



Review

Omniphobic membranes for distillation: Opportunities and challenges

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ABSTRACT

As an emerging thermal-driven membrane technology, membrane distillation (MD) has attracted immense attention for desalination and water purification. The membranes for MD generally have hydrophobic or superhydrophobic properties to enable vapor permeation without liquid passage (e.g., wetting). However, conventional MD membranes cannot undergo long term stable operations due to gradual wetting in practical applications where the feed solution often contains multiple low-surface tension contaminants (e.g., oil). Recently, omniphobic membranes repelling all sorts of liquids and typically having ultralow surface energy and re-entrant structures have been developed for robust MD to mitigate wetting and fouling. In this paper, we aim to provide a comprehensive review of recent progress on omniphobic membranes. Fundamentals, desirable properties, advantages and applications of omniphobic membranes are discussed. We also summarize the research efforts and methods to engineer omniphobic membranes. Finally, the challenges and future research directions on omniphobic membranes are discussed.

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1. Introduction

Water scarcity has become a major concern in many regions. More than 29% of people in the world have limited access to safe drinking water [1]. Apart from drinking and human (domestic) activities, a wide range of industrial and agricultural activities also require clean water. Thus, it is vital to find cost-effective ways to get fresh water. There are two main methods to produce fresh water: desalination and re-purification of wastewater [2–5]. The water sources, such as wastewater, seawater and brackish water may have: (1) high concentration of dissolved salts or metal ions, (2) oil/surfactants, (3) biological substances, and (4) other chemicals from specific industry [6–8]. Typical water purification methods include reverse osmosis (RO), multi-stage flash (MSF), multi-effect distillation, mechanical vapor compression, ion-exchange and forward osmosis [9–15].

Recently, an emerging membrane technology, membrane distillation (MD), has attracted growing attention [16–19]. MD is a thermally driven process in which a hydrophobic membrane is put between a hot stream (feed) and a cold stream (permeate) [20]. Theoretically, the hydrophobic membrane is not wetted by the feed solution, forming a vapor gap between the two streams. Feed water

on the hot side directly contacts the membrane and evaporates at membrane interface (liquid/vapor); the vapor transfers across the porous hydrophobic membrane and then condenses on the cold side (Fig. 1). Such a driving force is based on the vapor pressure difference induced by the temperature difference across the membrane. MD can operate at relatively mild pressures (~1 atm) and temperatures (30–80 °C) [21]. In addition, the theoretical salt rejection of MD can be up to 100%. Although the energy consumption of MD is higher than that of RO, low-grade heat and solar thermal energy could help minimize the energy cost of MD [22]. Most importantly, MD can deal with challenging solutions with high salinity and/or containing oil and surfactants which cannot be efficiently treated by other desalination technologies [23].

Conventional polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), polypropylene (PP) and polyethylene (PE) membranes have been used for MD [24–26]. These materials show reasonable hydrophobic properties (i.e., low surface energy) and MD performance. However, progressive wetting, fouling and scaling by various (inorganic/organic/biological) contaminants make these membranes ineffective for long-term MD operations. Thus, it is an emerging area in MD to develop novel robust hydrophobic membranes by new fabrication and/or surface engineering techniques. The former method focuses on improving the internal nanostructure of the membrane to enhance the mass transfer, while the latter one aims to enhance the hydrophobicity

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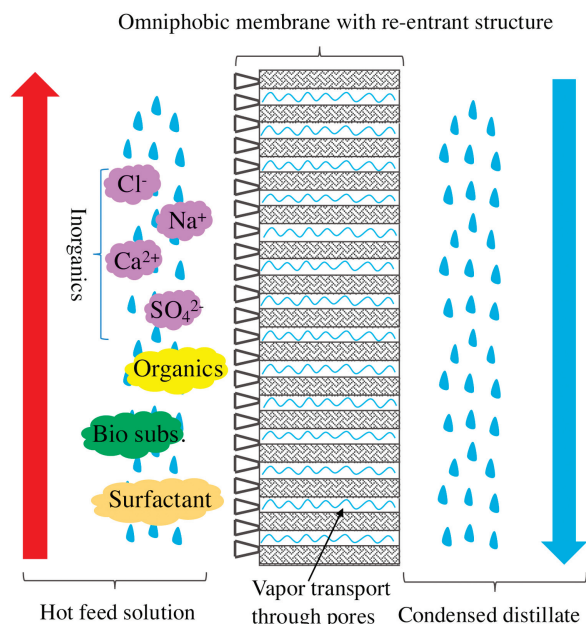


Fig. 1. Schematic diagram of membrane distillation by an omniphobic membrane.

and membrane repellence to a wide range of low surface tension liquids by surface modification.

To address the drawbacks of the “hydrophobic-only” membranes, omniphobic membranes (*i.e.*, repelling all sorts of liquids) have been proposed for MD. Their unique properties, such as re-entrant structures with ultralow surface energy make them repel a wide range of liquids even with low surface tension, exhibiting much better long-term stabilities than conventional hydrophobic membranes during the treatment of complex waste liquids (Fig. 1). Like conventional hydrophobic membrane, omniphobic membranes exhibit underwater oleophilic properties, but their re-entrant structures can effectively prevent the penetration of oil droplets into the membrane pores [27]. Omniphobic membranes provide new opportunities for more robust and stable MD applications compared with conventional hydrophobic membranes [28]. Thus, it is vital to provide an overview of omniphobic membranes in terms of design, modification, wetting and fouling prevention and applications.

In this review, we critically analyze the fundamentals of designing an omniphobic membrane from both parameter consideration and modification strategies. It starts with the fundamentals of wetting and fouling to emphasize the significance of omniphobic membranes and discuss the design perspective by analyzing the limitation of hydrophobic membranes and how omniphobic design helps. Following the theoretical aspect, we discuss the recent development of omniphobic membrane modification and evaluate the performance of omniphobic membrane in anti-fouling and anti-wetting during MD process. Finally, limitations of the omniphobic membrane are discussed and the potential pathways are suggested for enhancing the MD performance in the future.

