A review of membrane wettability for the treatment of saline water deploying membrane distillation

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Abstract

Membrane distillation (MD) is an alternative membrane technology that offers the capacity to treat highly saline water including industrial wastewater, seawater, brine water from other processes, and oil-gas field produced water. However, conventional hydrophobic membranes suffer fast wetting and severe fouling especially when low surface tension chemicals exist in saline water, which compromises the performance of MD. Recent advances in material science and nanomaterials research have led to the incorporation of special wetting properties on membrane surfaces. Membranes with special wettability can achieve high resistance against membrane fouling and wetting, as well as overcome the trade-off between membrane permeability and selectivity. This review summarizes the progress and recent development of studies on MD membranes with special wettability. Firstly, the fundamental concepts pertaining to membrane surface wettability including insights of their benefits and potential issues are highlighted in this review. Secondly, fabrication methods and applications of membranes utilizing various special wettability are discussed in detail, along with their challenges. Finally, this review concludes the advantages of membranes with special wettability and demonstrates potential solutions to the above-mentioned challenges for future research in high saline wastewater treatment.

Keywords: Membrane; wetting; superhydrophobic; omniphobic; special wettability; membrane distillation.

1. Introduction

Presently, significant research focus is being placed on next generation water and wastewater treatment technologies to address global water shortage issues [1, 2]. Among the current water and wastewater treatment technologies, membrane processes play a dominant role in the global market due to their relatively higher energy efficiency and smaller footprint [3, 4]. Conventional membrane technologies are mainly pressure-driven processes, such as reverse osmosis (RO) and nanofiltration (NF) [5, 6]. Recently, innovative membrane technologies driven by other driving forces have been extensively developed. Among them, membrane distillation (MD) has attracted wide attention [7]. MD is driven by vapor pressure gradient induced by temperature difference and since water vapor pressure is only modestly decreased by salinity it can operate at high concentrations [8-10]. Its distinct working mechanism makes it capable of treating challenging wastewater (e.g. brine) where conventional pressure-driven membrane processes are struggling to deal with the high osmotic pressure [11, 12]. The other major advantage of MD is its potential to be coupled with alternative heat sources such as solar and low-grade waste heat, making the process a low carbon option [13, 14]. Also, MD can be integrated with other water treatment technologies towards zero liquid discharge - an ideal condition for sustainable concentrate treatment [15, 16].

However, MD by and large is still in the stage of laboratory research and only has a few pilot-scale demonstrations with limited commercial success, due to a number of factors [17]. One such factor is the lack of suitable membranes [18-21]. Along with high permeability, an appropriate membrane for MD should have high wetting resistance, i.e., the feed solution should not wet the membranes internally in long-term operation and should only allow vapor to pass through the membrane structure [22, 23]. Typically, commercial hydrophobic microfiltration membranes have been widely evaluated in various MD applications. However, these membranes suffer relatively low permeation flux and are prone to wetting issues [24, 25], especially when treating wastewater, which contains high salinity or concentrations of low surface tension compounds including surfactants and oil (e.g., textile wastewater, produced water, seawater brine, municipal wastewater, etc.) [26, 27]. These feed solutions cause the membranes to suffer rapid wetting and fouling which may lead to membrane damage, necessitating early membrane replacement. This inevitably incurs additional operation cost [28-31]. Due to this inability of the commercial microporous membrane to have stable flux and rejection performance when exposed to challenging feed solutions, there is a need to develop new membranes that have high wetting and fouling resistance, while maintaining adequate flux and superior salt rejection [32, 33].

Considerable research efforts have been dedicated to developing MD membranes with the desired robust properties. Among them, membranes with special wettability characteristics have been found to be the most effective for the improvement of fouling and wetting resistance [34, 35]. Inspired by nature, the special wettability on MD membranes has been realized by adjusting surface roughness and chemical compositions via surface engineering, supported by the advances in nanomaterial synthesis and modification techniques [36].

Many researchers have made remarkable achievements in the fabrication of membranes with special wettability. Some researchers have successfully developed membranes with improved flux and stability in typical MD operations [37]; while others have developed membranes to deal with highly saline wastewater with low surface tension components [13, 38]. These membranes with special wettability were found to have high wetting and fouling resistance, which makes MD more viable in real applications [39, 40].

Recently, some researchers reviewed general advances in membrane fabrication and modification for MD applications [41, 42]. Some others studied MD membranes used for a specific application, the treatment of oil-containing feed streams, which involved the use of special wettability membranes [43-45]. A few review articles were published on MD membranes with individual special wettability such as superhydrophobic and omniphobic [46, 47]. These reviews either focused on applications or surface wettability but did not elaborate on membranes properties and their fabrication techniques. Advantages and disadvantages of each fabrication technique should be compared, and their challenges should be evaluated individually, which can give readers research directions towards solving such challenges. This is the first review that discusses collectively on membranes with special wettability for a variety of applications. This review includes an overview of surface wettability and its fundamentals, a literature review of various types of surface special wettability, and a summary of fabrication methods and MD applications of membranes with special wettability. Recommendations and future outlook have also been illustrated in this emerging field.

2. Membrane distillation and wetting phenomena

2.1 Principle of membrane distillation

MD is a membrane separation process where vapor instead of liquid passes through a hydrophobic, porous membrane and is condensed in the permeate side [48, 49]. The mass transfer of vapor is driven by a partial pressure difference between the two sides of the membrane. This unique mechanism makes MD viable in some applications where conventional technologies are not suitable [17, 50, 51]. Theoretically, the permeate of MD can reach 100% rejection of non-volatile components [52]. Moreover, the energy efficiency (in terms of carbon emissions) of MD can be significantly improved when low grade waste heat or solar energy are available [53-55].

The detailed transport mechanism of MD can be described in the following steps: (1) heat is transferred from the bulk solution to the membrane surface by boundary layer heat transfer;

(2) liquid evaporates at the hot feed-membrane interface; (3) driven by temperature gradient, the vapor passes through membrane pores; then, (4) the vapor condenses by coolants or cooling plates [56]. There are various MD configurations depending on how the vapor is condensed. Direct contact MD (DCMD) is the most studied configuration owing to the convenience of setup, where both feed and permeate are touching the membrane at both sides [57, 58]. For comparison, both air gap and permeate gap MD (AGMD & PGMD) configurations require condensation plates set inside modules, and vacuum and sweeping gas MD (VMD & SGMD) require external condensers to liquefy vapor [52, 59]. Generally, membranes used in the configurations of VMD and SGMD require higher liquid entry pressure (LEP) and wetting resistance owing to the external pressure gradient applied across the membranes; hence, membranes used in VMD usually have higher hydrophobicity and smaller average pore size [60-62].

2.2 Membrane wetting in membrane distillation

Membrane wetting is generally defined as liquid contacting with a solid membrane surface through intermolecular interaction between the phases of gas, liquid, and solid [63]. Specifically, wetting of porous membranes sees liquids penetrating the pores of the membrane. As a result, the flux either declines (blockage due to partial pore wetting) or steeply rises (liquid transport due to complete wetting) while salt rejection keeps decreasing sharply [64]. **Fig. 1** depicts the pore wetting potential (partially- or fully-wetted) for MD membranes. This wetting phenomenon is unique to MD since phase change is necessary, (i.e., formation of water vapor) rather than allowing liquid water to penetrate through the membrane. It is interesting to note that recent studies have found that some non-volatile organic compounds could still pass through membranes easily without the occurrence of membrane wetting via a so-called "adsorption-desorption-adsorption" mechanism [65-67].

