydrochloric acid to the feed after 10 days of operation has recovered the permeate flux, considerably. As the major scale-formatting agents present in seawaters are basic carbonate materials, such as calcium carbonate, addition of acid to the feed lowers the pH of the system and consequently dissolves the carbonates and increases the permeate flux. But the acidified feed could not affect the acidic scalants such as siliceous materials and here after these materials are the cause of scale formation and permeate flux reduction.

4. Conclusions

DCMD is a powerful, low cost, low temperature and clean method for seawater desalination. Flux decline in this process is mainly because of concentration and temperature polarizations in the feed side. The most important factors in this process are the feed temperature and then the feed flow rate, respectively. Cold stream condition has a lesser effect on the permeation flux.

Scale formation is the major reason for flux decline during long time runs. Periodical addition of acid and alkali to the feed solution may be considered as a proper way for online cleaning and flux recovery for this system.

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