2. Fundamentals of omniphobic membranes

2.1. Membrane wetting

Omniphobic membranes first came into attention in 2014 [29]. There are two major criteria for the omniphobic membrane: (1)

surface with ultralow surface energy, which can repel almost all sorts of low surface tension liquids and (2) re-entrant structures. Omniphobic membranes are developed to overcome the disadvantages of conventional hydrophobic membranes that are susceptible to wetting.

Wetting is defined as the penetration of feed solution into the membrane pores, which may result in the reduction of salt rejection and the contamination of distillate. It can be explained by liquid entry pressure (LEP) [6,30,31], which is the minimum hydrostatic pressure required to force a liquid to penetrate through pores. The governing equation is

$$LEP = \frac{-2B\gamma_L \cos\theta_0}{r} \quad (1)$$

where γ_L is the liquid surface tension (N/m), θ_0 is the equilibrium contact angle ($^\circ$), r is the effective pore radius (m) and B is a geometric factor that describe the morphology of the membrane pore (for cylindrical pores, $B = 1$). In general, pore wetting occurs when the transmembrane pressure ΔP is greater than or equal to LEP.

Membrane wetting can be either transient or stepwise, depending on the nature of the feed solution [27,32]. In transient wetting, as the pressure exceeds the LEP, the interfaces between the feed, air and the membrane are instantaneously disrupted. A sharp increase of distillate conductivity will be observed. Stepwise wetting happens in the scenario where the feed solution contains amphipathic organics (*e.g.*, surfactants), and the hydrophobic tail will form hydrophobic-hydrophobic interaction with the membrane surface [33]. As the adsorption of surfactants continues, the water/air interface is gradually pushed into the membrane pores since the surface tension and hydrophobicity largely decreases with the exposure of the hydrophilic head on the surface. The propagation is controlled by the kinetics of surfactant adsorption [33]. When the membrane inner pathway is fully filled by surfactants, the concentration of surfactants at the liquid-vapor interfaces increases, lowering LEP. Once the LEP is lower than the transmembrane pressure, the frontier eventually penetrates the membrane. An increase in surfactant concentration is expected to induce faster wetting. When the hydrophobic membrane also has repellence to surfactants, surfactant adsorption and thus pore wetting will be significantly minimized. Therefore, omniphobic membranes are excellent candidates to achieve stable MD performance for treating feed solutions containing liquids of low surface tension. Omniphobic membranes are typically oleophobic to repel a wide range of low surface tension liquids.

Membrane wetting can also be explained from the surface morphology aspect, defined by the Wenzel [34] and Cassie-Baxter [35] models. These two models explain the wetting state of a liquid droplet on a rough surface and the non-wetting scenario on a rough surface, respectively. It is difficult to maintain a stable Cassie-Baxter state especially for a low surface tension liquid as the threshold contact angle (critical angle that transform from the Wenzel to the Cassie-Baxter state [6]) needs to be greater than 90° on most solids [36]. According to the principle of wetting based on morphology, when a liquid contacts with a solid, the net traction on the interface governs the wetting phenomenon. For a surface with concave topography (re-entrant structure), the net traction is pointing upward to prevent a complete wetting on the surface (*i.e.*, the Wenzel State) [37].

In fact, the membranes fabricated today have non-regular textured surfaces, which means that wetting mechanisms of the hydrophobic membranes based on both points of view are still vague. Pore wetting of conventional hydrophobic membranes calls for the development of more robust omniphobic membranes.

2.2. Desirable properties for omniphobic membranes

An ideal omniphobic membrane has exceptional advantages over the conventional hydrophobic membrane. In general, a good omniphobic membrane should have a high water/oil contact angle (CA), a high LEP, high permeability (flux), excellent long-term stable performance and low fouling propensity.

2.2.1. Water/oil contact angle

An omniphobic membrane should be hydrophobic and oleophobic, namely, the water and oil contact angles on the membrane surface should be greater than 90°. Compared with omniphobic membranes, hydrophobic membranes ($CA_{\text{water}} > 90^\circ$) and superhydrophobic membranes ($CA_{\text{water}} > 150^\circ$) do not have the requirements for oil contact angles [38]. In fact, most fabricated omniphobic membranes are superhydrophobic and oleophobic (Table 1), because superhydrophobic and omniphobic membranes have similar surface treatments (e.g., surface fluorination); and re-entrant structures further enhance membrane repellence towards low-surface-tension liquids. Although there are no criteria for omniphobic membranes to achieve superhydrophobicity and/or superoleophobicity, higher water/oil CAs are still desirable for MD applications.

2.2.2. Liquid entry pressure (LEP)

A higher LEP indicates better wetting resistance, as illustrated above. Based on Eq. 1, LEP is generally related to the surface properties (e.g., geometry, surface tension, contact angle) and pore

radius. The surface properties actually dominate the LEP and wetting, since the pore radius has an inverse effect on the permeability, namely, a smaller pore radius leads to a larger LEP but significantly reduces the permeability. In general, hydrophobic membranes have LEPs of 0.5–3.5 bar, while the LEPs of omniphobic membranes are 1.5–5.5 bar (Tables 1 and 2).

2.2.3. Permeability

Permeability represents the ability of a membrane to transfer water vapor across the membrane. It can be described by [20]:

$$N \propto \frac{r^\alpha}{\tau \delta} \varepsilon \quad (2)$$

where N is the molar flux ($\text{mol cm}^{-2} \text{s}^{-1}$), r is the average pore radius (cm), α is used to describe different flow regimes (for Knudsen diffusion, $\alpha = 1$), ε is the porosity, τ is the membrane tortuosity and δ is the membrane thickness (cm).

