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Antiwettability and Performance Stability of a Composite Hydrophobic/Hydrophilic Dual-Layer Membrane in Wastewater Treatment by Membrane Distillation

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1 **Anti-wettability and performance stability of a composite**
2 **hydrophobic/hydrophilic dual-layer membrane in wastewater**
3 **treatment by membrane distillation**

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Abstract

This study investigated the performance and applicability of a composite dual-layer PTFE membrane coated with a dense hydrophilic polyurethane layer for treating wastewater containing surfactant and solvent in direct contact membrane distillation process. The influences of operating temperature and water recovery on bare and composite PTFE membranes were studied using simulated wastewaters containing sodium chloride together with sodium dodecyl sulfate or ethanol. In contrast to the significant wetting of bare PTFE membrane due to the adsorption of wetting agent on membrane surface, the composite membrane exhibited satisfied anti-wettability and desalination stability. The mechanism of anti-wettability of the composite membrane was related to the repellent effect of hydrophobic moiety of surfactant arrayed on the hydrophilic layer of the composite membrane, which prevented the wetting agent from reaching the hydrophobic layer of membrane. The results indicate that the dual-layer membrane could be potentially used to tackle organic solvent and/or surfactant containing wastewaters.

Keywords: Direct contact membrane distillation; Dual-layer PTFE membrane; Wetting; Surfactant; Organic solvent.

1. Introduction

Membrane distillation (MD) is a promising separation process for water purification¹, wastewater treatment and reuse², and food processing³. In MD process, a hot feed solution was separated by a hydrophobic microporous membrane from the permeate side at a low temperature and in most cases water molecules as the target component transport through the membrane pores to obtain pure water. The MD driving force for the water transport is the water vapor pressure differential arising from the temperature gradient across the membrane through the membrane pores⁴. MD has been paid increasing attention for water desalination and wastewater treatment, due to the excellent permeate quality and low sensitivity to salinity of feed solution⁵. The main advantages of MD are the theoretical 100% nonvolatile salt rejection, relatively low operating temperature (30-80 °C) compared to conventional distillation processes, capability of utilizing waste heat or alternative low-grade energy sources, lower requirement of membrane mechanical properties, and lower operating pressure than conventional pressure-driven membrane desalination processes such as reverse osmosis (RO)^{4,6}. MD process can be classified into four main configurations based on the operations on the permeate side to keep vapor pressure difference: direct contact membrane distillation (DCMD), vacuum membrane distillation (VMD), air gap membrane distillation (AGMD), and sweeping gas membrane distillation (SGMD)^{5,7}. Among the four configurations, DCMD is best suited for applications because it requires the least equipment and is simplest to operate⁷.

1 Up to now, MD has acquired only little commercial acceptance and is yet to be
2 widely applied in industry ⁸. The stable flux and salt rejection performance in
3 long-term operations are significant aspects to be taken into account for the MD
4 industrialization. Flux decline, however, is usually encountered in continuous MD
5 process, which is mostly induced by fouling and membrane wetting ⁹. Membrane
6 wetting, that is, membranes becoming gradually less hydrophobic during use causing
7 the pass of feed through the pores, is a serious problem affecting the MD performance,
8 which will cause the deterioration of the product water quality especially for
9 long-term operation. Thus, the performance and application of MD membranes for
10 water treatment are impeded by membrane wetting. Currently, membrane wetting has
11 been identified as one of the basic reasons why MD is not used industrially ¹⁰. When
12 MD is applied for wastewater treatment, membrane wetting becomes more
13 problematic as the wastewater may contain low surface tension substances such as
14 organic compound or surfactant ¹¹⁻¹⁴. Organic matters often possess lower liquid
15 surface tension values than that of water. Therefore, the water-organic mixture can
16 penetrate easily to the membrane pores and lead to the membrane wetting ^{12,13}. A
17 surfactant with a lower hydrophile-lipophile balance is more hydrophobic and readily
18 adsorbs to hydrophobic surfaces due to hydrophobic effects ¹¹. Thus, the hydrophilic
19 heads of adsorbed surfactants draw water towards the membrane pores and cause
20 membrane wetting ¹⁴.

21 Membrane wetting property can be measured by the Liquid Entry Pressure (LEP),
22 which depends on the diameter and the geometric structure of the pores, the contact

angle between the membrane surface, the liquid, and vapor phases, and surface tension of the liquid with vapor ¹⁵. LEP can be calculated according to the following LaPlace–Young equation ^{16,17}.

$$LEP = - \frac{4B\gamma_L \cos\theta}{d_{\max}} \quad (1)$$

where B is a geometric pore coefficient (equal to 1 for cylindrical pores), θ is the contact angle, γ_L is the surface tension of liquid (N/m), and d_{\max} is the maximum pore size of the membrane (m).

Wetting occurs when the pressure is large enough to impel the liquid through the hydrophobic membrane pores. High LEP value is favored by the membrane structural parameters such as small pore size and membrane properties with low surface energy and high surface roughness ¹⁸. To reduce the possibility of membrane wetting and feed penetration, membranes manufactured from hydrophobic materials such as polypropylene (PP), polytetrafluoroethylene (PTFE), and polyvinylidene fluoride (PVDF) with high contact angles, low surface energy, small maximum pore size and narrow pore size distribution are recommended for MD processes ^{9,19–21}. In general, the water contact angle (WCA) of a hydrophobic membrane should be greater than 90° ⁷. Some super-hydrophobic membranes with WCA of over 150° were also fabricated to overcome membrane wettability and increase permeate flux ²².

A large number of researchers have studied the influences of membrane wetting on the MD performance utilizing various types of membranes. The common methods to improve membrane anti-wetting property include membrane hydrophobic modification ^{23,24}, hydrophilic modification ^{11,25,26}, oleophobic modification ²⁷, and

1 omniphobic modification ^{28–30}. For example, Lee et al. ²³ reported a one-step versatile
2 electrospinning technique for incorporating functionalized TiO₂ nanoparticles into
3 organic polymer and found that the electrospun membranes exhibited enhanced
4 anti-wetting properties because of their high hydrophobicity. Lin et al. ¹¹ proposed a
5 novel approach to lessen the possibility of surfactant wetting during the MD process
6 using the PTFE membranes coated with a thin agarose layer and no wetting was
7 detected when testing against wastewaters containing dyeing. Wang et al. ²⁷ fabricated
8 a composite membrane by modifying a commercial hydrophobic PVDF membrane
9 with a nanocomposite coating comprising silica nanoparticles, chitosan hydrogel and
10 fluoro-polymer which significantly enhanced the surface anti-wettability when
11 dealing with the wastewaters containing high concentrations of hydrophobic
12 pollutants. Lin et al. ²⁸ fabricated an omniphobic membrane via modifying a
13 hydrophilic glass fiber membrane with silica nanoparticles for membrane distillation
14 process and found that the modified microporous membrane exhibited an enhanced
15 anti-wettability for both water and low surface tension substances such as organic
16 solvents. Even though great development has been made to exploit the composite
17 membranes to minimize organic solvents or surfactant adhesion and pore wetting, the
18 long-term MD process with full potential application in industries has not yet been
19 realized in operations with low surface tension feeds ³¹. In particular, only a very
20 limited amount of work has been reported on the influences of surfactants on
21 membrane wetting phenomenon ¹⁴.