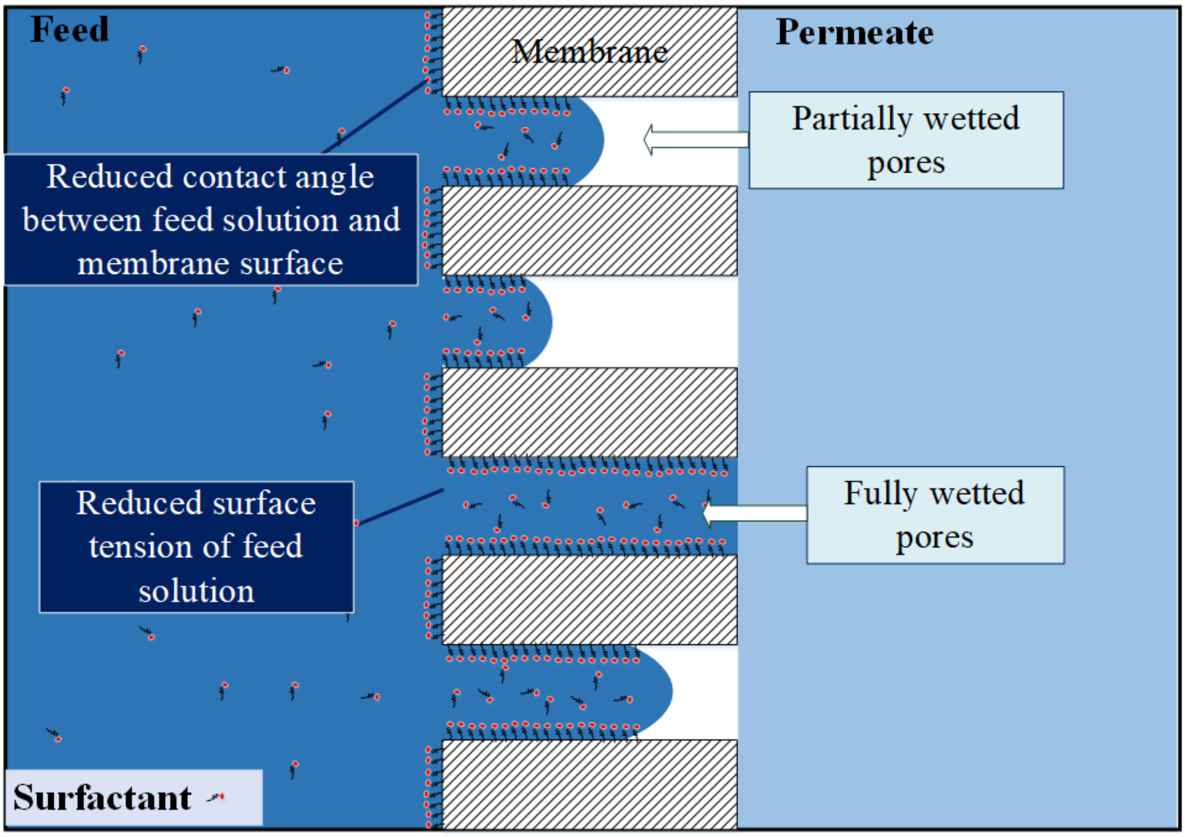


Fig. 1. Illustration of the occurrence of pore wetting (partially or fully-wetted) of a hydrophobic membrane when in contact with wastewater containing surfactants; the surfactants have hydrophobic tails and hydrophilic heads.

Hydrophobic membranes are widely used to lessen the possibility of liquid water penetration in MD. As a requirement, MD membrane should comprise at least one hydrophobic layer (generally, the side that is in direct contact to the feed solution). Therefore, hydrophobic polymers such as polyvinylidene fluoride (PVDF), polytetrafluoroethylene (PTFE), and polypropylene (PP) are favored to be used as MD membrane materials [68-71]. It is widely accepted that the primary metric for determining membrane wetting (wicking) resistance is the liquid entry pressure (LEP), and membrane wetting occurs when transmembrane pressure (ΔP) exceeds the LEP of membrane against a specific liquid [72]:

$$\Delta P \geq LEP \tag{1}$$

In other words, LEP is the maximum transmembrane pressure that a membrane pore can sustain (i.e. the minimum pressure for liquids to penetrate membrane pores). It is defined as [73, 74]:

$$LEP = -\frac{B\gamma_L \cos\theta}{r_{max}} \tag{2}$$

where γ_L is the surface tension of a liquid, θ is the apparent contact angle (CA) between feed solution and membrane surface, r_{max} is the maximum pore size of the membrane, and B is the pore geometry coefficient (e.g., B = 1.0 for a circular pore and stretched membranes such as PTFE with small curvature radius has B value of ~ 0.4 – 0.6).

Recent studies have established that the presence of low surface tension chemicals in feed solutions plays a significant role in membrane pore wetting as it can affect both membrane surface properties and feed characteristics [33, 75, 76]. As shown in **Fig. 1**, the deposition or adsorption of surfactants on membrane surfaces compromises its LEP by reducing both the membrane surfaces CA as well as the surface tensions of the feed solution. As a result, the membranes is highly susceptible to wetting [77].

2.3 Membrane properties deciding wettability

Key factors that influence fouling and wetting in MD can be classified by: (a) membrane surface properties (wettability, roughness, surface tension, pore size, surface charge, and surface functional group); (b) hydrodynamics (flow velocity, motion direction, temperature, local hydrostatic pressure gradient), and; (c) feed characteristics (mole fraction, diffusivity, nature of foulants, charge, pH) (see **Fig. 2**). The present review article focuses on the development of membranes with specific surface properties (special wettability) to address current MD application challenges treating impaired water sources.

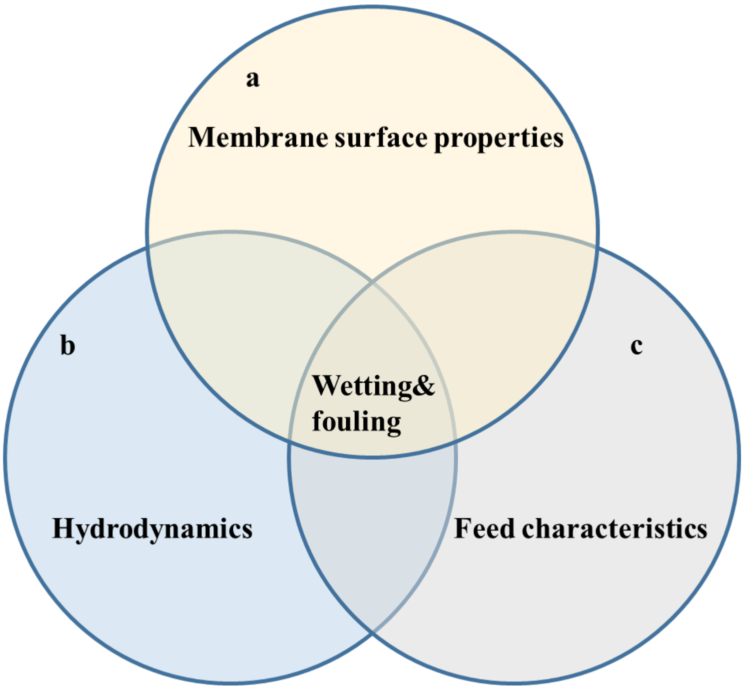


Fig. 2. Factors affecting membrane wetting: (a) membrane surface properties (wettability, roughness, surface tension, pore size, surface charge, and surface functional group); (b) hydrodynamics (flow velocity, motion direction, temperature, hydrostatic pressure), and; (c) feed characteristics (mole fraction, diffusivity, ion concentration, pollutant/surfactant content, electrokinetic potential charge, pH).

