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Application of superomniphobic electrospun membrane for treatment of real produced water through membrane distillation

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HIGHLIGHTS

- Modified nanofibrous membrane was fabricated through chemical vapor deposition.
- Superhydrophobic and superoleophobic surface was developed for MD.
- The modified membrane had an excellent antiwetting and antifouling property.
- High salinity produced water from hydraulic fracturing process was treated.
- The modified membrane exhibited high separation efficiency with good regeneration.

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ABSTRACT

A superomniphobic polyvinylidene fluoride (PVDF-F) membrane was fabricated through electronspinning to obtain an excellent antiwetting and antifouling property for the effective and efficient treatment of real produced water. Compared with pristine PVDF and hydroxyl functionalized PVDF (PVDF-O) membrane, PVDF-F membrane had a larger pore diameter, while its pure water flux was found to be lower than both. Neither liquids with high surface tension (water, ethanol) or low surface tension (sodium dodecyl sulfate (SDS) as surfactant, mineral oil) could wet the PVDF-F surface even up to 3 min of contact. During membrane distillation (MD) of 3.5 wt% of aquoues NaCl solution, PVDF-F could withstand 0.4 mM SDS solution without any wetting as seen from the conductivity of the permeate, which was not the case for the PVDF and PVDF-O membranes. After 18 h of MD operation using produced water, a significantly thick fouling layer was found on the PVDF and PVDF-O membranes containing $Ca_3(PO4)_2$, $Sr_3(PO_4)_2$ and $Mg_3(PO_4)_2$. However, PVDF-F had a very thin and reversible organic fouled layer, causing only 40% reduction in permeate flux and with a low permeate conductivity of 20 μS cm^{-1}. This layer was easily removed by cleaning using distilled water and 80% of the flux was recovered. On the 2nd and 3rd MD cycle, the reduction in permeate flux was within 10%. The superomniphobic PVDF-F nanofibrous membrane was run for three successful consecutive MD cycles during produced water processing without any significant fouling as well as wetting.

1. Introduction

To meet the increasing demand for energy, oil industries are exploring non-conventional sources of crude oil [1]. During hydraulic fracturing to extract crude oil and gas, water is injected to the well under pressure in order to provide suitable and commercially viable path for

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crude oil to come out to the surface [2,3]. This operations generate lots of produced water with high total dissolved solids and total organic content (polar or non-polar compounds), and total suspended solids [4]. Therefore, treating the produced water is mandatory not only for environmental concerns, but also for effective reuse of water [5,6].

Membrane based technology provides effective, environmentally benign, low energy, commercially viable, and adoptable technique to treat produced wastewater [7–10]. Among the membrane processes, direct contact membrane distillation (DCMD) is a promising separation technique because of its highly efficient and selective process for desalination. The driving force is based on the temperature gradient between feed and permeate side [11–14]. However, during the treatment of produced water a significant deterioration in membrane performance has been found due to membrane fouling and membrane wetting [15–17]. Polar and non-polar organic compounds and large quantity of salts in produced water interact with the membrane surface leading to membrane scaling and reversible/irreversible membrane fouling. Therefore, researchers have explored the possibility of modifying the membrane surface to achieve desirable performance.

Surface modification of MD membranes have been investigated previously by several approaches. Introducing hydrophilic moieties such as HEMA and EDA on the surface of a hydrophobic membrane reduced the fouling tendency [18,19]. Incorporating zwitterionic polymer or grafting poly (ionic liquid) brushes on hydrophobic membrane surface has been employed to improve antifouling property [20]. Recent investigations revealed enormous interest on the fabrication of MD membrane with very low surface energy, superhydrophobic, and omniphobic surface in nature [21,22]. This omniphobic membrane not only repels the water molecules, but also exhibits almost no interaction with oil, ethanol and even surfactant solution. On the other hand, this superomniphobic membrane surface significantly improves the antiwetting properties of membranes and moreover improves the antifouling characteristics due to lowered interactions.

Several studies have reported the modification of hydrophobic MD membranes to enhance the performance and antifouling properties. For example, Lin et al. [23] reported the fabrication of an omniphobic surface on hydrophilic glass fiber membranes through impregnation of silica nanoparticles followed by fluorination and polymer coating to improve the antiwetting and antifouling properties when treating produced water. Lu et al. [24] fabricated electrospun PVDF and fluorinated-decyl polyhedraloligomeric silsesquioxane based omniphobic membranes. Their modified membrane exhibited a high-water contact angle and a non-interacting surface in the presence of low surface tension liquids during processing of industrial wastewater. The direct surface functionalization of PVDF membrane by long-chained fluorododecyltrichlorosilane resulted in vigorous buds to intertwined fillets, which provided a robust barrier to low-surface-tension liquid penetration [25].

Wang et al. [26] demonstrated the tradeoff between the permeability and wetting of PVDF membrane by suitable coating with heptadecafluoro-1,1,2,2-tetrahydrodecyl trichlorosilane to form a particle-free monolithic omniphobic membrane. Qing et al. [27] modified PVDF nanofibers through coating of polydopamine anchored hierarchical nanofin structures for MD. The modified PVDF nanofiber exhibited a superantiwetting property, that could also resist mineral oil during MD. Boo et al. [22] reported omniphobic fluoroalkylsilane coated PVDF membrane for desalination of shale gas produced water by MD. Organosilane functionalized polyvinylidene fluoride-*co*-hexafluoropropylene and ZnO nanoparticle coated PVDF membrane was omniphobic and had a low surface energy. Furthermore, the modified MD membrane exhibited superior anti-wetting/anti-fouling characteristics with more than 99% salt rejection during desalination of low surface tension oily seawater streams [28]. The heat-pressing of electrospun nanofibrous PVDF membrane with subsequent dip coating in Teflon AF 2400 solution resulted in robust slippery omniphobic MD membrane. Moreover, it achieves antiwetting property by its omniphobic nature and suppressed scaling due to its 'slippery' surface [29].