22 The purpose of this work was to explore the anti-wettability and applicability of

1 a composite dual-layer PTFE (C-PTFE) membrane with hydrophilic/polyurethane
2 dual-layer when dealing with wastewaters containing surfactant or organic solvent in
3 DCMD process. Common surfactant sodium dodecyl sulfate (SDS) and organic
4 solvent ethanol were chosen to simulate wastewater for evaluating the membrane
5 performance in the DCMD experiment. The influences of operating temperature and
6 water recovery on the anti-wetting properties of the membrane were compared against
7 bare PTFE membrane. To understand the role of dense hydrophilic polyurethane layer
8 of C-PTFE membrane, the water uptake and water contact angle pre and post static
9 wetting treatment and pressurized filtration experiment using a series of feed solutions
10 were determined and discussed. It is expected that this work can help to understand
11 the mechanism of anti-wettability of dual layer membrane and provide guidance for
12 developing new anti-wetting membrane to broaden the application area of MD in
13 wastewater recycling and treatment.

14 **2. Experimental**

15 2.1. Materials

16 Sodium chloride (NaCl, 99.5%) and ethanol were purchased from Merck
17 Millipore. The sodium dodecyl sulfate (SDS) was procured from Sigma-Aldrich. The
18 reagents were used as received. The commercial microporous hydrophobic flat-sheet
19 polytetrafluoroethylene (PTFE) membrane was supplied by Porous Membrane
20 Technology (Ningbo, China). The commercial composite dual-layer PTFE membrane
21 with a dense polyurethane coating layer (C-PTFE) was supplied by Bruck textile.
22 Their structural parameters are listed in Table 1.

1 **Table 1.** PTFE and C-PTFE membrane parameters in this study.

Membrane	Property	Thickness, μm	Mean pore size, μm	Porosity, %	LEP, kPa	WCA
PTFE	Hydrophobic	14-20	0.45	90	450	142.6°
C-PTFE ^a	Hydrophobic ^b	14	0.39	90	>1000	142.2°
	Hydrophilic ^c	14	<0.01	--		15.2°

2 ^a Composite dual-layer PTFE membrane.

3 ^{b, c} The hydrophilic layer and hydrophobic layer of C-PTFE membrane, respectively.

4 2.2. Membrane characterizations

5 The morphology of PTFE and C-PTFE membranes were characterized by a
6 scanning electron microscope (SEM, Merlin ZIESS GEMINI2) with working distance
7 of 3.3-4.5 mm and voltage level of 5 kV. The membranes were frozen in liquid
8 nitrogen and then cut with a blade to create a clean cross section. Both the membrane
9 surface and cross section were imaged.

10 Pore size analysis of membranes was conducted via a Quantachrome Porometer
11 3G pore size analyzer, employing liquid expulsion technique using a wetting liquid
12 Porofil. Prior to pore size analysis, C-PTFE membrane was soaked in
13 dimethylformamide solvent and sonicated for 5 minutes in order to dissolve its upper
14 polyurethane layer, thus exposing the lower PTFE layer to enable pore size
15 comparison of the supporting PTFE layer of the C-PTFE membrane with bare PTFE
16 membrane.

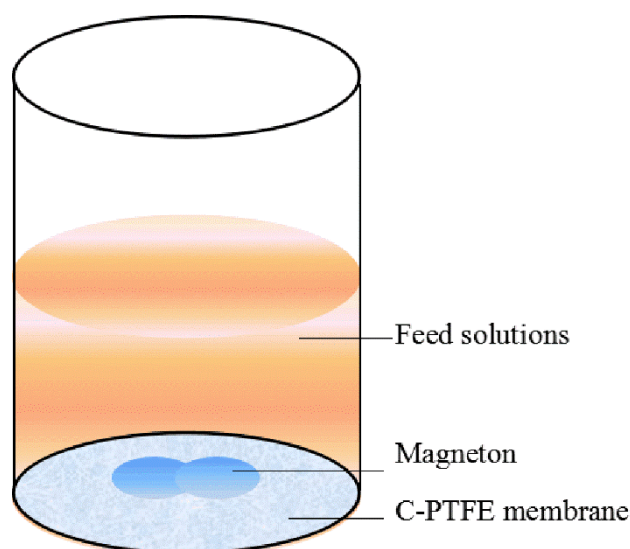
17 The water contact angles of PTFE membrane and C-PTFE membrane were

1 measured using a KSV contact angle meter (CAM200) connected with a video
2 capturing system. The measurement is depending on a sessile drop method, using an
3 optical system to capture the profile of the tested liquids ($\sim 9 \mu\text{L}$) on a horizontal
4 substrate membrane. The contact angles for each membrane were measured at three
5 different positions and the average value was taken as final result.

6 The water uptake of C-PTFE membrane hydrophilic layer was measured using
7 the following method. The dried C-PTFE membranes were weighed and then placed
8 into a custom designed apparatus (seen in Fig. 1), in which only the hydrophilic layer
9 of the C-PTFE membranes was allowed in contact with the liquid solutions which
10 were deionized water (DI water), 2 g/L NaCl aqueous solution, 100 g/L ethanol
11 aqueous solution, 40 mg/L SDS aqueous solution, 2 g/L NaCl aqueous solution
12 containing 100 g/L ethanol, and 2 g/L NaCl aqueous solutions containing 40 mg/L
13 SDS, respectively. The C-PTFE membrane was fixed at the bottom of the apparatus
14 and a magneton was used to stir the solutions to restrain the concentration polarization.
15 The hydrophilic surface of the C-PTFE membrane was exposed to the liquids for 24 h
16 at room temperature. After that, the membranes were blotted dry to remove surface
17 water and reweighed. Water uptake (g/m^2) is reported as the mass of water adsorbed
18 per unit membrane area.

19 Static wetting experiment for PTFE and C-PTFE membrane was conducted using
20 the same setup (Fig. 1). The immersion solutions were DI water, 40 mg/L SDS
21 aqueous solution, and 2 g/L NaCl aqueous solution containing 40 mg/L SDS,
22 respectively. After that, the membranes were dried at 40°C under vacuum for 24 h.

1 Then the contact angles of the dried membranes were measured with four kinds of
2 liquid droplets separately, including DI water, 2 g/L NaCl aqueous solution, 2 g/L
3 NaCl aqueous solution containing 100 g/L ethanol, and 2 g/L NaCl aqueous solution
4 containing 40 mg/L SDS.



5
6 **Fig. 1.** Schematic of the custom designed apparatus for water uptake test.