Some fabrication techniques help enhance the permeability by enlarging pore size while maintaining the mechanical strength of the membrane to prevent wetting. However, omniphobic membranes generally have smaller pore sizes after surface modification (e.g., fluorination), which results in a reduction of flux [39]. Thus, the reduced flux after omniphobic fabrication is a major obstacle to solve. Porosity is influenced by the fabrication method of the substrate membrane. Membranes fabricated by electrospinning generally have larger porosities compared with the membranes prepared by the phase inversion method [40]. From the discussion above, permeability itself is a relatively complex parameter.

Table 1
Recent developments in hydrophobic/superhydrophobic membranes.

Membrane substrate	Modification description	MD type	Mean pore size (μm)	Feed solution	WCA/OCA ($^\circ$)	LEP (bar)	Flux (LMH)	Ref.
PS	Enhanced electrospinning performance with external gas force added ("Electroblowing")	DCMD	0.562	NaCl: 35 g/L	154/-	0.386	~22.59	[59]
PTEE	Mixing with PEO for electrospinning, followed by sintering for decomposition of PEO	DCMD	0.45	NaCl: 35–150 g/L	155/-	2.5	29.1–30.3	[60]
PVDF	A thin PVDF and SiNPs outer layer and a thick porous hydrophilic PVDF-PEG inner layer	DCMD	N/A	Saline water with TDS 154, 220 mg/L	137.6 (Outer); 56.2 Inner/-	N/A	25.41	[61]
PVDF	Repeated layer of PEI and PSS layer (up to 3 times) on the original PVDF substrate, cross linked by GA solution	DCMD	0.0015	0.6 mol/L NaCl solution with SDS gradually added up to 0.4 mmol/L	32.1 $\pm$ 2.5/-	3.08 $\pm$ 0.38	16.7	[62]
PVDF/PTEE	Hybrid nanofibers with cellulose acetate (CA) and silica nanoparticles (SiNPs), followed by fluorination	DCMD	0.35 $\pm$ 0.07	3.5 wt% NaCl with 0.5 mmol/L SDS	155.6 $\pm$ 3.9/120	–	13.6	[63]
Kaolin hollow fiber	Grafting with fluoroalkylsilane (FAS)	DCMD	0.32	NaAsO ₂ solution at concentration of 1000 ppm, with HCl and NaOH added for pH adjustment	145/-	2	25–28	[64]
PVDF	Immersion precipitation with rolling embossing, which is fabricate by abrasive blating	VMD	0.34	Sea water with NaCl concentration of 24.85 g/L	151.2/-	3.97	24.81	[66]
Flat-sheet Al ₂ O ₃ ceramic membrane	Grafting with PFAS/PFDS followed by ultraviolet irradiation	VMD	–	1 wt% NaCl (75 $^\circ\text{C}$) aqueous solution	159/-	–	27.28	[65]
PVDF	Methanol induced phase induced fabrication	DCMD	0.72	35 g/L NaCl	164/-	1.03	~35	[67]
PVDF	CF ₄ plasma treatment	DCMD	0.232	10,000 ppm NaCl solution with SDS/TDBAC added as the surfactant (up to 2400 ppm)	162/~100	–	20.6	[68]
PVDF	Addition of TiO ₂ (either blending in PVDF casting solution or post deposition after phase inversion), followed by silane modification	DCMD	0.37 $\pm$ 0.04	phenolic rich solution (100 g/L gallic acid)	151.9 $\pm$ 1.5/-	0.67 $\pm$ 0.03	2.5	[69]
PTFE	External ultrasonic irradiation during MD process	DCMD	0.26	50 mg/L humic acid	–	–	2.25	[70]
PVDF	Cast solution variation	VMD	1.502–1.941	NaCl: 100,000 ppm	–	–	~10	[71]
PVDF	Argon plasma pre-treatment followed by CF ₄ plasma treatment	DCMD	0.246	4 wt% NaCl solution	162.4 $\pm$ 1.2	3.1	~24	[72]

Table 2

Recent development in omniphobic membranes.