Electrospun membranes exhibited better MD performance compared to flat sheet membrane because of their large degree of controllable porosity, high surface roughness, high surface to volume ratio, and a reentrant structure [30,31]. A large variety of hydrophobic polymer like polytetrafluoroethylene (PTFE), polyvinylidene difluoride (PVDF), and polydimethylsiloxane (PDMS) can be used for preparation of electrospun membranes with the desired size, shape, and thickness. The active layer can also be fabricated on the porous support to tune the membrane surface properties.

In view of this, the present study deals with the fabrication of superomniphobic nanofibrous PVDF membrane having fluorosilane on the membrane surface. Its potential application was explored for processing of produced water from the petroleum industry. Moreover, its efficacy in regeneration and sustainability were also studied. The modified membrane not only showed excellent antiwetting property, but even after 24 h of MD operation with produced water only marginal reversible organic fouling was observed, which is easily washable. Its antiwetting characteristics were demonstrated for water as well as low surface tension surfactant solution. It could resist 0.4 mM sodium dodecyl sulfate (SDS) solution during MD operation.

2. Material and methods

2.1. Materials

All chemicals were ACS reagent grade used without any purification. Powder form poly (vinylidene fluoride-*co*-hexafluoropropylene) (PVDF-HFP), tetraethyl orthosilicate (TEOS), ammonium hydroxide solution ($NH_3{\bullet}H_2O$), and sodium chloride (NaCl) were purchased from Sigma-Aldrich (St. Louis, MO). PVDF Kynar 761A was provided by Membrane Science Inc., Hsinchu, Taiwan. Sodium hydroxide (NaOH), dimethylformamide (DMF), and SDS were purchased from VWR (Atlanta, GA). Trichloro(1H,1H,2H,2H-heptadecafluorodecyl)silane (TFS) (TCI America) was used for fluorination of the membrane.

2.2. Fabrication of pristine and modified electrospun PVDF membrane

A lab-scale electrospinning instrument was utilized for the fabrication of the electrospun nanofibrous membranes. The syringe pump (Model No: NE-1000) was procured from New Era Pump System Inc., USA. The power supply was procured from Gamma High Voltage Research Inc., USA. The collector drum was purchased from Falco Co., Ltd., Taiwan. The horizon reciprocating stage was purchased from Membrane Science Inc., Taiwan. A PVDF-HFP (8 wt%) solution was taken in a mixture of DMF and acetone with relative composition 7:3 by continuous stirring for a duration of one day at 315 K. After overnight degassing, the solution was placed into the syringe of the electrospinning instrument installed with a stainless-steel needle. The flow rate was optimized at 1 $mL{\bullet}h^{-1}$, whereas the applied voltage was kept constant at 18 kV. The distance between the needle and the Al foil collector was 15 cm. The spinning rotation speed was optimized to 145 rpm. The membrane was electrospun for 9-h and subsequently collected from Al foil. Afterwards, it was air and vacuum dried to remove the excess solvent. The pristine membrane was denoted as PVDF.

Hydroxyl functionalyzed PVDF (PVDF-O) membrane was prepared similarly with the pristine PVDF membrane. Aside from that, the PVDF-O solution was electrospun on top of the electrospun PVDF support. Herein, the PVDF support and the PVDF-O were spun for 5 h and 4 h respectively. The total electrospinning time was 9 h, which was similar to the unmodified membrane. To obtain the PVDF-O solution, the PVDF-HFP powder was first hydrolyzed using NaOH. Specifically, a mixture containing 761A PVDF powder, 30 g of NaOH and 100 g of water was stirred at 343 K for 3 h. Afterwards, the modified powders were rinsed several times using deionized (DI) water until the pH remained unchanged. Then, these powders were oven dried for 48 h before use.

The superomniphobic PVDF (PVDF-F) membrane was fabricated through fluorination using TFS. Fig. 1 illustrates the schematic diagram for fabrication of electrospun membranes. Briefly, a solution containing 4 mL of TEOS, 20 mL of 8% PVDF-O (precursor solid for fabrication of PVDF-O membrane as discussed above) was electrospun for 4 h on top of PVDF support. Afterwards, the membrane and NH_3•H_2O solution (in petri dish) were both placed inside a vacuum oven at 90 °C. This would result in the chemical vapor deposition on the active site of the membrane to form surface hydroxyl functionality. Another stage of chemical vapor deposition was performed at 100 °C inside the vacuum oven in the presence of TFS solution. This was to convert the surface functionality to fluoro functionality as shown in scheme.

2.3. Membrane characterization

Prior to membrane characterization, all the membranes were thoroughly washed with DI water and dried overnight. Fourier Transform Infra-Red (FTIR) spectroscopic investigation was carried out to investigate the modification in functional groups on the surface of the membranes using FTIR spectrometer in ATR mode, Perkin Elmer Spectrum 100 FT–IR procured from Perkin Elmer, USA. Scanning Electron Microscopic imaging was employed to understand the surface morphology of and cross-sectional view of the membranes surface before and after use for MD (FESEM S-4800, procured from Hitachi Co., Japan). The contact angles of different liquids on these membrane surfaces were investigated to understand the interaction of the liquids with the surface using the instrument for measuring contact angle having model No. OCA15EC procured from Future Digital Scientific, USA.