7 The liquid entry pressure (LEP) of the PTFE membranes was determined by the
8 same method as described in the literature ²². The measurement was conducted with a
9 cylindrical pressure filtration cell (110 ml) with an effective surface area 10.2 cm²
10 linked with a pressurized air bottle through a pressure regulator and a pressure gauge.
11 A dry membrane was placed in the pressure filtration cell followed by pressurizing
12 NaCl aqueous solution containing ethanol or SDS as feed with air. The pressure was
13 gradually increased by 10 kPa every 10 min starting from 30 kPa. The pressure value
14 at which the first liquid droplet of the feed leaves the permeate side of the pressure
15 filtration cell is determined as LEP. The tests were repeated at least twice.

16 In order to investigate whether the wetting agents can be sterically rejected by

1 the C-PTFE's hydrophilic layer or not, the pressurized filtration of the wetting agent
2 through the C-PTFE membrane was tested using the same setup as in LEP
3 measurement. The 100 mL aqueous solutions containing 40 mg/L SDS or 100 g/L
4 ethanol was fed to the cylindrical cell for filtration under 200 kPa. 20 mL permeate
5 was collected and the penetration of wetting agent through the membrane was
6 determined based on total organic carbon (TOC) measurement of feed and permeate
7 with TOC analyzer (Shimadzu CSH E200 analyzer, TOC V with TNM-1 unit).

8 2.3. Membrane performance in DCMD process

9 Fig. 2 presents the schematic diagram of the laboratory scale DCMD
10 experimental set-up. The flat sheet membrane cells made of acrylic plastic can
11 minimize the heat loss to surroundings. The flow channels of the feed and permeate
12 semi-cells were engraved in each of two acrylic blocks. Each semi-cell possessed a
13 flow channel with depth, width, and length of 0.15, 6, and 9.5 cm, respectively, and
14 formed an active membrane surface area of 57 cm². Two variable-speed peristaltic
15 pumps were used to circulate the feed and permeate through the membrane cell with
16 flow rates monitored by rotor flow meters. Polypropylene spacers (thickness, 0.75
17 mm, and porosity, 87%) were used in both feed and permeate side to guide the flow
18 and improve flow turbulence. The feed and permeate temperatures were adjusted by a
19 heater integrated water bath and a chiller, respectively. The temperatures at the inlet
20 and outlet of the membrane module on both feed and permeate side were measured by
21 K-type thermocouples with ± 1 °C accuracy. The feed was directly contacted with the
22 hydrophilic layer of the C-PTFE membrane when using C-PTFE membrane in DCMD

experiment. The penetration of solute was measured depending on the conductivity measurement of the permeate solution with a digital conductivity meter (model no: HI 98192 supplied by Hanna Instruments). The weight increment of the permeate was determined by a digital balance. The average water permeate flux, J (kg/(m²·h)) was expressed according to the following equation:

$$J = \frac{\Delta W}{At} \quad (2)$$

where ΔW (kg) is the mass variation of distillate over a given time t (h), and A (m²) is the effective membrane area.

The normalized water flux (J/J_0) was calculated as follows:

$$J / J_0 = \frac{Flux_f}{Flux_0} \quad (3)$$

where $Flux_f$ is the flux obtained with simulated wastewaters containing NaCl and wetting agents and $Flux_0$ is obtained with pure water under the same operating conditions.

For each experiment, water recovery (Rec) is calculated by equation (4) as

$$Rec = \left(1 - \frac{V_t}{V_o}\right) \times 100\% \quad (4)$$

The corresponding NaCl concentration (C_{NaCl} , g/L) can be determined by

$$C_{NaCl} = \frac{m_{NaCl}}{V_o(1 - Rec)} \quad (5)$$

where m_{NaCl} (g) is the NaCl mass in feed solution, and V_o (L) and V_t (L) are the initial feed volume and volume of feed at time t (h), respectively.

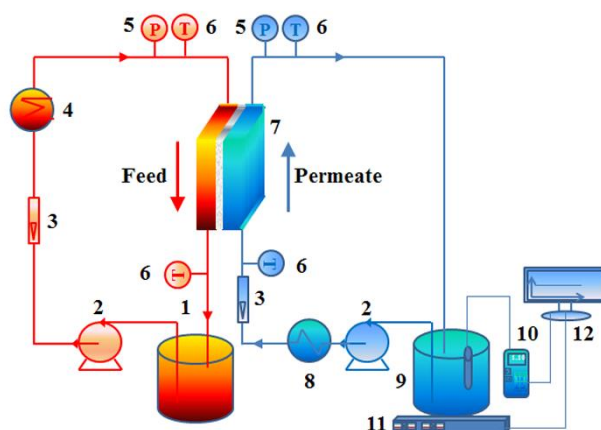


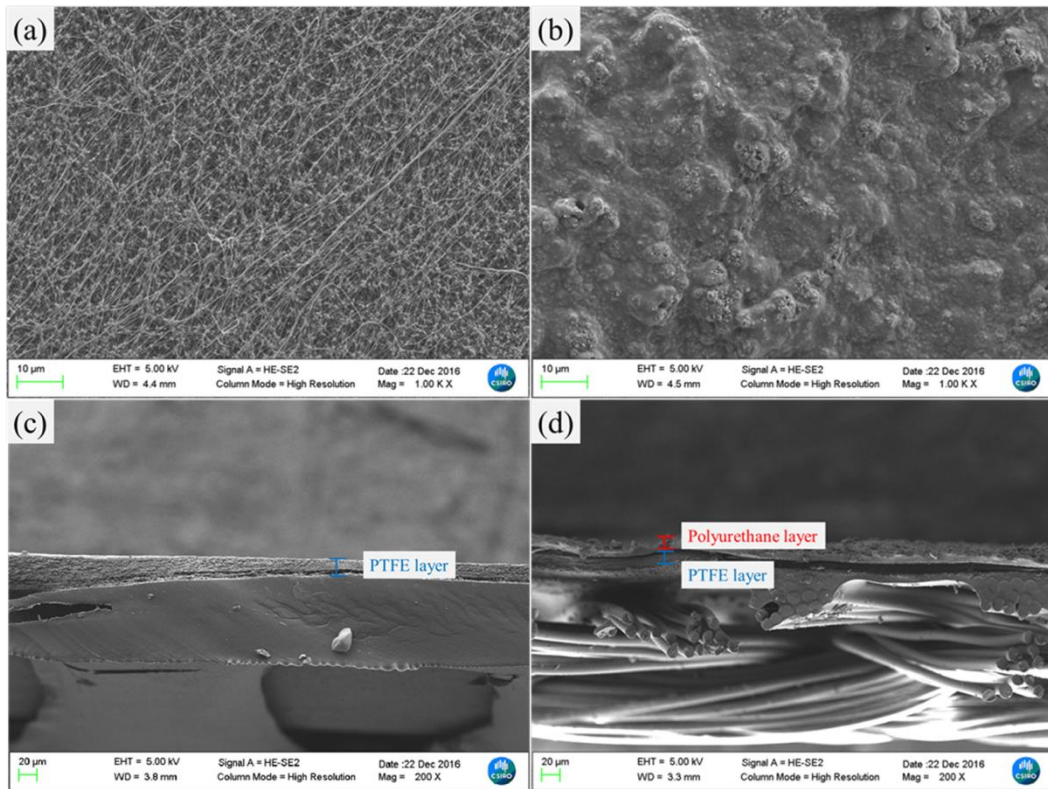
Fig. 2. Schematic diagram of DCMD setup: (1) feed tank; (2) peristaltic pumps; (3) rotameters; (4) heater; (5) pressure gauge; (6) thermocouples; (7) flat sheet membrane module; (8) chiller; (9) permeate tank; (10) conductivity meter; (11) analytical balance; (12) computer.