2.3.1. Contact angle (CA)

CA is the angle where the liquid-vapor interface meets the solid-liquid interface. It is generally used to quantify the wettability of a membrane surface against specific liquids [78]. As the CA in equilibrium reflects the strength of molecular interaction between solids, liquids, and vapors, the surface tension of a material can be calculated based on the Young equation with the CA acquired on a rigid surface [79, 80]:

$$\gamma_{SL} - \gamma_{SV} - \gamma_{LV} cos\theta_{c} = 0 \tag{3}$$

where γ_{SL} is solid-liquid interfacial energy, γ_{SV} is solid-vapor interfacial energy, and γ_{LV} is liquid-vapor interfacial energy.

Wenzel or Cassie-Baxter models should be introduced when CA is measured on a rough surface such as the surface of porous membranes [81]. A relationship between the Young CA and the apparent CA of liquid on a rough surface has been developed depending on the state of surface wettability (Wenzel or Cassie-Baxter) [82, 83]. In both models, roughness plays an important role determining apparent CA. Wenzel state, a homogeneous wetting regime, occurs when liquids completely reach roughness valleys (**Fig. 3a**), which is represented by the following equation:

$$cos\theta_{C} = r cos\theta_{Y} \tag{4}$$

where r is the roughness ratio, defined as the ratio between actual and projected solid surface areas, θ_Y is the Young CA when the liquid is placed on ideal smooth surface in thermodynamic equilibrium systems, and θ_C is the apparent CA.

Cassie-Baxter, on the contrary, is a heterogeneous wetting regime as air remains trapped inside the roughness valleys under liquids (see **Fig. 3b**), expressed as:

$$cos\theta_{C} = r_f f cos\theta_{Y} + f - 1 \tag{5}$$

where f is the fraction of solid surface projections under liquid droplets, and r_f is the roughness ratio of wetted areas; θ_Y is the Young's CA when the same ideal solid surface is applied in thermodynamic equilibrium systems, and θ_C is the apparent CA. The Cassie-Baxter equation can be converted into the Wenzel equation when f = 1, r_f = r.

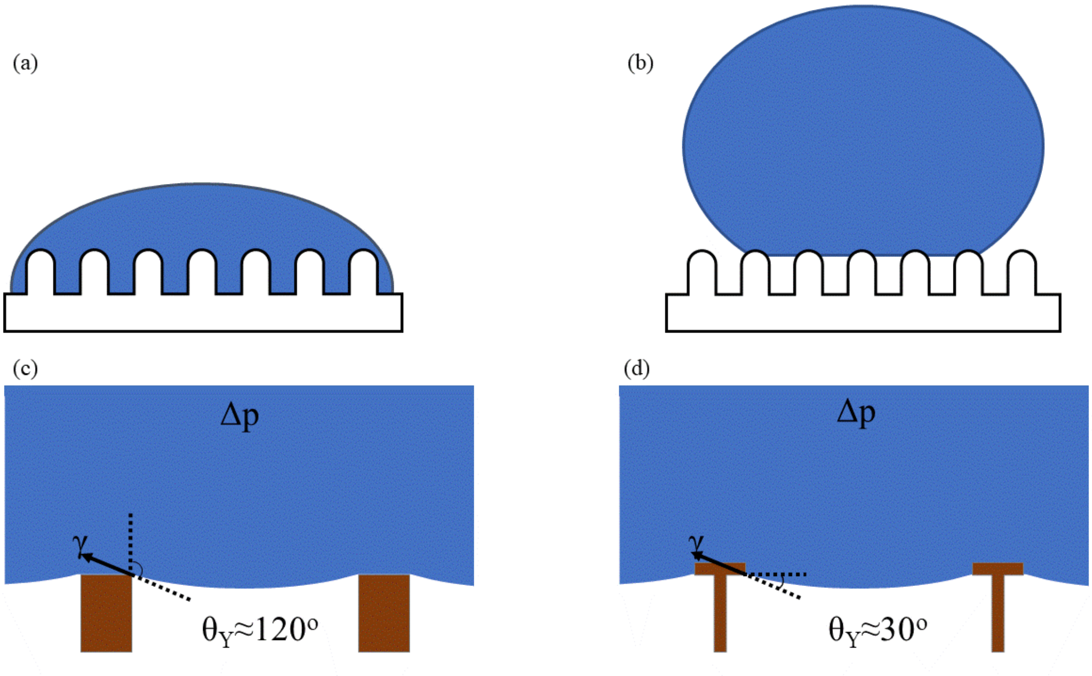


Fig. 3. (a) Wenzel and (b) Cassie-Baxter model of surface wetting regime. Requirement of CA to suspend liquid: c) simple topology; d) re-entrant topology.

In addition, the 'sliding angle' is also applied to characterize the surface wettability, defined as the minimum tilt angle required for liquid droplets to slide down an inclined plate. Lower sliding angles can be observed when membrane surfaces have higher apparent CAs. The Cassie-Baxter state of surface has much lower sliding angle than the Wenzel state at the same apparent CAs due to air trapped in surface structures [84].

It can be concluded that surface wettability is strongly affected by surface roughness and morphology. The Kao diagram (**Fig. 4**) has been introduced to illustrate the relationship between the Young CA (representing surface tension) and the apparent CA in terms of the surface wettability state (Wenzel/Cassie-Baxter) of membranes [85, 86]. The Kao diagram illustrates that the hydrophobicity of hydrophobic surfaces or hydrophilicity of hydrophilic surfaces is amplified by surface roughness. The cosine values of the apparent CA (θ_r) is plotted against the cosine values of the Young CA on rigid smooth surfaces (θ_s). Given a fixed surface roughness, changes in the Young CA (i.e. the change of surface tension) results in amplified changes in the apparent CA. However, the effects of the Young CA on the apparent CA diminishes dramatically at both ends of the $\cos\theta_r$ ranges [85, 87]. Usually, a larger surface roughness leads to a sharper gradient in terms of relationships between the apparent CA and the Young CA due to the effects of additional air trapped in surface structures [86]. It is concluded that both low surface tension and high roughness contribute to the Cassie-Baxter state on membrane surface, which is generally necessary for superhydrophobic and omniphobic surfaces having high CA and low sliding angle of liquid droplet. While the effect of trapped air is beneficial in terms of the Cassie-Baxter wetting phenomenon there is a potential down side. It has been shown that by deaerating the feed in MD the diffusive transport of water vapor in the pores can be enhanced [88]; modelling showed a significant increase in flux.