2.4. Membrane performance

MD was performed using a set up with a capacity to process 1 L feed solution kept at 60 °C by a heating mantle, while the temperature of the permeate side was maintained at 20 °C using an external chiller procured from PolyScience, USA. The permeation side containing 1 L of distilled water was kept on a computer controlled analytical balance procured from Mettler Toledo, Columbus, USA. After each finite time, the balance would record the weight on the permeate side and by monitoring the weight change for known time and then the flux was calculated. The effective surface area for the membrane was 8 cm^2. The conductivity of the permeate side was measured using a conductivity meter procured from VWR, USA. The custom-made MD module made from polycarbonate was used. Spacers with 2 mm deep channels made up of polycarbonate procured from XN4510, Industrial Netting, Minneapolis, USA were employed as mechanical support for the membrane sandwiched between the polycarbonate slabs. Two gear pumps were used on the feed and permeate side in opposite direction having a speed of 0.5 L min^{-1}. These pumps were procured from Masterflex I/P, Cole Parmer, Vernon Hills, USA. The flux (J) was calculated as volume of the permeate passed through the unit effective area of membrane in unit time as follows (Eq. (1)).

$$J = \frac{V_P}{A \times t} \tag{1}$$

$$R(\%) = \left(1 - \frac{\frac{V_P \times C_P}{J \times A \times t}}{C_f}\right) \times 100 \tag{2}$$

where, V_p is the volume of permeate, A is effective surface area and t is the time of MD operation.

The rejection, R, was calculated using Eq. (2). C_P is the salt concentration in the permeate, and C_f is the salt concentration in the feed.

2.5. Produced water analysis

The produced water used in the present case was characterized in Arkansas Water Resources Center, University of Arkansas and the results were given in Table 1. Prior to MD operation the produced water was

Table 1
Quality of produced water.

Parameter	Number	Unit
TDS	36,714.28	mg L^{-1}
TOC	140.8	mg L^{-1}
TSS	62.3	mg L^{-1}
Turbidity	49.1	NTU's
pH	6.0	–
Conductivity	6100	μS/cm

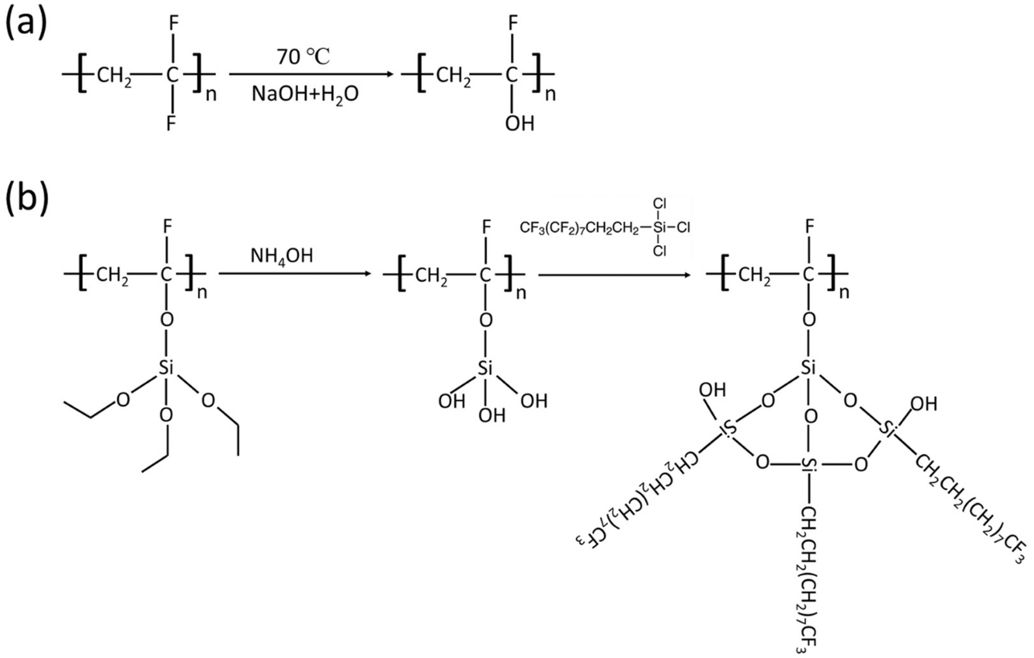

Fig. 1. (a) Hydrolysis reaction of PVDF to PVDF-O polymer and (b) fabrication of superomniphobic PVDF-F membrane through chemical vapor deposition (CVD).

heated at 60 °C and the feed volume was 500 mL. All the membranes were initially tested with short term operation period (18 h). The membrane with best performance was then challenged by repeated MD runs with 24 h operation time for three consecutive cycles.