Membrane substrate	Modification description	MD type	Mean pore size (μm)	Feed solution	WCA/OCA	LEP (Bar)	Flux (LMH)	Ref.
PVDF flat sheet	Immobilizing SiNPs on PVDF membrane, followed by fluorination.	DCMD	0.3 ± 0.01	Mixed salt solution ($\text{NaCl} + \text{CaCl}_2$) with acid/surfactant	169.0/112.1	5.5	~ 37	[74]
PVDF-HFP substrate	Direct fluorination by FDTS employing vapor deposition	DCMD	0.55	3.5 wt% NaCl solution with 0.4 mmol/L SDS	154.1/129.7	2.25	10.5	[75]
PVDF	Solvent-thermal treatment followed by fluoroalkylsilane coating and fluorination	DCMD	0.358 ± 0.035	3.5 wt% NaCl with 0.4 mmol/L SDS	173.2/153.8	2.19 ± 0.26	~ 25	[76]
PVDF	PEA/PEI solution modified with the addition of silica particle contained acetate buffer, followed by crosslinking and fluorination	DCMD	0.3	20 wt% NaCl feed solution	158/-	0.84	25.48	[77]
PVDF-HPF/APTES	SiNP <i>in-situ</i> growth by immersing into ammonium/ethanol solution followed by TEOS/ H_2O /ethanol solution, silanization by FDTS at 100°C	DCMD	0.35	3.5 wt% NaCl solution with 0.4 mmol/L SDS	151.49/140.64	2.23	19.11	[78]
PVDF	One-step spraying using a waterborne coating solution comprising FS, FAS and SiNPs with a ratio of 20:40:5 g/L	DCMD	0.354 ± 0.013	3.5 wt% NaCl with 0.4 mmol/L SDS	164.4 ± 0.95 / 153.31 ± 2.09	4.09 ± 0.16	~ 27	[79]
Commercial PVDF	Deposition of ZnO nanoparticles composite	DCMD	0.39	3.5 wt% NaCl with 0.4 mmol/L SDS	152.2 ± 3.1 / 119.8 ± 3.1	1.89 ± 0.04	24.74	[80]
PVDF-HFP substrate	PDA Coating, TiO_2 nanorods deposition on PVDF-HFP substrate followed by fluorination	DCMD	0.52 ± 0.03	3.5 wt% NaCl with 0.4 mmol/L SDS	168/153	2.54 ± 0.12	21.3	[41]
PVDF-HFP substrate	Mixing F-POSS powders with PVDF-HFP substrate	DCMD	–	1.0 mol/L NaCl, with SDS added progressively (up to 0.3 mol/L)	154.5 ± 2.6 / 148.8 ± 3.7	–	~ 8	[81]
PVDF flat sheet	SiNPs and PS microsphere attachment by electrostatic interaction, followed by fluorination	DCMD	0.267 ± 0.021	Mixture of SDS:hexadecane: NaCl at a concentration ratio of 240:2400:10000 mg/L in water	176.5 ± 0.1 / 138.4 ± 1.9	4.12 ± 0.08	~ 8.5	[82]
PES	Dip coating of fluorinated silica nanoparticles	DCMD	–	5 g/L NaCl, 0.5 mmol/L SDBS, and 200 ppm hexadecane oil (NSH-Feed)	147/-	2.42	~ 10	[83]
PVDF	CF_4 plasma treatment	AGMD	0.82 ± 0.02	RO brine with TDS = 15354 mg/L, SDS added up to 0.7 mmol/L	160.9 ± 0.9 /-	1.87 ± 0.02	15.3 ± 0.8	[84]
PVDF-HFP substrate	Mix BTEAC with base substrate as a charged electrospun nanofiber scaffold, followed by SiNPs grafting, silanization and thermal annealing	DCMD	0.42 ± 0.09	1 mol/L NaCl solution with SDS gradually added till 0.3 mmol/L	150/133	–	~ 24	[85]
Glass fiber	SiNPs deposition followed by polymer coating and fluorination	DCMD	–	1.0 mol/L NaCl with SDS gradually added	140/110	–	15.8 ± 2.7	[29]

Desirable omniphobic membranes should have an optimal balance between permeability and wettability.

2.2.4. Long-term performance

Long-term performance is one of the outstanding advantages of omniphobic membranes. It refers to exceptionally long and stable performance compared with conventional hydrophobic membranes, which largely reduces the costs of membrane replacement and/or cleaning. Unfortunately, few studies on engineering membrane materials have extended the process duration to a few days or weeks. Potential wetting and fouling still exist for omniphobic membranes and thus the vapor flux and salt rejection will decline after a certain time, especially when the feed contains a lot of contaminants. However, the enhancement of omniphobicity can effectively postpone the flux and salt rejection decline for long-term MD [41]; and thus largely reduce the costs for membrane replacement and/or cleaning.

2.2.5. Low fouling propensity

Fouling refers to the accumulation of unwanted contaminants on the membrane surface and/or in the membrane pores. A low fouling rate enables smooth transport of water vapor without contaminants flowing through. The mechanism of fouling varies based on foulant types. The pollutants can be categorized into three types: (1) inorganic pollutants, (2) organic pollutants and (3) biological pollutants [42].

Inorganic fouling refers to the soluble minerals that could scale on the membrane surface by crystallization and gelation. As the

feed solution becomes more concentrated, mineral precipitates form after the concentration exceeds the solubility. The precipitates will form in the bulk solution and membrane surface. The bulk mineral nucleation (homogeneous nucleation) can be mitigated by simple pre-treatment, while the surface scaling (heterogeneous nucleation) causes the partial pore blockage or even pore penetration as the crystal structure is able to cause pore deformation [43,44]. Superhydrophobic-omniphobic membranes with low sliding angles reduce the residence time of precipitates on the surface and prevent nucleation. The slippery surface plays an important role in scaling prevention as the slippery hydrophobic surface enables a fast flow velocity at the surface, leading to better mixing, and enhances anti-wetting and anti-scaling performance of the membrane (Fig. 2) [45–48]. However, superhydrophobic-only membranes are still prone to wetting induced by surfactants, as wetting by low-surface-tension liquids is thermodynamically favorable for surfaces with low surface energy. Thus, the implementation of omniphobicity (e.g., superhydrophobic-omniphobic membranes) can facilitate the superior anti-wetting and anti-fouling properties by developing the re-entrant structure to act as a “kinetic barrier” to prevent the transition from the meta-stable Cassie-Baxter to Wenzel state for all liquids [49].

Organic pollutants usually include substances like oils, humic acid, proteins in the feed solution. Organic fouling can be attributed to the hydrophobic-hydrophobic interactions. Omniphobic membranes are often underwater oleophilic [50]. However, the omniphobic membrane is still able to prevent oil wicking by its re-entrant structure on the surface (Fig. 3). Addition of surfactants

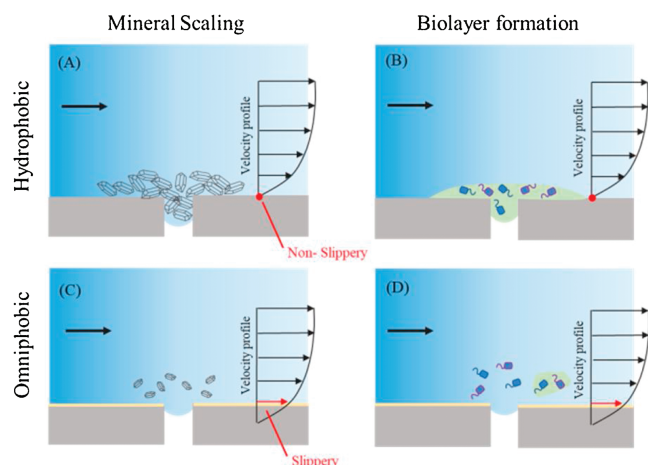


Fig. 2. Influence of velocity profile of feed solution on (A, C) mineral scaling and (B, D) biolayer formation using (A, B) hydrophobic and (C, D) superhydrophobic-omniphobic membranes. The velocity profile at the surface of the superhydrophobic-omniphobic membrane is not zero, indicating a flow movement along the surface, thus lower the residence time for both scaling and biolayer formation.