3. Results and discussion

3.1. Membrane surface characterizations

Fig. 3 presents the surface and cross-sectional SEM images of both PTFE and C-PTFE membranes. It is observed that the changes in surface morphology of the PTFE membrane after hydrophilic modification by coating with a dense polyurethane layer on its top surface are rather evident. There are abundant pores on the PTFE membrane (Fig. 3 (a)), but no pores were observed on the dense hydrophilic polyurethane layer of the C-PTFE membrane which thoroughly covers the surface of PTFE substrate (Fig. 3 (b) and (d)). Fig. 3 (d) indicates that the polyurethane layer has a thickness of around 14 μm and does not penetrate into the bulk of the PTFE substrate. In addition, it can be seen that the hydrophobic PTFE layer of C-PTFE membrane has similar thickness to that of PTFE layer of PTFE membrane shown in Fig. 3 (c).

1 The difference in pore size between the PTFE membrane and the hydrophobic
2 layer of the C-PTFE membrane measured by liquid expulsion technique is presented
3 in Fig. 4. It can be observed that the PTFE membrane has a mean pore size of 0.45
4 μm , and hydrophobic layer of C-PTFE membrane has a comparable mean pore size of
5 0.39 μm and a narrower pore size distribution.



6 **Fig. 3.** SEM images of surface (a) PTFE and (b) C-PTFE membranes and cross section (c) PTFE
7 and (d) C-PTFE membranes.
8

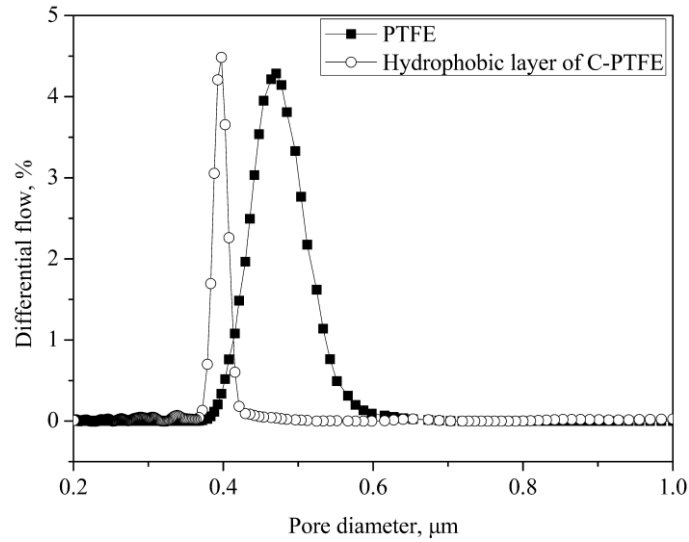


Fig. 4. Pore size distribution of PTFE and hydrophobic layer of C-PTFE membranes.

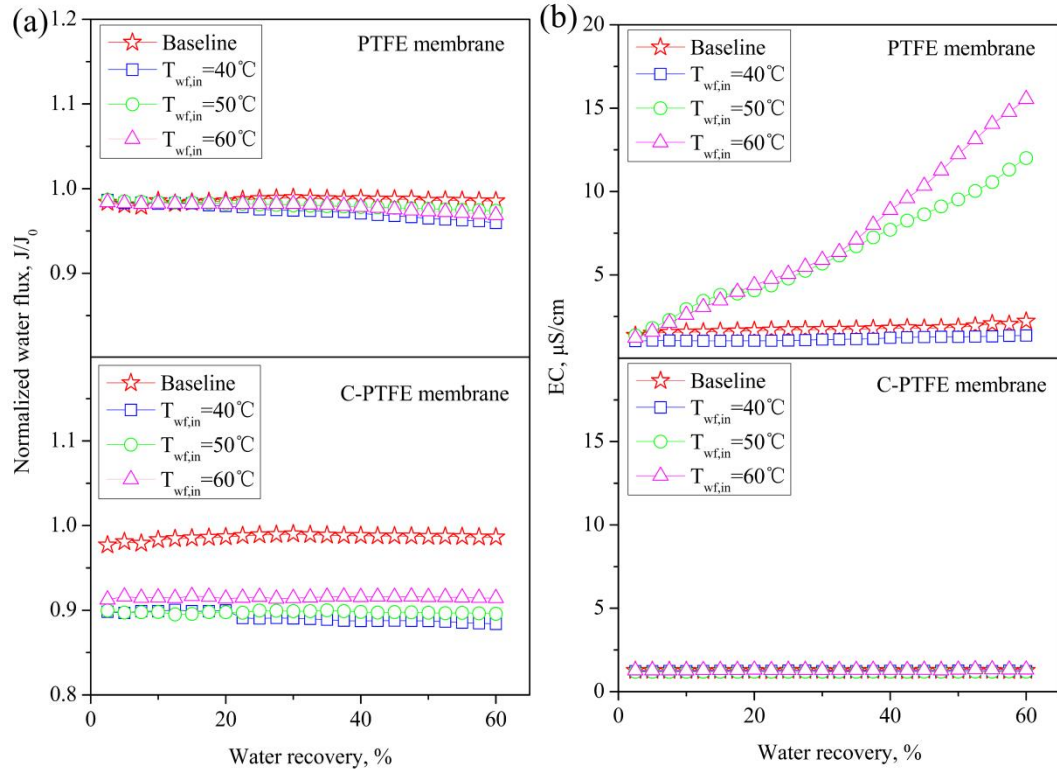
3.2. Anti-wettability of C-PTFE membrane

3.2.1. Effect of ethanol and SDS on membrane wetting

Fig. 5 shows the effect of water recovery on the normalized water flux (J/J_0) and permeate electrical conductivity (EC) using PTFE and C-PTFE membranes. A baseline test was first conducted using 2 g/L NaCl aqueous solution at 50°C, as shown in Figs. 5 (a) and (b). The purpose of running a baseline test was to ascertain the stable performance of the MD system during desalination process. As can be seen, the J/J_0 was steady (~ 0.98) and the EC was constantly in range of 2-4 $\mu\text{S}/\text{cm}$.