3. Results and discussion

3.1. Physicochemical properties of the nanofibrous membranes

FTIR spectroscopic analysis was carried out to understand the nature of the functional groups present on the surface of the nanofibrous membranes (PVDF, PVDF-O and PVDF-F). Fig. 2 reveals that the surface functionalities of all three membranes were not the same. The change in relative intensity, appearance of new peaks and shifting of existing peaks indicates the successful modification of the membrane surfaces. PVDF had a peak at 1180 cm^{-1}, which was attributed to symmetrical stretching of CF_2 group [17]. The peak at 890 cm^{-1} was ascribed to the mixed mode of $–CH_2$ rocking and CF_2 asymmetric stretching in β or γ phase [32,33]. The peak ~1400 cm^{-1} corresponded to plane bending or scissoring of CH_2 groups. The small peak ~1250 cm^{-1} was ascribed to the presence of γ phase of PVDF [32]. The peak at 1070 cm^{-1} was from the bending of C-C-C bonds. PVDF-F membrane had a new peak at ~1140 cm^{-1}, indicating the presence of silanol groups on the membrane [34]. The peaks at 807 cm^{-1} and 956 cm^{-1} are due to the symmetric and asymmetric stretching frequencies for Si-O-Si moiety in PVDF-F membrane [35], whereas the peak at 1091 cm^{-1} is attributed to Si-O-C moiety. Furthermore, the peaks at 1250 cm^{-1} and 934 cm^{-1} in PVDF-F membrane are ascribed to C-O-C and Si-OH moiety [36].

Table 2 lists the elemental composition of the membranes from the EDX analysis before and after MD operations for processing produced water. The EDX analysis of PVDF-F membrane was also carried out after cleaning with DI water to understand the nature of fouling and washing efficacy. The base PVDF membrane was found to have 49.81% of C peak and 50% of F peak. As for PVDF-O membrane surface, additional peak for O atom was observed with 0.31% of composition, while no significant modification in relative compositions of C and F was observed after hydrolyzing the PVDF. In the case of PVDF-F membrane, C occupancy was drastically reduced to 32.53%, whereas a significant enhancement in F occupancy was observed up to 58.9%. For Si and O, the PVDF-F membrane only had 3.97% and 4.61%, respectively. This confirmed the desired modification on the PVDF surface and revealed the fact that the surface density of modification in PVDF-O membrane was less compared to that of PVDF-F membrane.

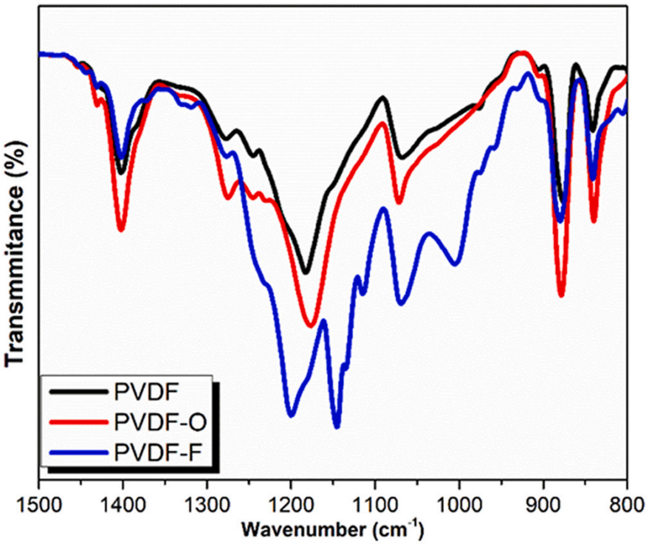

Fig. 2. FTIR spectra of PVDF, PVDF-O and PVDF-F membranes.

Table 2
Elemental composition of PVDF, PVDF-O and PVDF-F membranes before and after MD cycles using produced water from EDX analysis.

Element	Fresh membranes			After short-term run			After a long-term run
	PVDF	PVDF-O	PVDF-F	PVDF	PVDF-O	PVDF-F	PVDF-F
C	49.81	50.46	32.53	20.54	19.08	34.82	32.77
O	–	0.31	4.61	39.72	33.18	3.94	3.94
F	50.19	49.23	58.9	–	–	58.07	51.83
Si	–	–	3.97	–	1.73	3.17	3.32
Mg	–	–	–	1.76	1.73	–	–
P	–	–	–	12.85	15.46	–	–
Ca	–	–	–	21.72	26.69	–	–
Sr	–	–	–	3.42	3.85	–	–
Zr	–	–	–	–	–	–	8.15

Fig. 3 shows the morphology of the pristine and modified membranes. There was a clear difference in surface morphology after modification. The PVDF-O membrane had a thicker fiber than that of PVDF. PVDF-F membrane had a web-like network on each fiber. The thickness of the PVDF, PVDF-O, and PVDF-F membranes was 115 μm, 140 μm, and 135 μm, respectively.

3.2. Membrane hydrophobicity and antiwetting behavior

Fig. 4(a) depicts the contact angles of water, SDS solution, ethanol and mineral oil on the surface of PVDF, PVDF-O and PVDF-F membrane. The initial contact angles for water and the SDS solution on PVDF were found to be similar (137 to 142°), indicating a hydrophobic surface. Even after 180 s, the contact angles for water and SDS on PVDF remain the same. When ethanol and mineral oil were dropped on the PVDF surface, their contact angles were similar (21 to 23°). After 30 s, the droplet disappeared on the surface of PVDF, suggesting a strong hydrophobic-hydrophobic interaction between the liquid (i.e. ethanol and mineral oil) with the PVDF surface. PVDF-O membrane displayed a similar result to the PVDF membrane. However, the droplet for mineral oil was still present after 30 s in contact with the surface of PVDF-O, and then disappeared at 60 s. PVDF-O had less hydrophobic interaction with the liquids because of the presence of some oxygen groups on the membrane surface. Consequently, it took more time for the mineral oil to disappear on the surface of PVDF-O membrane than that on the PVDF membrane. It was also noted that, the water contact angle did not change, revealing no hydrophilic interaction was induced.