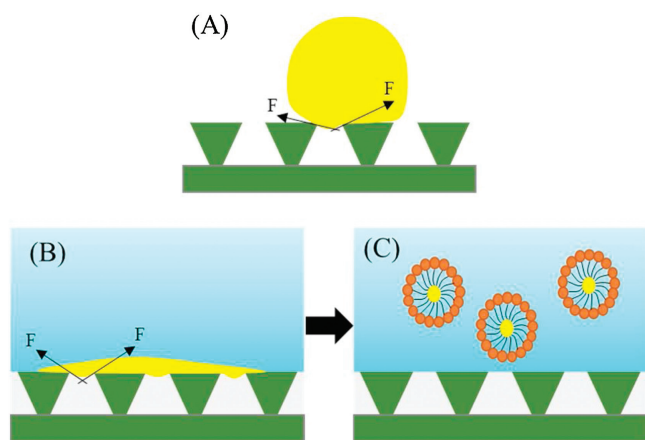


Fig. 3. (A) Oil droplet on a re-entrant structured surface in air, (B) oil droplet on a re-entrant structured surface underwater (re-entrant structures prevent pore wicking), and (C) addition of surfactant to stabilize the oil underwater, which forms micelle that has a hydrophilic outer layer.

can prevent the oil covering on membrane by stabilizing the oil-in-water emulsion. This action is feasible for omniphobic membranes while conventional hydrophobic membranes can be easily polluted by surfactants. With the use of omniphobic membranes, effective treatment of oily water can be implemented by adding surfactants as pre-treatment for better distillation performance.

Biological fouling refers to the growth of the micro-organisms on the membrane surface. The developed biofilm could be fully reinforced and hard to remove (gel-like structure). Like the nucleation in mineral scaling, biological pollutants also require time to aggregate. Thus, the slippery surface and re-entrant structure of omniphobic membranes can generate turbulence to reduce the potential growth of biofilms.

Overall, a desirable omniphobic membrane should have high wetting resistance (i.e., large LEP), reasonable vapor permeability, long-term stable performance, and low fouling propensity. However, long-term stability and fouling studies of omniphobic membranes are still scarce, requiring more research efforts in the future. Omniphobic membranes generate more opportunities for desalination and industrial wastewater treatment as they provide

more functionalization potential in processing a wide range of liquids due to the unique structures and properties of the membranes.

3. Advantages and applications of omniphobic membranes

Omniphobic membranes have some advantages over conventional hydrophobic membranes. Conventional hydrophobic MD membranes are only effective for the feed with simple components/contaminants and have limited duration due to their low stabilities related to wetting. Omniphobic membranes show strong repellence to a wide range of low surface tension liquids and thus their pores are prevented from wetting during the operation. In addition, repelling-all-induced fouling prevention towards inorganic, organic, and biologic contaminants open new opportunities for omniphobic membranes to be used in more complex situations. Omniphobic membranes could be more effective than conventional hydrophobic MD membranes in the following applications.

3.1. Seawater desalination

Seawater desalination provides an unlimited source for pure water production. Seawater contains various minerals. MSF and RO are the major methods for desalination [51]. However, the huge heat requirement for MSF and the strict feed water quality requirement for RO make them cost-ineffective for some complex seawater. Recently, MD as an emerging desalination technology can use waste heat and has a low requirement for the feed solution but a high-water recovery (up to crystallization for the feed). With the introduction of omniphobic membranes, MD for seawater desalination have the potential to be industrialized at large scales in the future due to the improved robustness, long-term stability and fouling resistance of the membranes.

3.2. Ultrapure water production

Ultrapure water production (UPW) has increased its significance in advanced high-tech productions, such as semi-conductor, microelectronics industry and medical applications [52]. UPW is commonly produced by ultraviolet radiation to reduce micro-organisms [53]. UPW can also be produced by MD due to the hydrophobicity of the membrane and its distillation mechanism [54]. Omniphobic membranes may provide more long-lasting and stable distillation performance for UPW compared with conventional hydrophobic membranes.

3.3. Wastewater treatment

MD has been examined in treating wastewater from textile, mining, mineral processing, etc. [55–57]. One of the advantages of MD over other wastewater treatment methods is that it can treat the solution containing high concentrations of contaminants, such as phenol, methanol and other organic matters [58]. Omniphobic membranes, with higher repellence towards various contaminants, could provide better MD performance in wastewater treatment.

4. Omniphobic membrane fabrication methods

With the growing interest in MD, arrange of hydrophobic/superhydrophobic modifications have been conducted in the past decades (Table 1) [59–72]. Key parameters including the membrane pore size, water/oil contact angle, LEP and flux, are determinant factors for an MD membrane [73]. Some superhydrophobic membranes with smooth and unpolluted surfaces show good MD performance when using single-component feed

solutions. Omniphobic membranes can be applied to challenging feed solutions containing multiple components. Most studies use 3.5 wt% of NaCl solution (i.e., simulating seawater) as a benchmark for MD. Moreover, the addition of sodium dodecyl sulfate (SDS) or other organic additives aims to mimic industrial wastewater. Table 2 summarizes the developments and performances of omniphobic membranes in recent years [29,41,74–85]. There are three typical strategies to engineer omniphobic membranes: (1) substrate fabrication, (2) surface modification and (3) other methods.