Figs. 5 (a) and (b) demonstrates the performance of the PTFE membrane and C-PTFE membrane challenged by 2 g/L NaCl feed solution containing 100 g/L ethanol. As can be found, at 40 °C of $T_{wf,in}$, EC of PTFE membrane was almost constant with increasing water recovery, however, at 50 and 60 °C of $T_{wf,in}$, EC increased with water recovery. This indicates that the high feed temperature facilitates the wetting of PTFE membrane. The phenomenon is related to the surface tension reduction of ethanol/water mixture solution with temperature³². It is reported that the

1 net inward pull will become less with the increase of temperature, thus weakening the
2 molecular interactions and then reduced the surface tension ³². In this case, low
3 operating temperature is preferred. By comparison, as for C-PTFE membrane, the J/J_0
4 was slightly lower than the results with PTFE membrane and exhibited a slight
5 decrease with water recovery, but the ECs were constant for all temperatures and
6 water recovery considered. The slight decrease of the J/J_0 with water recovery is
7 related to the reduction of the driving force of the MD process, which is caused by the
8 increase of the feed concentration with water recovery.



9
10 **Fig. 5.** Normalized water flux (J/J_0) (a) and permeate electrical conductivity (EC) (b) versus water
11 recovery using PTFE and C-PTFE membrane of DCMD with 2 g/L NaCl feed solution containing
12 100 g/L Ethanol. (10 °C of permeate inlet temperature and 450 mL/min of feed and permeate flow
13 rates).

14 Furthermore, another feed solution containing 2 g/L NaCl and 40 mg/L of SDS

was employed and the normalized water flux (J/J_0) and permeate EC versus water recovery are shown in Figs. 6 (a) and (b), respectively. As can be seen, the permeate EC of PTFE membrane increased significantly with water recovery, especially for water recovery exceeding 30% (NaCl concentration of 2.9 g/L). Similarly, the higher the feed temperature, the faster the EC increases, creating more severe membrane wetting. By contrast, the ECs of C-PTFE membrane remained relative constant at all test temperatures.

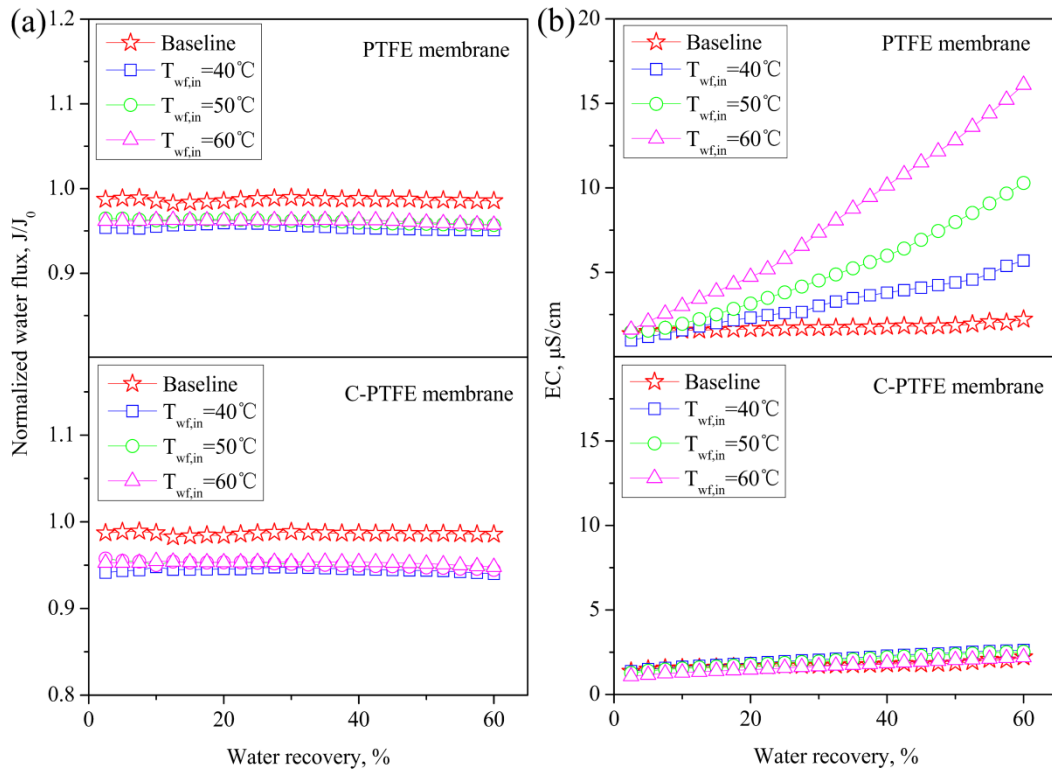


Fig. 6. Normalized water flux (J/J_0) (a) and permeate electrical conductivity (EC) (b) versus water recovery using PTFE and C-PTFE membrane of DCMD with 2 g/L NaCl feed solution containing 40 mg/L SDS. (10 °C of permeate inlet temperature and 450 mL/min of feed and permeate flow rates).

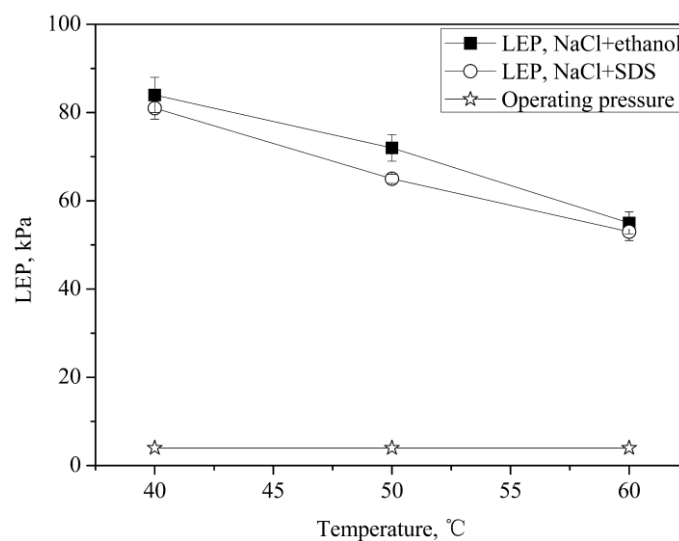
3.2.2. Membrane wetting mechanism

It is known that wetting is related to feed surface tension decline when

1 containing surface active component compared with the surface tension of pure water
2 ¹². The surface tension of pure water is equal to 72.66 mN/m (at 25 °C), whereas that
3 of ethanol is equal to 22.14 mN/m (at 25 °C) ^{32,33} and that of SDS solution (40 mg/L)
4 is 64.89 mN/m (at 25 °C) ³⁴. Therefore, the presence of ethanol and SDS at the PTFE
5 membrane surface breaks the hydrogen bonds between the water molecules and thus
6 lowers its surface tension. With the increase of surfactant concentration, more
7 molecules will adsorb at the membrane surface, thus lowering the surface tension
8 further ³⁵. Furthermore, an increase of feed temperature also decreases the feed
9 surface tension ³⁶, which leads to a decrease of LEP. Therefore, the PTFE membrane
10 is more vulnerable to be wetted at high ethanol and SDS concentration and high feed
11 temperature.