However, the benefit of mitigating surface wetting by entrapped air could override this in many applications.

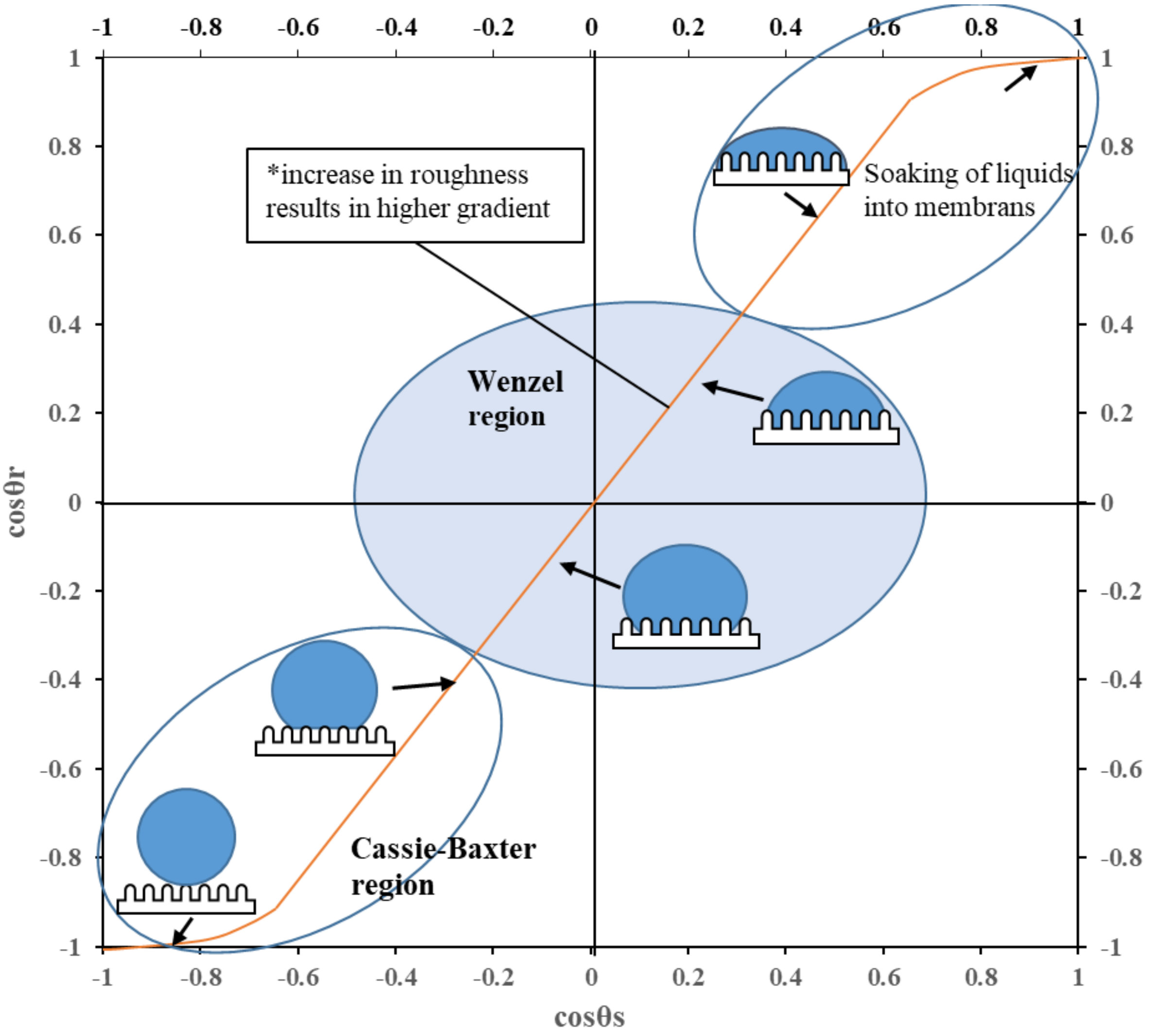


Fig. 4. Kao diagrams of a sample membrane with fixed roughness showing the relationship between surface tension and wetting regimes.

2.3.2. Surface roughness and morphology

Surface roughness is used to represent irregularities at the surface of the material during the fabrication process [89]. Roughness statistics obtained from instrumental analyses (atomic force microscopy) give quantitative insights into membrane morphology. Generally, R_{RMS} and $R_{average}$, which are both functions of height deviations from mean surface levels, are used to represent membrane surface roughness.

In addition to surface roughness, membrane morphology is another physical property affecting surface wettability. Generally, the achievement of multi-scale surface structures leads to improved hydrophobicity on membrane surfaces. Re-entrant structures are most favored for MD membranes as such morphology can easily achieve Cassie-Baxter state against most liquids even it has low surface tension, owing to the large amounts of air pockets on the membrane topology [90, 91]. **Fig. 3(c)** shows that a topology without re-entrant structures requires surface materials having higher than 90° Young CA to suspend liquid. On the other side, re-entrant topology can suspend liquid with a surface material having the Young CA much lower than 90° by reducing solid-liquid contact (**Fig. 3(d))**. It means that, by changing surface structure alone, a membrane can suspend or repel low surface tension liquids including oil and surfactants [92]. In summary, for membranes with hierarchical topology, increases in the fraction of trapped air greatly reduce the requirement of material's inherent wettability for the suspension or repellency of liquids. If the air fraction is extremely high (>94%), a membrane made of hydrophilic materials but with re-entrant topology can repel very low surface tension liquids, although the achievement of such topology is very difficult [93].

2.3.3. Surface tension

Surface tension (surface energy) quantifies the required energy to create a surface by disrupting intermolecular bonds [94]. Surface tension plays a critical role in surface wetting: a solid surface with low surface tension has generally less wetting tendency. Surface tension can be worked out using Eq. (3) with Young's CA, which is stated in Section 2.3.1.

Commercial hydrophobic membranes widely used in MD experiments are made of polymers with low surface tension. However, these membranes are prone to fouling by organic contaminants and to wetting by surfactant due to hydrophobic interaction [28].

2.3.4. Surface charge

The surface charge of a membrane surface is the electrical potential difference between the membrane surface immersed in a conducting liquid and the bulk of the liquid [95]. The surface charge of a membrane considerably affects the wettability against low surface tension liquid due to hydration forces, which can be explained by Extended Derjaguin Landau Verwey Overbeek (x-DVLO) [96]. The surface charge of a membrane varies significantly depending on feed water chemistry including pH, electrolyte concentrations, and the presence of organic compounds. Surface charge is determined by zeta potential measurements.

Surface charge has strong impacts on the wettability of certain compounds. For example, a positively-charged composite membrane had low underwater oil CA after 30 min while a negatively-charged composite membrane maintained underwater superoleophobicity although both composite membranes were coated with hydrophilic layers [95].