4.1. Substrate membrane fabrication

An omniphobic membrane typically has a hydrophobic substrate. The hydrophobic substrate layer can be prepared by two techniques: phase inversion and electrospinning. The phase inversion method has the advantages of simple operation and controllable surface and internal structures of the membrane [86]. Compared to the electrospinning technique, membranes fabricated by phase-inversion method are more wetting resistant due to the denser structure and hydraulic perturbation of the phase inversion formed membrane [87]. Electrospun fibrous MD membranes have interconnected pores, which are more prone to be wetted as wetting for one pore can lead to the wetting of the whole structure. However, membranes fabricated by electrospinning are still popular as it does not require solvent exchange for pore formation. Also, the electrospun membranes have higher porosity (>80%) and high hydrophobicity, providing a better flux [88].

Omniphobic membranes are often composite and need more than one steps for fabrication. Conventional MD membranes (e.g., PVDF, PTFE and PP) only have one layer [82]. A common modification is to mix other polymers with the base polymer. For example, emulsion polymerization of PVDF and hexafluoropropylene (HFP) was used to prepare the PVDF-co-HFP membrane [89]. The incorporation of HFP increases the hydrophobicity and mechanical strength of the membrane due to the introduction of fluoro groups [90]. The substrate membrane can also mix with other chemicals for omniphobicity development. Lu *et al.* created a mixture of PVDF-co-HFP and F-POSS (fluorinated polyhedral oligomeric silsesquioxanes) by thiol-ene click reaction for electrospinning of membranes [81]. The mixing of F-POSS with the substrate replaces conventional fluorination requiring hazardous fluoroalkyl solution. The prepared omniphobic membrane showed a water CA of 154.5°, an oil CA of 148.8° and an MD flux of 8 LMH. Although F-POSS has been investigated since 2008 for surface modification [91], its application in membrane fabrication is rare. The drawback of F-POSS is its poor adherence on the membrane substrate, but it can be overcome by blending F-POSS with the substrate polymer without sacrificing liquid repellence [92,93].

Similar to pre-mixing the doping solution, Xu *et al.* developed an *in-situ* silica nanoparticle assembly technique by mixing (3-aminopropyl)triethoxysilane (APTES) in the PVDF-HFP doping solution for growing SiNPs on the fibrous membrane and achieved omniphobicity ($CA_{\text{water}} = 151.49^\circ/CA_{\text{oil}} = 140.64^\circ$) with a stable MD flux of 19.11 LMH [78]. Compared with the conventional mixing method for the polymer solution, *in-situ* growth does not reduce the porosity of the membrane significantly after modification (Fig. 4A). This method not only takes the advantage of electrospun membranes with re-entrant structures, but also makes deposition in a relatively quick and simple step.

In summary, mixing polymers and modifiers for substrate fabrication can increase membrane hydrophobicity and introduce re-entrant structures, leading to omniphobicity without sacrificing mechanical strength and permeability of the membrane. Other

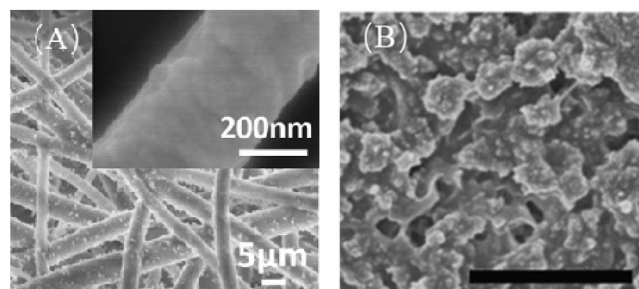


Fig. 4. SEM images of the omniphobic membranes modified by (A) *in-situ* growth of SiNPs. Reproduced with permission [78]. Copyright 2020, Elsevier. (B) Waterborne coating with a solution comprising FS, FAS and SiNPs. Reproduced with permission [79]. Copyright 2019, Elsevier.

modifiers, such as $LiCl_2$ and $CaCl_2$ for improving electrospinnability [75] and FAS for enhancing adhesion [80] can also be added in the polymer solution.

4.2. Surface modification

Surface modification has been widely investigated for MD membranes to increase the roughness and/or hydrophobicity by lowering the surface energy. Omniphobic membranes can be obtained *via* constructing surfaces with re-entrant structures and/or lowering the surface energy to achieve robust MD performance. Deposition of nanomaterials and surface fluorination are two effective ways to achieve omniphobic membranes.

4.2.1. Nanomaterial functionalization

Inorganic nanoparticles (NPs), carbon nanomaterials (CNM) and metal organic frameworks (MOFs) have been used to engineer omniphobic membranes by surface functionalization. Re-entrant structures can be built on the membrane surface after nanomaterial deposition, and the modified membranes become repellent to liquids with low surface tension [63].

Inorganic NPs, such as TiO_2 [41], ZnO [80] and SiNPs [85], have been deposited onto pre-treated membrane substrate. The pre-treatment can be alkylation using NaOH or KOH (introducing $-OH$ groups) [74,79,82], or surface charge deposition (e.g., $-NH_2$ groups for surface positive charge deposition provided by polydopamine (PDA) or APTES) [76,78], or coating with fluoroalkyl silane solution.

Apart from the conventional deposition, other methods have also been investigated. Zheng *et al.* reported an omniphobic membrane prepared by spray-coating of SiNPs and polystyrene sphere (PS) onto a PVDF porous membrane [82]. The prepared membrane with micro- and nanostructures showed great anti-wetting and fouling performance in MD.

CNM and MOF nanomaterials have also been investigated for hydrophobic membranes. However, the modified membranes with these materials cannot reach omniphobicity and robust MD performance due to hydrothermal instability of these nanomaterials [23]. Nanomaterial surface functionalization often endows the membranes with re-entrant structures, which can not only assist a meta-stable Cassie-Baxter state, but also enhance the surface roughness. The meta-stable Cassie-Baxter state provides excellent wetting resistance for the membrane; the enhanced surface roughness leads to the rise in both hydrophobicity and evaporation areas. Also, the functionalized particles can promote the shear force and thus reduce the fouling potential by mitigating scale agglomeration.