12 To understand the wetting phenomenon of the PTFE membrane, the liquid entry
13 pressure (LEP) of the PTFE membrane was measured at 60% water recovery and
14 different temperatures with feed solutions containing 5 g/L NaCl and 250 g/L ethanol,
15 or 5 g/L NaCl and 100 mg/L SDS. Since the ethanol is volatile, it will also permeate
16 through the membrane with water vapor during the DCMD experiment and thus the
17 ethanol concentration at the water recovery of 60% will be lower than 250 g/L. It
18 means that the LEP for the actual DCMD experiment will be larger than the measured
19 values using the feed solutions containing 5 g/L NaCl and 250 g/L ethanol, which
20 means that the DCMD process will be safe from the occurrence of breakthrough of
21 feed solution under the current conditions. The LEP measurement results are shown in
22 Fig. 7. It shows that the LEP decreases with increasing temperature. Nevertheless, as

1 can be seen, the LEP was still higher than 50 kPa when temperature increased to 60
 2 °C. However, the operating pressure on feed side during the current DCMD
 3 experiments was lower than 5 kPa. Obviously, the feed pressure is less than the LEP
 4 of the membrane. Therefore the increase of conductivity with water recovery and
 5 operating temperature is not resultant from the possible entry and passing of bulk feed
 6 solution into and through the membrane.



7
 8 **Fig. 7.** Effect of temperature on liquid entry pressure (LEP) tested with aqueous feed solutions
 9 containing 5 g/L NaCl and 250 g/L ethanol, and containing 5 g/L NaCl and 100 mg/L SDS,
 10 respectively.

11 Thus, PTFE membrane wetting in Figs. 5 (b) and 6 (b) should be related to the
 12 interaction between the wetting agents and PTFE membrane surface. Since the
 13 ethanol or SDS consists of both hydrophobic alkyl chains and hydrophilic hydroxyl
 14 and/or sulfate groups, when the ethanol or SDS contacts with the PTFE membrane,
 15 the hydrophobic tail would attach to the hydrophobic membrane surface and the
 16 hydrophilic head would face to the water molecules ¹¹. This will reduce the
 17 hydrophobicity of the PTFE surface, and bridge the water into the membrane pore.

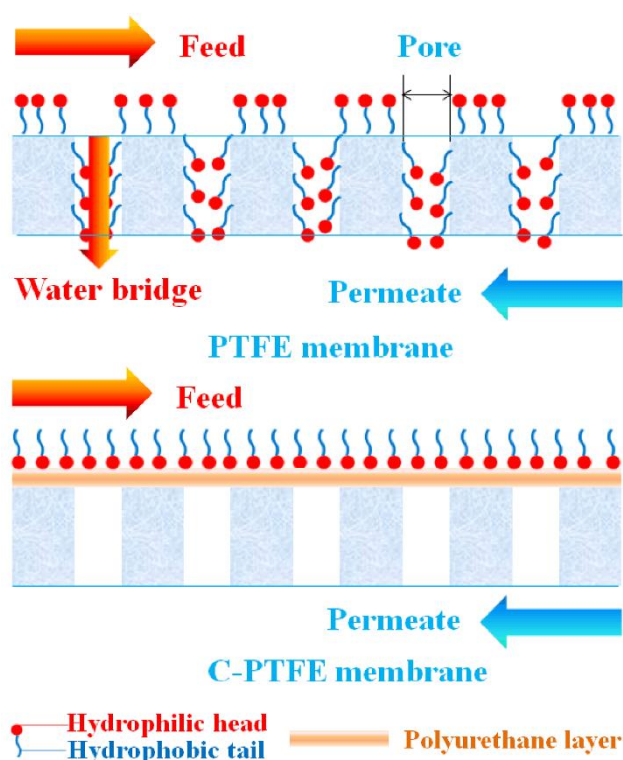
1 Membrane wetting behavior can start through the larger pores spontaneously, while
2 the water will be driven into the narrowest pores gradually by capillary forces,
3 eventually causing the partial wetting ¹⁰. This can explain the observed wetting
4 phenomenon in the DCMD experiment, which is consistent to the results reported by
5 Gryta ³⁷. Meanwhile, the “water bridges” generated by the membrane wetting will
6 allow the transportation of solutes to the permeate side, resulting in the worsening of
7 distillate quality.

8 To understand the anti-wettability mechanism of the PTFE membrane, firstly, the
9 pressurized filtration experiment using the C-PTFE membrane was conducted using
10 the salt feed solution containing ethanol or SDS to investigate the penetration of
11 wetting agent through the membrane. As shown in Table 2, the comparable
12 concentration of ethanol or SDS to that of feed can be detected on the permeate side,
13 indicating that these wetting agents cannot indeed be sterically rejected by the
14 C-PTFE’s hydrophilic layer. Therefore, the phenomenon of relatively stable EC with
15 C-PTFE in Figs. 5 (b) and 6 (b) should also be explained by surface interaction. It is
16 assumed that when ethanol or SDS contacts the C-PTFE membrane, the hydrophilic
17 head would attach to the hydrophilic membrane surface and the hydrophobic tail
18 would face the water and reduce membrane wetting. Fig. 8 illustrates the adsorption
19 and array posture of wetting agent molecules on the C-PTFE membrane surface, as
20 well as on PTFE membrane surface for comparison.

21 **Table 2.** Total organic carbon (TOC) measurement results for evaluating penetration of wetting
22 agents through C-PTFE membrane in pressure filtration under 200 kPa.

Wetting agent	Sample	TOC, mg/L
--	DI water	0.9
Ethanol	Feed	52341.5
	Permeate	51895.8
SDS	Feed	14.7
	Permeate	12.9

1



2

3 **Fig. 8.** Illustration of the adsorption of wetting agents on the PTFE and C-PTFE membrane

4 surfaces.

5 Based on this hypothesis, the hydrophilic surface of polyurethane layer of the
6 C-PTFE membrane will partially become hydrophobic. As a result, it is expected that
7 the water uptake of the surfactant and/or ethanol containing feed should be less than
8 that of the deionized water. To demonstrate the theory, the water uptake of the
9 C-PTFE membrane was measured with different solutions and the results are shown

1 in Fig. 9. It is observed that the water uptake values of the C-PTFE membrane with
 2 NaCl solution are only slightly decreased compared to that with the deionized water,
 3 while the values with ethanol or SDS solutions and salt solutions containing ethanol
 4 or SDS is considerably lower. This suggests that the ethanol or SDS at
 5 water/membrane interface impeded the contact of water with membrane surface, thus
 6 reducing the water wetting and uptake on membrane surface. This can be illustrated
 7 by the array of the wetting agent on membrane surface that their hydrophobic moiety
 8 of molecules face liquid water phase as shown in Fig. 8.