3. Special wettability

Various types of special surface wettability have been demonstrated to improve the MD stability against wetting and fouling issues (**Fig. 5**). In this section, special wettability on membrane surfaces for MD applications is discussed. Novel Janus membranes with special wettability are also covered in this section. Details about their definition, working principles, and fabrication approaches are presented and analyzed. Evaluation and insights of the special wettability are also discussed.

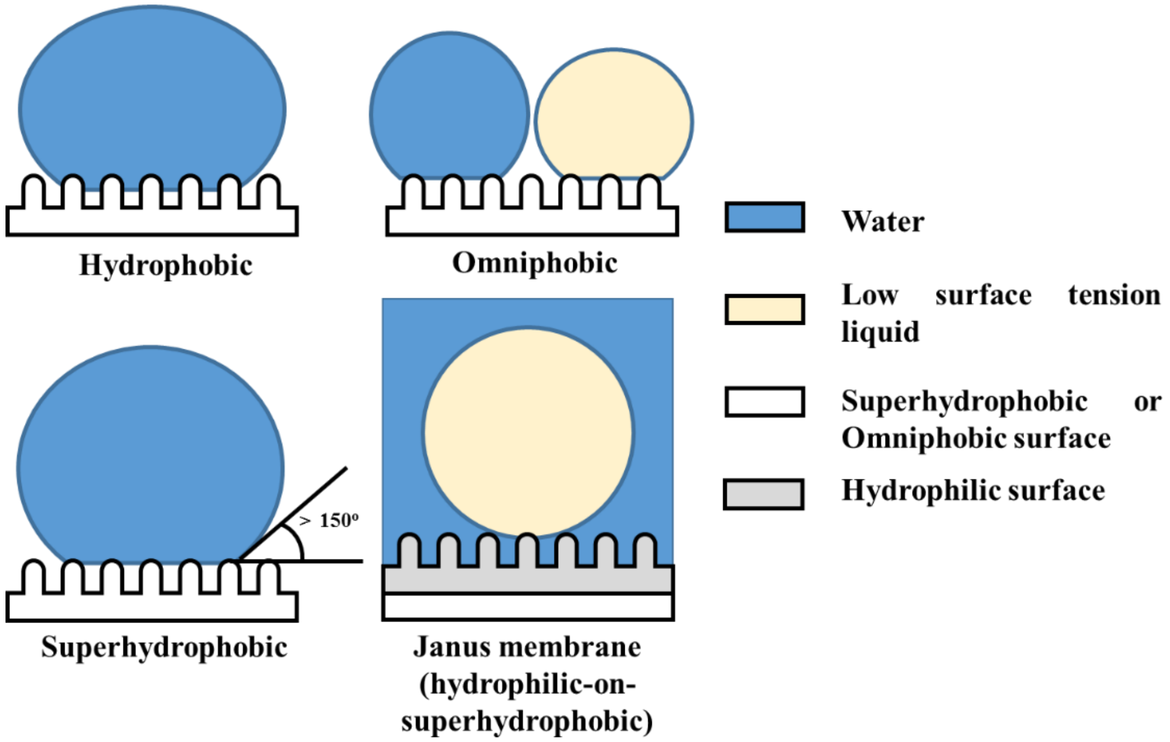


Fig. 5. Summary of membranes with special wettability for membrane distillation.

3.1 Superhydrophobic membrane surfaces

A superhydrophobic surface is generally defined by an apparent water CA of more than 150° [39, 97]. However, the CA varies depending on various measurement techniques. In addition, two distinctly different wetting states, Wenzel and Cassie-Baxter, can share the same apparent angles. To clear the ambiguity, some researchers argued that superhydrophobic membranes should have a Cassie-Baxter wetting state. Therefore, a more explicit definition of superhydrophobicity is that in addition to high apparent CAs, water droplets should be able to bounce or have very low sliding angles (i.e. tilt angle) on the superhydrophobic surfaces

[97, 98]. Superhydrophobic surfaces are inspired from natural phenomena such as the lotus effect for its self-cleaning property.

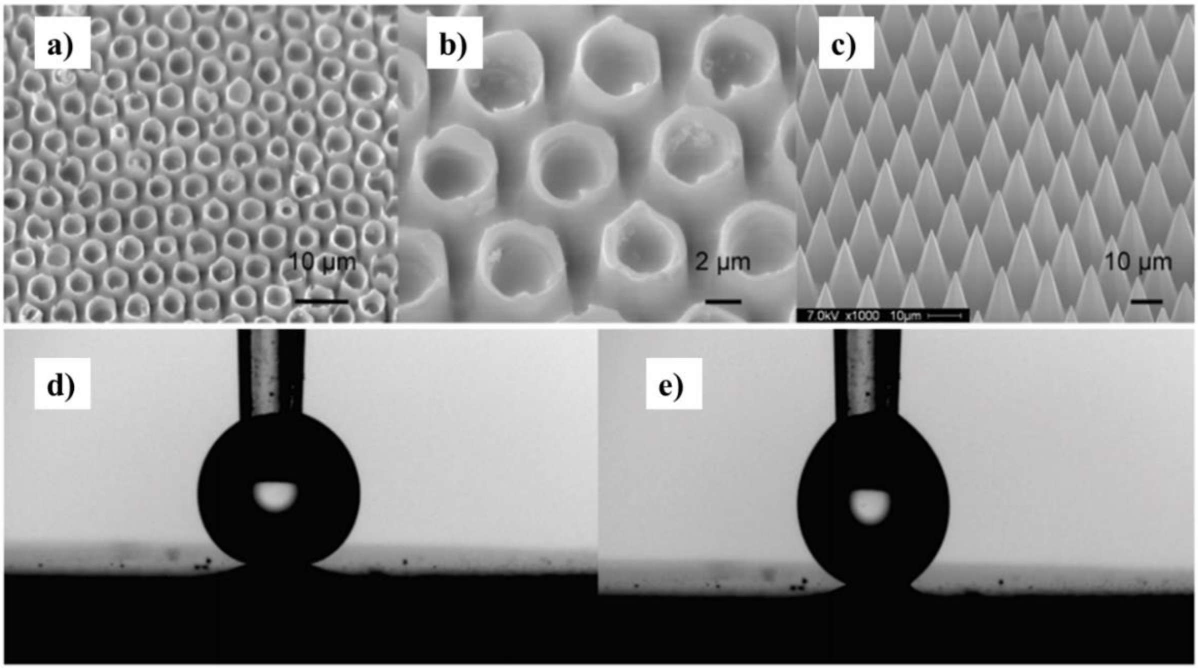


Fig. 6. a) Low- resolution scanning electron microscopy (SEM) of nano-spiked microchannels on glass membrane surface that are etched in 1% hydrofluoric acid for 30 mins; b) high-resolution SEM of nanospiked microchannels; c) array of cone-shaped nanospikes; d and e) high CAs (>160°) on superhydrophobic membranes. Image is reproduced with permission. Copyright 2009, American Chemical Society [99].