The fluorination of the PVDF membrane (PVDF-F) changed the surface property to superomniphobic. PVDF-F membrane had a water contact angle of more than 150°, indicating its superhydrophobicity. When SDS solution, ethanol, and mineral oil were contacted with the membrane surface, their contact angles remained the same for 180 s. These results revealed that the surface of PVDF-F membranes significantly reduced its interaction with water, zwitterionic surfactants, polar aprotic solvent like ethanol and even large molecular weight organic compound (mineral oil). Furthermore, surface of PVDF-F membrane acquired super antiwetting characteristics and was superomniphobic in nature as it exhibited antiwetting properties against polar solvents (water, ethanol) as well as low surface tension liquids (SDS, mineral oil etc.).

The antiwetting behavior for PVDF, PVDF-O and PVDF-F membranes was monitored using different concentration of SDS as shown in Fig. 4 (b). The initial MD experiment was carried out using 3.5 wt% NaCl solution for a duration of 0–50 min. In the next 50 to 100 min, the feed solution was converted to 3.5 wt% NaCl solution with addition of 0.1 mM of SDS. The next 50 min duration i.e. 100–150 min, the SDS concentration was raised to 0.2 mM. In the next 50 min duration, i.e. from 150 min to 200 min, the SDS concentration was further increased to 0.4

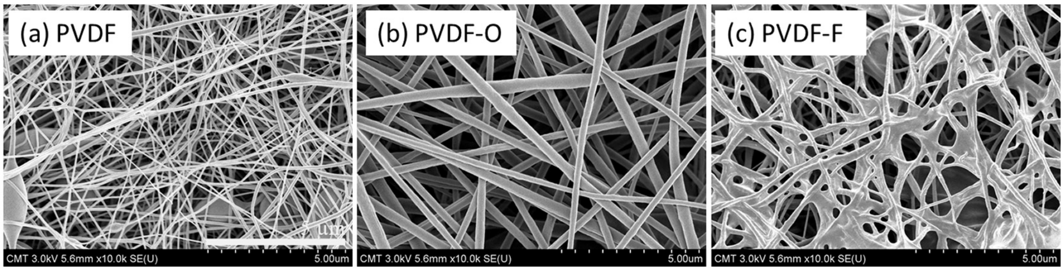

Fig. 3. SEM images of (a) PVDF; (b) PVDF-O and (c) PVDF-F membranes.

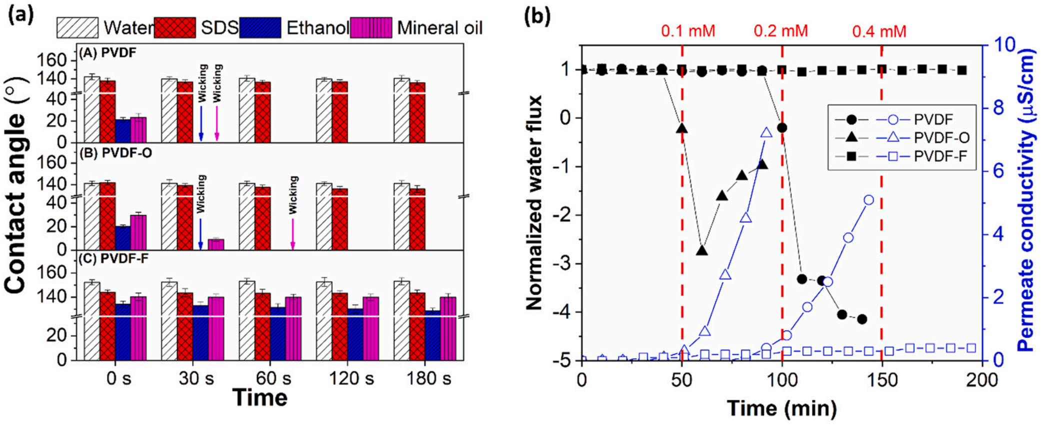

Fig. 4. (a) The dynamic contact angles of water, SDS, ethanol and mineral oil on the PVDF, PVDF-O and PVDF-F membrane surfaces. (b) Monitoring of normalized water flux and the conductivity of the permeate solution under MD operation at various concentration of low surface tension surfactant—SDS solution. The initial vapor flux of PVDF, PVDF-O, and PVDF-F were 20.4, 26.5, 17.0 L m^{-1} h^{-1}, respectively.

mM. Normalized flux was calculated by dividing the time-dependent permeate flux with the initial permeate flux without SDS. For pristine PVDF membrane, there was no change in normalized water flux for the first 90 min. In 100th min, the normalized water flux dropped to almost zero followed by negative normalized water flux, indicating wetting of the membrane. This was further confirmed by the conductivity of the permeate side. From 0 to 100 min, the conductivity in permeate was almost zero, revealing that the permeate has good quality of water. However, more than 100 min, the permittivity suddenly increased, indicating wetting of the membrane. After 140 min, the permeate side has high conductivity of 5 μS•cm^{-1}.

The PVDF-O membrane wet earlier than the other membranes. For up to 40 min contact of the feed with the PVDF-O, there was no change in normalized water flux or conductivity. However, from 50 to 60 min, the normalized water flux decreased from −0.23 to −2.75. Up to 90 min, the normalized water flux reached −0.97, suggesting that the membrane was unstable (feed containing SDS) for a long period of time. Moreover, the permeate conductivity of PVDF-O membrane reached a maximum of 7.2 μS•cm^{-1}after 90 min. It could not sustain even 0.1 mM of SDS solution. However, the antiwetting property for virgin PVDF membrane was found to be better. It could sustain at least up to 0.1 mM of SDS solution. The fluorinated PVDF-F membrane had a superomniphobic surface. For a long period of time (200 min), PVDF-F membranes maintained a constant normalized water flux and conductivity as well as high concentration of SDS (0.4 mM). Thus, the PVDF-F membrane was ideal for MD process.