4.2.2. Surface fluorination

To further lower the surface energy of the hydrophobic membranes, surface fluorination is often an important final step

to prepare omniphobic membranes after other modifications. The omniphobicity (both hydrophobicity and oleophobicity) can be further enhanced by introducing long fluoroalkyl chains. Surface fluorination can be performed by different methods, such as surface coating, grafting and plasma modification [21].

Surface coating refers to the physical or chemical covering of solvents and other additives, followed by curing or drying. The coated layer is adhered by intermolecular force between the coating material and membrane substrate. Khan *et al.* applied a mixture containing perfluorodecyltriethoxysilane (FDTES), polydimethylsiloxane (PDMS) as cross linker and fluorinated SiNPs on an APTES treated PES membrane by dip-coating and achieved membranes with anti-oil-fouling and anti-wetting abilities regardless of zeta potential charges near the membrane interface [83]. Li *et al.* spray-coated a mixture of SiNPs, FS and FAS onto amino functionalized PVDF membranes with a water contact angle of $160.40^\circ \pm 0.95^\circ$ (Fig. 4B). The process combined both nanoparticle deposition and surface fluorination into one step to reduce the fabrication time but increase the omniphobicity [79]. Another fluorination method for coating is vapor deposition (VD), and the fluorination coating by VD is harder and more durable. Wu *et al.* proposed a direction fluorination process by vapor deposition of FTDS after electrospinning of PVDF-HFP dope solution [75]. Interestingly, the prepared membrane showed omniphobicity but did not have re-entrant structures. Compared with the control electrospun PVDF-HFP membrane, the fluorinated membrane by VD displayed more robust MD performance [41].

Compared to surface coating, grafting enables bond formation with the substrate, which increases the membrane mechanical stability as well. Zhang *et al.* reported a grafting method to deposit SiNPs by immersing the membrane into IPA solution containing PFOTS and achieved an omniphobic membrane with a water contact angle of 169° and a relatively high flux MD performance (~ 37 LMH) [74]. The modified membrane also showed a high stability in a wide range of pH (2–12) and relatively long-term MD performance (up to 300 h of continuous operation).

Fluorination can also be achieved by CF_4 plasma treatment, which effectively lower the surface energy by the introduction of a fluorinated layer onto the membrane [72,94]. Electrospun membranes followed by CF_4 plasma treatment showed omniphobicity with a water contact angle of $160.9^\circ \pm 0.9^\circ$ for AGMD [84]. The modified membrane also showed excellent anti-wetting performance using salt solution with 0.7 mmol/L SDS, which is the highest surfactant concentration tested so far. Therefore, CF_4 plasma treatment of electrospun membranes has the potential to increase MD performance by endowing the membrane with excellent anti-wetting and anti-fouling performance.

4.3. Other methods

Apart from the modification methods discussed above, other methods have also been introduced for omniphobic membrane fabrication. Zhu *et al.* proposed a membrane fabrication pathway that integrated both advantages from fibrous membranes (inter-connected pores) and phase inversion formed membrane (anti-deformable pores) to fabricate a superhydrophobic-omniphobic membrane [77], which could achieve the greatest effectiveness in mitigating wetting, scaling and fouling. The process started with immersing a PVDF substrate into a PDA/PEI solution, followed by the deposition of SiNPs by dip-coating. A second immersing process was then performed by immersing the SiNP modified membrane into a 17-FAS/PDMS precursor solution, followed by thermal welding. Silica NP deposition, surface fluorination and PDMS welding were three key steps to fabricate stable omniphobic membranes (Fig. 5). Crosslinking by PDMS effectively tightened the internal loose fibers and maintained the pore stability for long

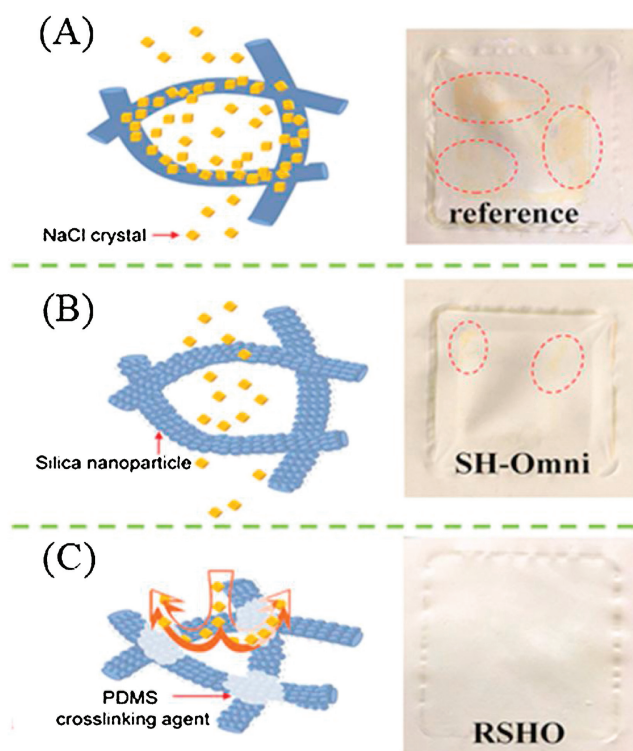


Fig. 5. Schematic diagram of pore structure and its anti-wetting demonstration for (A) pristine PVDF membrane, (B) membrane modified by SiNPs deposition and surface fluorination with 17-FAS (denoted as SH-Omni), and (C) membrane SH-Omni with PDMS welding. The welding of the fiber increases its LEP, water contact angle and mechanical strength. Reproduced with permission [77]. Copyright 2020, Elsevier.

term fouling resistance without a significant sacrifice of the overall flux (~ 25.48 LMH). In their another work, similar fabrication processes were conducted on different substrates, including inorganic, metal or polymer materials [95]. The prepared surfaces showed omniphobicity, suggesting the universality of the method.