Recently, superhydrophobic MD membranes have been developed to address challenges in MD applications. Membranes with superhydrophobic surface tend to have improved flux and suffer much less flux reduction in long-term MD operation due to their much higher wetting resistance and self-cleaning properties. In some cases, superhydrophobic membranes also have improved wetting resistance against feed solutions containing low surface tension components [100].

One of the first superhydrophobic membranes for MD was developed by Ma et al. in 2009 by creating ordered arrays of nano-spiked microchannels on a glass membrane surface followed by the fluorination on membrane surfaces [99] (see **Fig. 6**). The membrane surface had a high water CA of over 160°. It is believed that the nanostructures at the membrane surface contributed to the improvement of CAs. Varying surface morphology by increasing cone angles led to much improved superhydrophobicity.

Razmjou et al. developed a superhydrophobic membrane by incorporating fluorinated TiO_2 nanoparticles (NPs) onto PVDF membranes [39]. The membrane surface had a hierarchical structure with multilevel roughness, exhibiting a water CA of 163°, a glycerol CA of 166°, and a 30% (vol.) mono-ethanol amine CA of 150°. In principle, a superhydrophobic surface can be achieved in two steps: 1) increasing surface roughness with hierarchical structures, and; 2) decreasing surface tension with tailored chemical compositions on the membrane surface.

Although better MD performance has been achieved with superhydrophobic membranes for its improved permeability and wetting resistance, there are still challenges due to its intrinsic limitations. Like hydrophobic surface, superhydrophobic surfaces are prone to severe organic fouling especially when oil emulsion exists in the feed water. Flux will quickly decline when membrane fouling occurs, which is caused by oil adsorption on membrane surfaces.

3.2 Omniphobic membrane surfaces

Omniphobic surfaces can repel liquids over a broad range of surface tensions and polarities, exhibiting high CA of these liquids such as mineral oils, decane, ethanol, etc. Compared with superhydrophobic surfaces, omniphobic surfaces generally have even lower surface tension. In addition, hierarchical structures with reentrant features are generally found on omniphobic surfaces, leading to a Cassie-Baxter state on membrane surfaces [101]. Such wettability has properties including self-cleaning, bio and mineral fouling resistance, and stain resistance [102, 103]. To address fouling and wetting issues when treating low surface tension feeds via MD, omniphobic membranes have been developed. Hydrophobic PTFE and omniphobic membranes show different wetting behavior when liquids with various surface tension are applied on their surfaces: PTFE membranes are susceptible to rapid wetting against low surface tension liquids while omniphobic membranes are able to repel the liquids [104].

Lin et al [104] fabricated the first omniphobic MD membrane by coating silica nanoparticles on glass membranes followed by fluorination (see **Fig. 7**). The modified surface illustrated high CA towards low surface tension chemical liquids including mineral oil, ethanol, and decane, due to the air trapped inside reentrant structures.

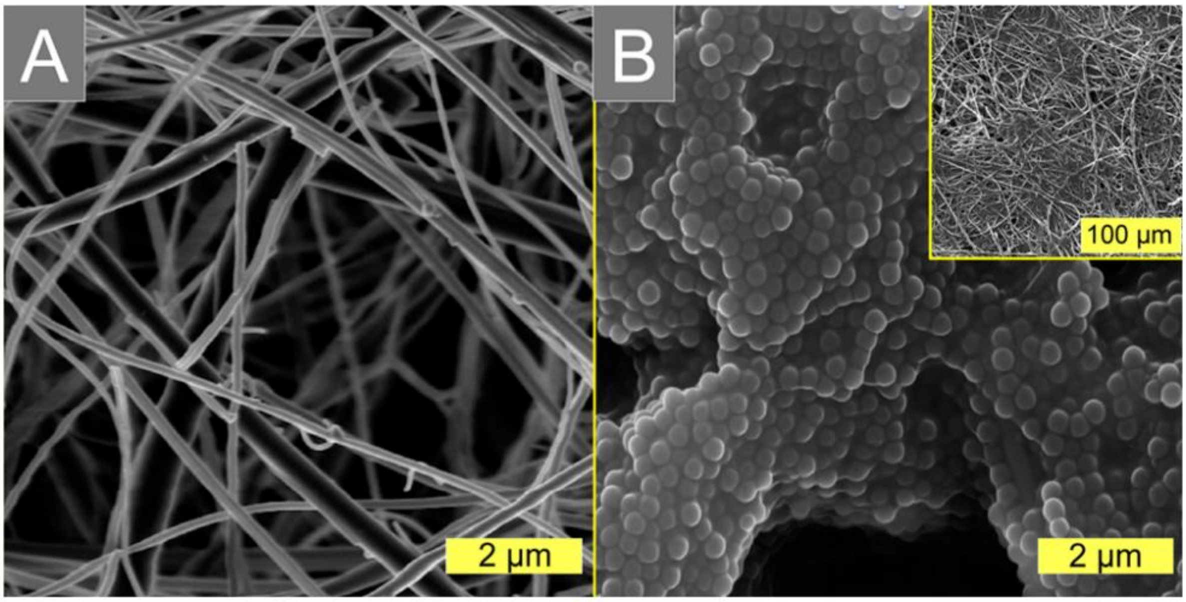


Fig. 7. SEM images of the surface morphology of A) pristine glass fiber membrane; B) omniphobic surface on glass fiber after modifications. The inset image in B displays the same

sample at lower magnification. Image is reproduced with permission. Copyright 2014, American Chemical Society [104].

Woo et al. developed omniphobic MD membrane surfaces without reentrant structures by modifying the electrospun nanofiber membranes with CF_4 plasma treatment. The omniphobic surface displayed water CA > 160°, and high CA (147 – 149°) towards methanol, ethylene glycol, and mineral oil. Longer duration of CF_4 plasma treatment led to higher omniphobicity by reducing surface tension by promoting the formation of CF_3 and CF_2-CF_2 bonds.

Omniphobic membranes provide additional fouling resistance against feedwater containing low surface tension contaminants, and the wetting issues are hence mitigated as well. However, it is challenging to fabricate chemically and mechanically robust omniphobic membranes. Moreover, omniphobic membranes usually contain toxic compounds (e.g. fluorine) which pose potential risks to potable water production if they leach or lose coating materials.

3.3 Janus membranes

Janus membrane structures allow opposing properties at the two sides working collaboratively, exhibiting distinctive mass transfer mechanism with integrated selectivity. In a broad sense, the properties of both sides in a Janus membrane can differ in chemical and physical aspects such as morphology, surface charge, material component, etc. Recently, the definition of Janus membrane has become more specific. To be in line with the literature, Janus membranes are defined as having opposing wettability at each side [105] and can be configured in three approaches: 1) A-on-B: one side is significantly thinner than the other; 2) A-and-B: Both sides share similar thicknesses; sandwich membrane including one additional middle layer is also counted as one special form of Janus membrane; 3) A-to-B: gradient across the membrane cross-section can be observed between the two sides. In general, there are two approaches to fabricate Janus membranes: asymmetric fabrication and asymmetric decoration, depending on whether Janus structures are achieved during the formation of membranes [106]. Depending on the configurations and the composition of each layer, Janus membranes can exhibit various surface wettability and mass transfer mechanisms.