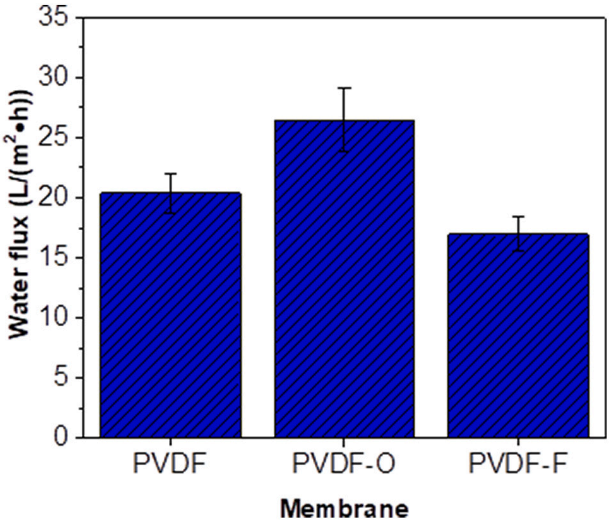

Fig. 5. The pure water permeation flux for PVDF, PVDF-O and PVDF-F membranes.

3.3. Intrinsic membrane performance

Fig. 5 compares the pure water flux of PVDF, PVDF-O and PVDF-F membranes. The feed and permeate temperature were kept at 60 and 20 °C, respectively. Using a feed solution of 3.5 wt% of NaCl solution, pristine PVDF membrane had a water flux of 20 L•m^{-2}•h^{-1}, whereas PVDF-O had a water flux of 25 L•m^{-2}•h^{-1}. The membrane LEP and mean pore size is shown in Table S1. Because PVDF-O (1.60 μm) membrane had a larger mean pore radius than that of PVDF (0.44 μm) membrane, its water flux was higher. However, PVDF-F membrane had a mean pore radius in between that of PVDF and PVDF-O membrane. The lower flux of PVDF-F (16 L•m^{-2}•h^{-1}) was probably because of its surface properties. The liquid entry pressure (LEP) was estimated for all these three membranes. Pristine PVDF membrane had LEP of 113.8 kPa, which was significantly reduced for the PVDF-O membrane 84.8 kPa. The presence of hydroxyl groups on the surface might be responsible for such a reduction. However, the LEP for PVDF-F membrane was estimated as 132.4 kPa. Such a high LEP was an indication of superoleophilic membrane surface. The behavior of non-interacting surface of PVDF-F membrane corroborated with results obtained by dynamic water contact angle measurement. The reduction in water permeation flux compared to unmodified and modified PVDF-O membrane might be due to the superoleophilic characteristic of the PVDF-F membrane surfaces. All membranes exhibited more than 99% rejection of NaCl, indicating the hydrophobic nature of the membranes. Huang et al. [37] reported that the fabrication of anti-scaling PVDF membrane by liquid like surface modification. They demonstrated that the enhancement in surface roughness of the membrane pore walls increased the probability water molecules collide with the pore walls. This would provide an additional mass transfer resistance, resulting in reduction of water flux through the membrane. In their modified membrane, the surface roughness of the membrane pores was found to remain unchanged, thus, a higher water flux was achieved compared to the pristine membrane.

3.4. Processing real produced water

The real produced water was characterized in Table 1 for total dissolved solid (TDS), total organic content (TOC), total suspended solid (TSS), turbidity, pH and conductivity prior to MD. The TDS was estimated as 36.71 g•L^{-1}, while TOC was found to be 140.8 mg•L^{-1}. The overall pH was ~6, indicating a slightly acidic nature of the feed. The feed turbidity was determined as 49.1 NTU's, while TSS was found to be 62.3 mg•L^{-1}. The feed solution also exhibited a conductivity of 6.1 mS•cm^{-1}. These results revealed that produced water has both ionic and organic solutes. Hence, it might have significant effect on the MD performance after a finite time of operation due to fouling on the membrane surface.

Fig. 6(a) reports the performance for PVDF, PVDF-O and PVDF-F membranes during the processing of real produced water. The normalized water flux was found to decrease significantly during the initial 8 h of operation for both PVDF and PVDF-O membranes. The normalized flux values were decreased to 0.3 at 8 h for both membranes, however, the greater reduction was observed for pristine PVDF membrane.

During the first 0–8 h of operation, the normalized flux values for PVDF membrane were found to be lower than that of PVDF-O membrane. Beyond 8 h, both of membranes behaved similarly. There was a continuous increase in the conductivity in the permeate side for both the membranes. After 18 h of operation the conductivity of the permeate side was 45 μS cm^{-1} for the PVDF membrane, whereas PVDF-O membrane was 38 μS•cm^{-1}. This behavior could be attributed to extensive fouling of PVDF and PVDF-O membranes in presence of real produced water. The MD performance for the PVDF-F membrane was significantly better than PVDF and PVDF-O membrane. After 12 h of MD operation using PVDF-F membrane, there was only 15% reduction of normalized water flux. The normalized water flux became 60% of its original value after 19 h of continuous operation. Furthermore, its permeate conductivity was increased only to 10 μS•cm^{-1} after 8 h of operation; and after 19 h it became 20 μS•cm^{-1}. The results indicated the superiority of the superomniphobic PVDF-F membrane when treating real produced water. The superomniphobicity was responsible for the enhanced antifouling characteristic of the membrane. To understand the nature of fouling, the PVDF-F membrane was cleaned by distilled water and reused, for three consecutive MD cycles.