Another solvent-thermal induced roughening method was introduced by immersing the base PVDF membrane into a mixture of water, HCl and *n*-pentanol to induce the deformation and roughness fins formation by heating, followed by fluorination to reduce surface energy [76]. The prepared membrane had superhydrophobicity ($\text{CA}_{\text{water}} = 173.2^\circ$) and superoleophobicity ($\text{CA}_{\text{oil}} = 153.8^\circ$).

The two methods discussed above are examples only. To engineer omniphobic membranes, new facile fabrication methods should be developed in the future. Although some methods, such as electroblowing [59], and phase separation [71] only showed effectiveness in obtaining superhydrophobicity, they can still provide useful insights into developing high-performance omniphobic membranes for MD.

5. Concluding remarks and perspectives

MD has been an emerging technology for many applications (e. g., desalination, ultrapure water production and industry wastewater treatment) and plays an important role in sustainable water purification. The key challenge of MD is its low stability due to wetting and fouling under practical operation conditions. Omniphobic membranes, are a promising solution to the key challenge of MD, since they have the superiorities in excellent wetting and fouling resistance, high stability, and durable performance with superhydrophobic and/or superoleophobic surfaces and re-entrant structures. The highlights of this review are summarized below.

- (1) Omniphobic membrane should have both hydrophobicity ($CA_{\text{water}} > 90^\circ$) and oleophobicity ($CA_{\text{oil}} > 90^\circ$). Superhydrophobic-omniphobic membranes are desirable for MD due to their superior anti-wetting and anti-scaling properties. A desirable omniphobic membrane should have a reasonably large pore size (e.g., 0.3–0.8 μm), a high LEP (e.g., 2–6 bar), high water and oil CAs, and high permeability. However, there are trade-offs between these factors. Thus, optimization of different factors is vital in developing omniphobic membranes.
- (2) Omniphobic membranes have huge potential for robust MD applications, particularly for treating challenging liquids containing a range of contaminants and/or a high concentration of salts.
- (3) The preparation of omniphobic membranes consists of substrate membrane fabrication and surface modification. The fundamentals are based on lowering surface energy and increasing surface roughness of the membrane. Electrospinning, phase separation, nanoparticles functionalization and surface fluorination are the widely used methods for engineering omniphobic membranes.

However, omniphobic membranes also face some challenges that call for more research efforts in the future.

5.1. Limitations of the omniphobic membrane

The major limitation of the omniphobic membrane, like the conventional membrane, is its low flux as the omniphobic membrane has relatively small pore size and low porosity, which reduce the MD flux and overall performance. Additionally, the fabrication process is still complex and some chemicals (e.g., fluorinated solvents) used are costly and have a long-lasting environmental impact, which is not suitable for large-scale production. In the applications/investigations of omniphobic membranes, the feed solution is often synthetic and simple. Very limited studies used real wastewater (e.g., RO brines [96], petrochemical wastewater [97], or municipal wastewater [98]), thus the challenges and mechanisms of wetting and fouling in MD using real waste liquids have not been fully revealed.

5.2. Future research

5.2.1. Multi-layer omniphobic membrane

The present omniphobic membranes are mainly based on a single layer or its further modification or functionalization. New omniphobic membranes with multiple layers to achieve different functions for each layer could be feasible. For example, the Janus membrane, having a hydrophobic substrate and a hydrophilic surface, has shown great promise in MD due to less mass transfer resistance on the hydrophilic layer [99–101]. Since it is underwater oleophobic, it can also effectively repel organic contaminants with second re-entrant protection. The Janus-omniphobic membrane was fabricated and showed a decent performance with a water flux of 27 LMH [102]. In addition, the dual layer omniphobic nanofiber membrane by electrospinning is worth investigating in the future [21,103].

5.2.2. Improve existing methods

There is still room to improve existing methods for omniphobic membrane fabrication. Nanoparticle deposition has the problem of poor adhesion with the base membrane. Surface fluorination generally decreases the permeability of the membrane due to reduced pore sizes and increased mass transfer resistance. Some methods, such as CF_4 plasma treatment have the requirements for the equipment and likely decrease the mechanical stability of the membrane. Therefore, more strategies should be innovated to overcome these issues.

The strategies of constructing superhydrophobic membranes for MD, air purification and oil-water separation, such as spray-coating [104], surface fluorination [105] and bioinspired fabrication [106,107], could be also effective in developing omniphobic membranes. For example, deposition of nanocarbon materials has shown great potential due to the unique properties in transfer and geometric features of the prepared membranes [108,109]. 3D printing technology has emerging applications for membranes. However, its application for omniphobic membranes is still limited. In the future, 3D printing combining with other surface engineering techniques could lead to high-performance omniphobic membranes by printing unique structures to lower the mass transfer resistance and minimize the fouling and nucleation potentials [110–112].

In the fabrication of the omniphobic membranes, the mass transfer related membrane pore size and porosity should not significantly reduce so that reasonable flux can be maintained. At the same time, the heat transfer related heat loss should not be high. Fluorinated materials typically have low thermal conductivity, while some nanomaterials (e.g., graphene) may have high thermal conductivity, which should be paid more attention during their functionalization as they could increase the heat loss of the MD process.

5.2.3. System integration

In practical applications, system integration can be vital in improving overall performance and minimizing the system costs [113,114]. Integration of MD with other membrane technologies (e.g., nanofiltration, electrodialysis and reverse electrodialysis) can be a promising solution for desalination of saline water [115–117]. In addition, pre-treatment of the feed water before MD can help mitigate scaling and fouling, thereby extending the lifespan of the omniphobic membrane.

5.2.4. Improvement in evaluation methods

To date, most water CA and oil CA studies are carried out in air, which is far from the real situation where the membrane contacts with liquids. Therefore, evaluation of the underwater properties of the membrane may be more insightful. Moreover, long-term experimental evaluation (e.g., a few months even longer) using real waste liquids should be conducted as durability and stability are the key factors for the industrialization of the omniphobic membrane.

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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