Khayet et al. developed a flat-sheet Janus membrane for MD with a configuration of “hydrophobic layer over hydrophilic layer”. The membrane was prepared by a single phase inversion casting step with a hydrophilic polymer dope solution containing hydrophobic fluorinated surface-modifying macromolecules [107]. Bonyadi and Chung also developed a Janus membrane but in a hollow fiber membrane configuration with similar structure: hydrophobic layer on hydrophilic layer [19]. **Fig. 8** shows the contact angle measurements of the hollow fiber Janus membrane, having two different values at opposite sides of the membrane.

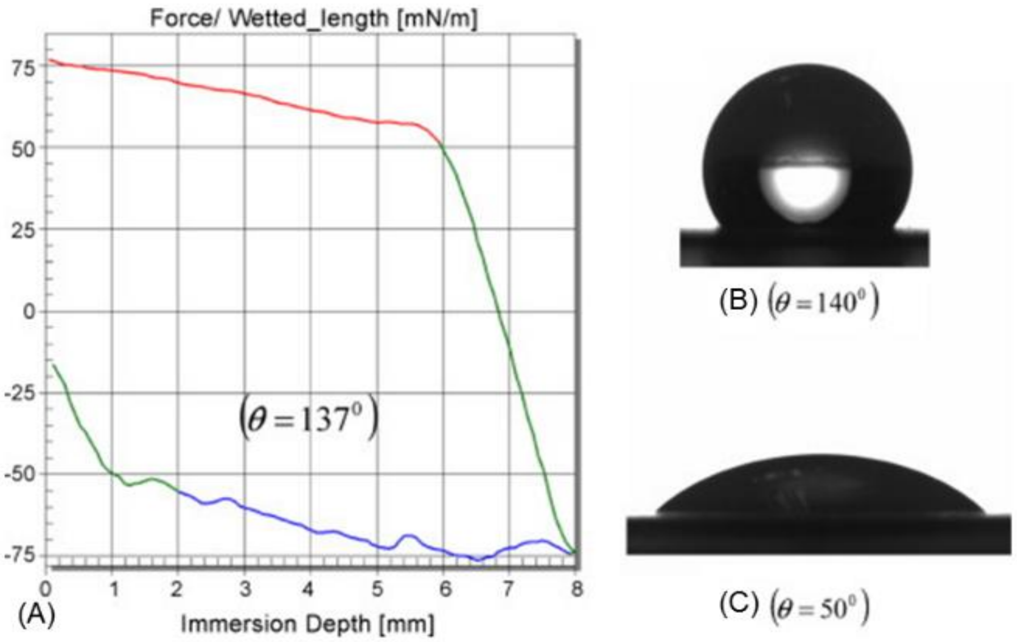


Fig. 8. Contact angle measurements of the developed hollow fiber. A) Force per unit length of fiber vs. immersion depth. Wetting state and contact angle of water droplet on flat sheet membrane using dope solution B) for hollow fiber shell layers; C) for hollow fiber lumen layers. Image is reproduced with permission. Copyright 2007, Elsevier [108].

In contrast, Peng et al. reversed the layer design and fabricated a membrane with hydrophilic layer on hydrophobic layer [109]. The approach was to design PVA/PEG hydrophilic layers with a thickness of 6 µm coated on top of hydrophobic PVDF substrates [109]. A similar hydrophilic layer on hydrophobic substrate was developed for an Osmotic Distillation (OD) process. (In OD the vapor pressure difference is generated by osmotic pressure differences). A thin PVA coating on the PVDF or PP membrane eliminated wetting by an oily feed solution [110]. Recently, interest in this configuration has been increasing due to their improved wetting and fouling resistance against oils and other low surface tension liquids, which is essential for the potential usage of MD in the treatment of produced water. Zuo and Wang conducted a detailed investigation on the development of Janus membrane with the configuration of “hydrophilic layer on hydrophobic layer” in terms of fouling resistance. The hydrophilic layer exhibited very low in-air water CA but high underwater oil CA. The membranes were fabricated by grafting a hydrophilic layer made from PEG on top of a hydrophobic PVDF flat sheet membrane [111]. The top and bottom sides of Janus membrane showed water CA of 25.2^{o} and 120.1^{o}, respectively, as the deposition of TiO$_2$ particles on hydrophilic layers further improved the hydrophilicity of the membrane surfaces by the incorporation of multi-level structures. Plasma was then applied on the coated membrane to improve the stability of the hydrophilic layer. The Janus membrane showed strong attachment between the hydrophilic layer and the hydrophobic layer as it can be observed that surface morphology hardly changed after 5 min of ultrasonic treatment. Janus membranes with “hydrophilic layer on hydrophobic layer” configuration exhibit improved fouling resistance against low surface tension liquids and wetting resistance against surfactants. Moreover, such membranes have improved resistance against oil fouling, the only foulant types which omniphobic membranes are susceptible to because of the hydrophobic-hydrophobic interaction [106, 112].

Although Janus membranes exhibit unique properties beneficial to MD applications, the special wettability coating on hollow fiber membranes at a large scale is still challenging. Also, some unknown influencing factors such as stimuli-responsive effects on Janus configurations need further investigation [113].

4. Membranes with special surface wettability for membrane distillation

The development of MD membranes with special wettability has drawn significant attention in recent years. In addition to the satisfaction of the desired membrane properties, the provision of special wettability on MD membrane surface contributes to synergetic effects which may benefit the overall MD processes. For example, superhydrophobic MD membranes designed with anti-wetting property usually have improved permeability and selectivity [39, 114]. This section comprehensively discusses details on the fabrication methods to achieve MD membranes with special wettability. Further, enhancement in MD performance for various applications using the MD membranes with special wettability features is highlighted.

We categorized the membrane fabrication techniques to produce surfaces with special wettability into four subgroups: nanocomposite membranes, surface-modified commercial polymer membranes, surface-modified synthesized polymer substrates, and surface-modified inorganic membranes. Nanocomposite membranes are one-step fabricated membranes, by which the membrane matrix and the special wettable membrane surface features are created simultaneously. Meanwhile, the other three subgroups are membranes requiring surface modification, which are categorized based on the types of their substrates. **Table 1** summarizes main features of various special wettability membranes for comparison. For each category, fabrication methods, available special wettability, benefits, challenges and applications are selected based on literature developing special wettability membranes, which will be detailed in following sections. For example, regarding applications of surface modified commercial membranes, researchers have applied them for desalination, oil/water separation, and surfactant removal [111, 115, 116]. As they have not been tested for brine treatment, such membranes are assumed unsuitable for brine treatment although they may treat it.

Table 1. Category representation of special wettability membranes based on fabrication methods, available special wettability, benefits, challenges and applications (references provided in subsequent tables).