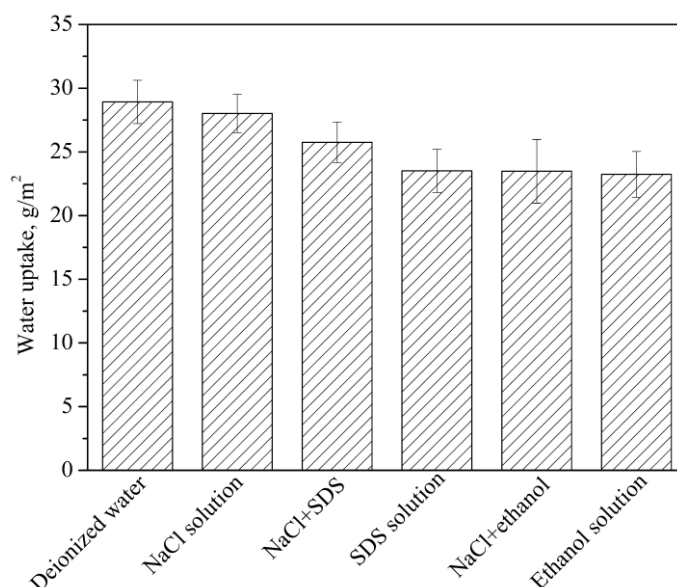


Fig. 9. Water uptake test of C-PTFE membrane at room temperature.

11 Furthermore, the hydrophobicity/hydrophilicity of the PTFE and C-PTFE
 12 membrane surface exposed to the ethanol and SDS solutions were inspected by
 13 measuring the water contact angle for the PTFE and C-PTFE membranes pre and post
 14 DCMD experiments. The results are shown in Table 3. Because the ethanol is easy to
 15 volatilize, the water contact angle for membranes after DCMD experiments with
 16 ethanol was not conducted. Table 3 shows that the contact angle for PTFE membrane

always decreased after the DCMD experiment, indicating the reduction of surface hydrophobicity due to the wetting agents adsorption. However, it is interesting to observe that the water contact angle of the C-PTFE membrane surface is significantly increased, which means the increased hydrophobicity of the membrane than the virgin one after the DCMD experiment.

Table 3. Water contact angle of PTFE and C-PTFE membranes pre and post DCMD experiments under different operating temperatures (2 g/L NaCl solutions with 40 mg/L SDS).

Membrane	Feed temperature, °C	Water contact angle	
		Pre	Post
PTFE	40	$143.5 \pm 3.0^\circ$	$131.8 \pm 6.1^\circ$
	50	$141.2 \pm 7.5^\circ$	$132.6 \pm 3.5^\circ$
	60	$142.3 \pm 7.6^\circ$	$132.4 \pm 6.4^\circ$
C-PTFE	40	$15.5 \pm 0.5^\circ$	$87.8 \pm 3.6^\circ$
	50	$15.2 \pm 0.6^\circ$	$88.1 \pm 4.1^\circ$
	60	$15.2 \pm 0.3^\circ$	$92.1 \pm 2.1^\circ$

3.2.3. Static wetting test

In addition, the contact angles for PTFE and C-PTFE membranes after static wetting treatment with DI water, SDS solution and NaCl solution containing SDS, respectively, were also measured with a series of solutions as droplet solutions in contact angle measurement to probe the effect of wetting agent on the hydrophobicity/hydrophilicity of the PTFE and C-PTFE membranes. The results were shown in Fig. 10. It can be observed that the contact angles for PTFE membrane challenged by SDS solution or NaCl solution containing SDS were lower than those treated by DI water, no matter what the droplet solutions were employed in the

1 contact angle measurement. By contrast, the contact angles of C-PTFE membrane
2 significantly increased after static wetting challenge with SDS solution or NaCl
3 solution containing SDS compared to the results with DI water, when testing with all
4 of different solutions as droplet solutions. The phenomenon of decreased contact
5 angles of bare PTFE membrane and increased contact angles of C-PTFE membrane
6 after wetting treatment is consistent with the results in Table 3 obtained by
7 challenging membrane via DCMD experiment. It means that, being opposite to the
8 case of bare PTFE membrane, when wetting agents exist in wastewater or on the
9 C-PTFE membrane surface, the membrane surface will convert to more hydrophobic
10 one during wastewater treatment. This can be explained by the proposed array posture
11 of wetting agent molecules on membrane surface in Fig. 8. Furthermore, from Fig. 10
12 (b), it can be observed that, for C-PTFE membrane challenged by SDS solution or
13 NaCl solution containing SDS, the contact angles measured with NaCl solution
14 droplet were slightly lower than those measured with DI water droplet. This should be
15 related to ionic interaction of salt with $C_{12}H_{25}O_4S^-$ which enhances the transfer of salt
16 solution to membrane surface. However, with the addition of ethanol or SDS into the
17 salt solution, the situation becomes relieved with the contact angle being increased.
18 This further verifies that the wetting agents act to impede the contact of water
19 molecules with hydrophilic membrane surface and thereof decreased its hydrophilicity.
20 It is interesting that in case of hydrophobic pristine PTFE membrane, the wetting
21 agent in wastewater decreased the hydrophobicity of membrane, leading to membrane
22 wetting, while as for hydrophilic C-PTFE membrane, the hydrophilicity of membrane

was decreased, which enable the stable performance of membrane. Therefore, it is obvious that the adsorption of the wetting agents on the C-PTFE surface functions to adjust the hydrophilicity/hydrophobicity of membrane and prevent serious water adsorption and solution into membrane to induce membrane wetting. Moreover, it is definitely that the thin dense hydrophilic layer can effectively keep bulk water as well as the wetting agent from reaching the hydrophobic surface, thus preventing the membrane wetting and avoiding penetrating effect as observed for PTFE membrane.

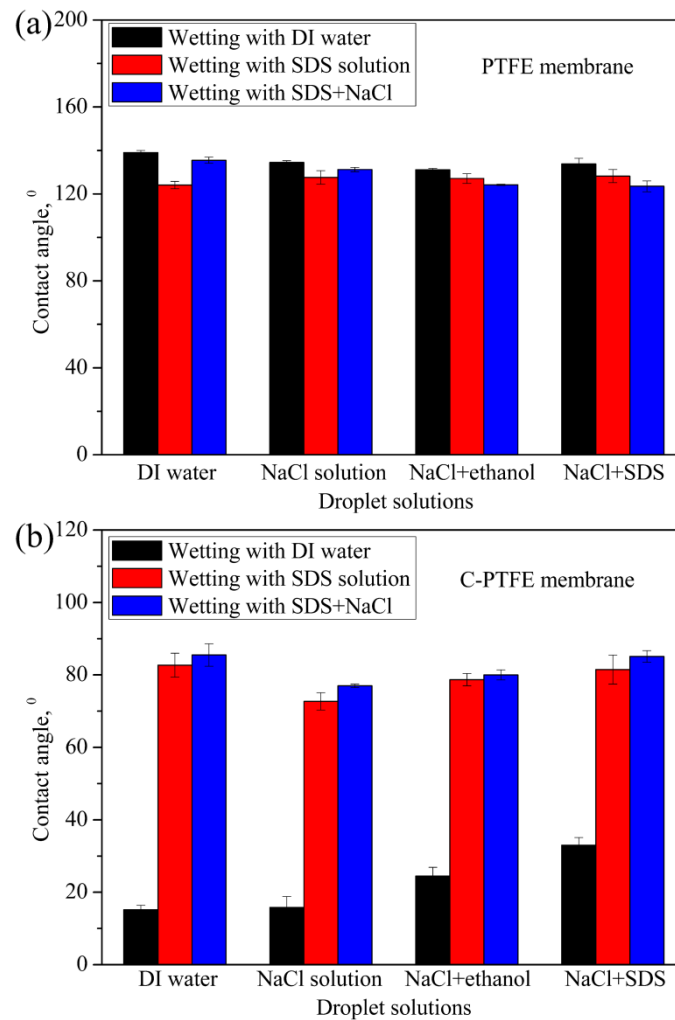


Fig. 10. Contact angles of (a) PTFE and (b) C-PTFE membranes after the static wetting experiments.