Fig. 6(b) presents the 3 repeated MD cycles with flushing of DI water between each run. After 24 h of MD operation and subsequent washing with DI water; 80% recovery of normalized water flux was observed. The fouling on the PVDF-F membrane surface might be irreversible in nature, hence the performance deterioration could not be quantitatively recovered. Only 10% reduction in normalized water flux was observed in next 24 h of operation. This time the washing resulted in an almost quantitative normalized flux recovery. This implied that the initial fouling on PVDF-F membrane surface resulted in irreversible fouling. However, once it was done, no further permanent damage was observed. There was also a slow increase in conductivity that was noticed in the permeate side during each MD cycle. After first two cycles of 24 h MD operation, the conductivity of permeate side reached 20 μS cm^{-1}, whereas after 3rd cycle the conductivity became 12 μS cm^{-1}. The results suggest that the PVDF-F membrane could be easily regenerated and reused. Many previous studies indicate that once fouled the membrane is very difficult to regenerate [20,38–40].

Fig. 7 displays the surface cross sectional SEM images of PVDF, PVDF-O and PVDF-F membranes after 12 h of MD operation using real produced water. Among the membranes, PVDF-F membrane had least foulant on the membrane. Its superomniphobic surface helped the membrane prevent attachment of foulants. The PVDF membrane was covered by a thick foulant layer, leading to an unclear image of the PVDF membrane. For PVDF-O, an 8 μm layer of foulant was presented on top of the membrane. Therefore, PVDF-F membrane had good antifouling property. Fig. 8 shows the actual photographic images of the membranes after using the membrane for MD. PVDF and PVDF-O membrane had a very thick dark brown foulants on the surface. However, the extent of fouling for PVDF-O was less compared with PVDF base membrane. In the case of PVDF-F membrane, only marginal deposition of foulant was observed.

The FESEM and actual images of the membranes were corroborated well with the MD performance, revealing that superomniphobic PVDF-F

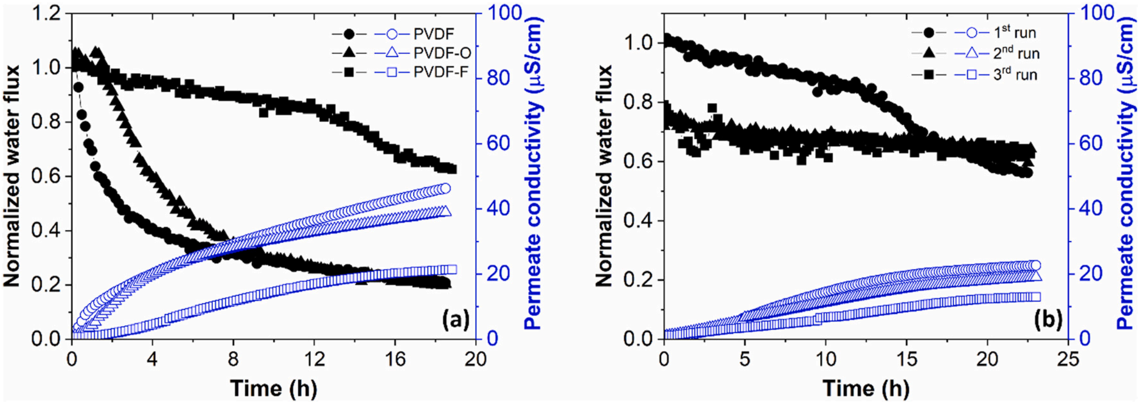

Fig. 6. MD performance using real produced water by (a) PVDF, PVDF-O and PVDF-F membranes for a duration of 18 h. The initial vapor flux for PVDF, PVDF-O, and PVDF-F were 23.7, 28.8, 17.9 L m^{-1} h^{-1}, respectively; (b) Three consecutive cycles by PVDF-F membrane for 72 h of operation. Membrane was flushed using DI water after each run.