3.3. Long term performance

1 To investigate the long-term stability of MD process for the wastewater treatment,
2 the DCMD experiments with a 90 h period for the bare PTFE membrane and C-PTFE
3 membrane were performed with feed containing 2 g/L NaCl and 40 mg/L SDS. Fig.
4 11 shows how the normalized water flux (J/J_0) and permeate electrical conductivity
5 (EC) change with time in the long-term experiment. For the PTFE membrane, the EC
6 increases significantly and a constant steady-state EC curve slope of 2.09 is reached
7 after 25 h. The J/J_0 decreases slightly and jumps rapidly after 50 h. The wetting
8 behavior can start through the larger pore mouths spontaneously while water would be
9 gradually driven to the narrowest pores by capillary forces, eventually inducing partial
10 wetting¹⁰. This can explain the membrane wetting and the consequent increase of
11 DCMD flux in the long-term experiment. Eykens et al.³⁸ also reported the gradual
12 partial pore wetting of PTFE membrane by the surfactant with feed solutions
13 containing SDS in the long-term experiment (3 days). Meanwhile, the “water bridges”
14 formed by the membrane wetting in DCMD process will allow the transportation of
15 solutes to the permeate side, leading to the worsening of distillate quality. By contrast,
16 the J/J_0 for commercial dual-layer PTFE membrane is stable and the increase of EC is
17 slight and close to only 20 $\mu\text{S}/\text{cm}$ after the long-term experiment. Its slope of the EC
18 curve after 25 h is only 0.26. It means that the commercial dual-layer PTFE
19 membrane has excellent anti-wetting property and can be applied for the wastewater
20 treatment containing low surface tension substances. In addition, it should be noted
21 that the water flux of C-PTFE membrane is lower than PTFE membrane. This is
22 related to its higher thickness than PTFE membrane as shown in Table 1, smaller pore

size as shown in Fig. 4, and also the transport resistance from the polyurethane hydrophilic layer with much smaller pores. The thickness of the hydrophilic layer of the C-PTFE membrane is 14 μm which still has much space to be decreased. So it is expected the dual-layer membrane will be more promising for application when the membrane thickness especially the hydrophilic layer thickness is decreased in the future effort.

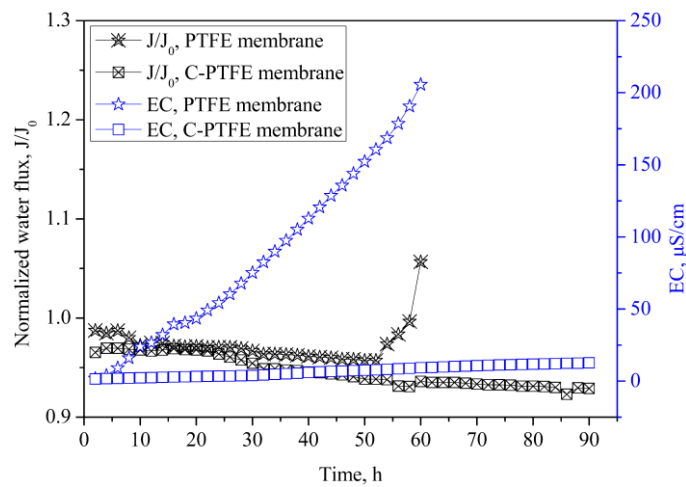


Fig. 11. Long-term experimental results for 2 g/L NaCl solutions containing 40 mg/L SDS at 50 °C and 10 °C of feed and permeate inlet temperatures, respectively, and 450 mL/min of feed and permeate flow rates.

4. Conclusions

In this study, commercial C-PTFE with a dense polyurethane layer coating on the surface of PTFE substrate membrane was evaluated and compared with bare PTFE membrane to investigate its anti-wettability and applicability of treating wastewaters containing organic solvent or surfactant in direct contact membrane distillation process. High water recovery with high temperature resulted in easier wetting of the PTFE membrane. By contrast, the C-PTFE membrane showed stubborn anti-wetting

1 properties. The results of the liquid entry pressure (LEP) measurement, pressurized
2 filtration experiment, water uptake test, and water contact angle measurement all
3 indicate the adsorption mechanism of membrane wetting and anti-wettability which
4 are ascribed to the interaction between the wetting agents and membrane surface. It is
5 deduced that, as for C-PTFE membrane, the hydrophobic moiety of the surfactant is
6 repelled by the hydrophilic layer of membrane to face aqueous feed solution, and
7 therefore, the dense hydrophilic layer could keep organic solvent and surfactant from
8 reaching the hydrophobic layer of the C-PTFE membrane to avoid membrane wetting.

9 The long term stability experiment further confirms that the membrane wetting
10 due to the reaching and adsorption of organic solvent or surfactant on hydrophobic
11 PTFE membrane can be effectively prevented by coating a dense hydrophilic
12 composite layer on membrane surface. This study indicates that the application of
13 hydrophilic/hydrophobic dual-layer membrane in MD process is a feasible way for the
14 wastewater recycling and treatment. The membrane with a thinner hydrophilic layer is
15 expected to be extremely competitive in improving water flux of membrane for MD
16 process.

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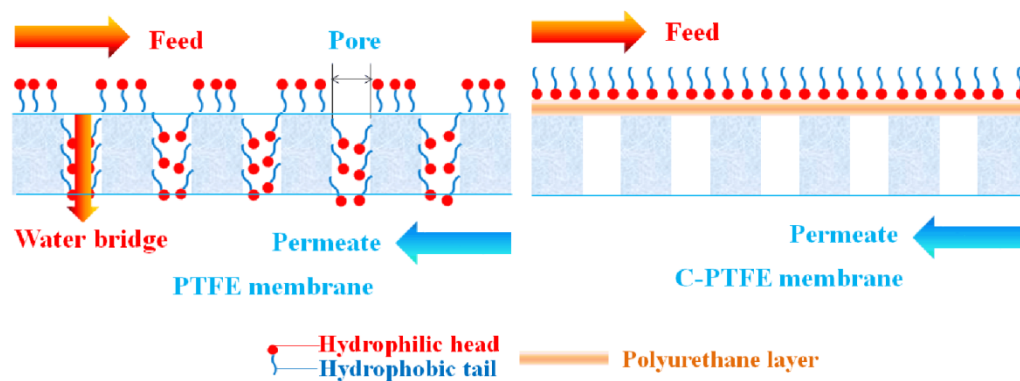
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