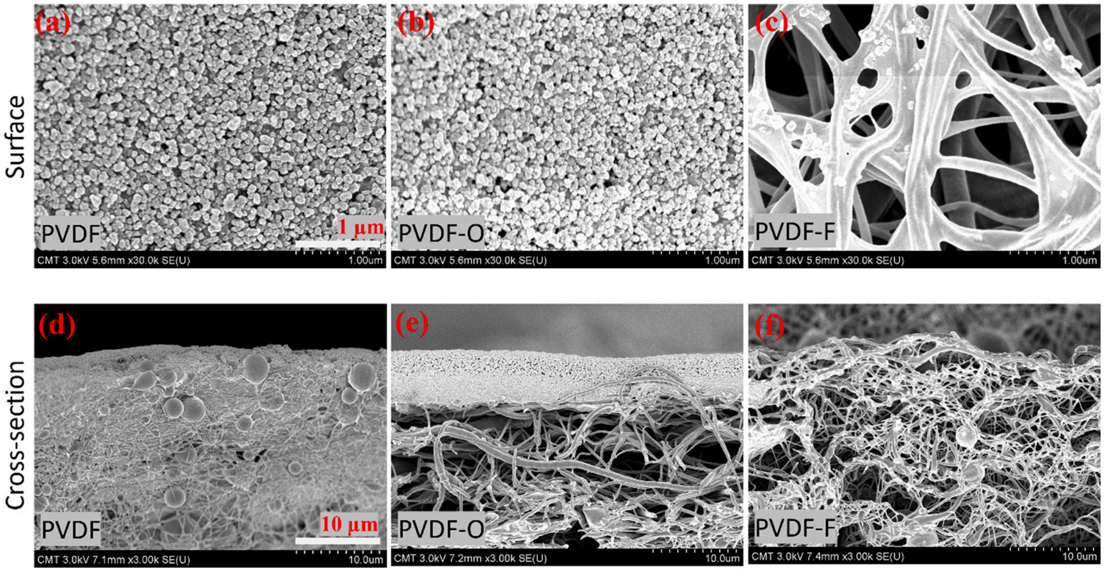

Fig. 7. SEM images for (a) surface view of PVDF; (b) surface view of PVDF-O; (c) surface view of PVDF-F membranes; (d) cross sectional view of PVDF; (e) cross sectional view of PVDF-O; (f) cross sectional view of PVDF-F membranes.

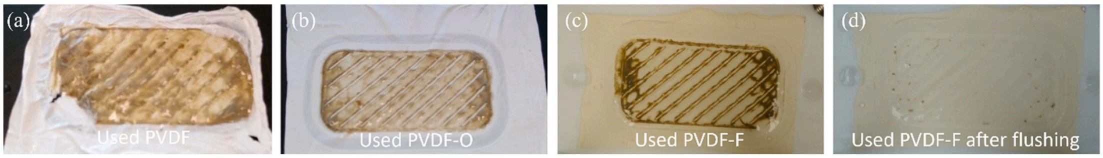

Fig. 8. Digital images of PVDF, PVDF-O, and PVDF-F membrane after 18 h MD operation of produced water.

membrane had superior performance. After flushing the PVDF-F membrane for 30 min (Fig. 8(d)), most of the foulant were disappeared, indicating the good regeneration property of the modified membrane. This visual change also agreed well with the SEM images of the surface as well as of the cross-sectional images. Furthermore, Fig. S1 shows that the PVDF-F membrane did not deteriorate after using again in MD operation for processing produced water. Therefore, PVDF-F had excellent antifouling and regeneration property.

Table 2 tabulates the relative elemental composition of the membranes before and after 18 h of MD operation using produced water. Pristine PVDF membrane had large reduction of C from 49.81 to 20.54%, after short-term run. Furthermore, the F element was completely disappeared, whereas almost 40% of O peak was appeared. Apart from that, 1.76% Mg, 12.85% P, 21.72% Ca and 3.42% Sr were also found in pristine PVDF. This indicates that the fouling layer might predominantly contain $Ca_3(PO_4)_2$, $Sr_3(PO_4)_2$ and $Mg_3(PO_4)_2$ salt. The fouling layer was also thick enough, that F from PVDF completely disappeared. PVDF-O membrane had a similar fouling property with PVDF, with relative composition of 19.08% C, 33.18% O, 1.73% Mg, 15.46% P, 26.69% Ca, and 3.85% Sr. However, a distinct peak of Si (1.73%) appeared on the fouling layer of PVDF-O membrane. This peak was absent in fouling layer of the PVDF membrane. This suggested that, although both PVDF and PVDF-O membranes exhibited similar types of fouling with respect to salt deposition; however, PVDF-O membrane had strong affinity with Si from produced water. In case of PVDF-F membrane, no other element was found, but only ~2% enhancement in C content was observed in fouled membrane, indicating that PVDF-F membrane could not interact with ionic substance. However, a slight fouling from organic matter could not be avoided. After flushing using DI water, the extra C content had disappeared. This revealed that the high efficacy of washing, and the fouled layer deposited on PVDF-F membrane were reversible in nature and can be easily get rid of.

4. Conclusions

Electrospun PVDF nanofibrous membranes were fluorinated through CVD to attain superomniphobic surface for MD of real produced water. PVDF-F membrane exhibited non-wetting property for liquid with high and low surface tension (water, ethanol, SDS, and mineral oil). The PVDF-F membrane could sustain up to 0.4 mM SDS in MD operation without getting wet using 3.5 wt% brine solution. During processing of real produced water, PVDF and PVDF-O membranes showed a drastic reduction in permeate flux and an increased in permeate conductivity due to significant fouling on their membrane surfaces. Ca, P, Mg and Sr were mainly found in the fouled layer. A significant enhancement in antifouling as well as anti-wetting properties could be demonstrated while processing produced water using superomniphobic PVDF-F membrane. The modified membrane sustained 24 h of MD operation with produced water without much fouling on its membrane surface. The PVDF-F membrane could survive for three consecutive MD cycles without significant deterioration in the membrane performance. Therefore, superomiphobic PVDF-F membrane could be potentially used for treating produced water.

CRediT authorship contribution statement

Yu-Hsuan Chiao: Conceptualization, Methodology, Validation, Investigation, Formal analysis, Experiment execution, Writing. **Micah Belle Marie Yap Ang**: Conceptualization, Investigation. **Arijit Sengupta**: Visualization, Investigation, Writing-review & editing. **Yuhe Cao**: Conceptualization, Methodology, Project administration, Supervision, Writing-review & editing. **S. Ranil Wickramasinghe**: Funding acquisition, Writing-review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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