	Nanocomposite membranes	Surface modified commercial membranes	Synthesized membranes	Ceramic membranes
Fabrication Method				
-Electrospinning	●	●	●	
-Nanoparticle coating		●	●	●
-Templating			●	
-Plasma treatment		●	●	
-Fluorination		●	●	●
Special Wettability Type				
-Superhydrophobic	●	●	●	
-Omniphobic		●	●	
-Janus (hydrophilic-on-hydrophobic)			●	
-Janus (hydrophobic-on-hydrophilic)			●	●
Benefits				
-One-step fabrication	●			
-Strong robustness		●		●
-High permeability	●		●	
-Anti-wetting (water)	●	●	●	●
-Anti-wetting (surfactants)		●	●	●
Anti-fouling		●	●	●
Challenges				
-Low LEP	●			
-Low permeability		●		●
-Scale-up	●	●	●	
-Use of toxic chemicals		●	●	●
-Membrane swelling	●	●	●	
-High thermal conductivity				●
-Energy intensive				●
Applications				

-Desalination	●	●	●	●
-Brine treatment	●		●	●
-Oil/water separation		●	●	●
-Industrial wastewater treatment			●	●
-Surfactants removal		●	●	●

4.1 Nanocomposite membranes

This section covers all MD nanocomposite membranes with special wettability which are fabricated via one-step fabrication methods. All of these membranes have superhydrophobic surfaces (**Table 2**).

Table 2. Published reports in the literature about nanocomposite membranes with special wettability(superhydrophobicity) categorized by application.

Polymer and additives	Fabrication method	Water contact angle (º)	Mean pore size (µm)	Application and MD configuration	Claimed benefit	Ref.
PVDF /hydrophobic silica	Electrospinning	150	0.36	DS by DCMD	AW	[117]
PVDF	Electrospinning (electrospraying hydrophobic silica simultaneously)	163	n/a	DS by DCMD	HP	[114]
PVDF/ PTFE	Electrospinning	152	0.49±0.15	DS by VMD	AW	[118]
PVDF-HFP /carbon nanotubes	Electrospinning	159	0.29±0.01	DS by DCMD	AW	[119]
PVDF-HFP /graphene	Electrospinning	163	0.86±0.02	DS by AGMD	AW	[120]
PS	Electrospinning	150	1.15	DS by DCMD	HP	[121]
PMMA/PDMS	Electrospinning	163	8.03	DS by DCMD	AW	[122]

Note: DS = desalination, IW = industrial wastewater, AF = anti-fouling, AW = anti-wetting, HP = high permeability

4.1.1 Fabrication methods

A facile way to fabricate nanocomposite membranes is by using an electrospinning technique to obtain nanofiber membranes with rough surfaces. This technique offers a relatively easy and straightforward fabrication method for achieving nanocomposite membranes with large pore sizes, high porosity, and superhydrophobicity. The membranes have largely improved wetting resistance while maintaining high permeability. For nanofiber membrane fabrication, the material parameters (such as dope solution concentration), process parameters (such as applied voltage, tip-to-collector distance and fabrication time), and environmental parameters (such as humidity) should be optimized to attain the desired membrane morphology that will effectively enhance MD performance.

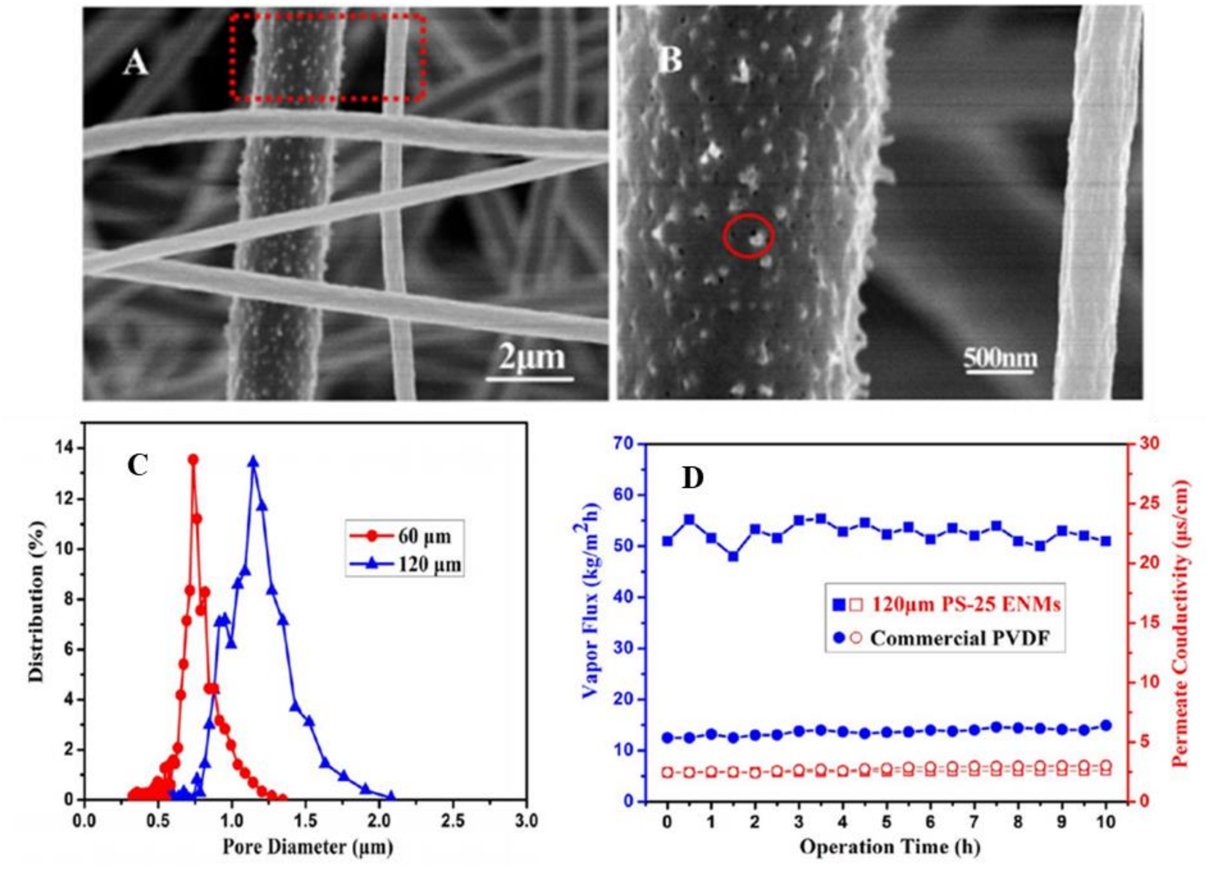


Fig. 9. a) SEM images of dual-biomimetic PS nanofiber membranes; b) the dotted circle shows nanopapillose and nanoporous structures; c) the effect of membrane thickness on pore size distribution; d) the comparison of flux between superhydrophobic nanofiber PS membrane with a commercial PVDF membrane. Image is reproduced with permission. Copyright 2014, American Chemical Society [121].

Hierarchical structures on the surface of nanocomposite membranes can significantly enhance MD permeation performance. Li et al. successfully developed electrospun polystyrene (PS) nanofiber membranes with micro/nanoscale roughness, which are inspired by the lotus effect (**Fig. 9**). The nanofiber membranes showed high CA (~150°), which led to very high flux (105 Lm^{-2}h^{-1} or LMH) due to high feed temperature [121]. A common method for creating hierarchical structures on the surface of nanocomposite membranes is by adding hydrophobic micro/nanoparticles into electrospinning dope solutions. For instance, Woo et al. added two-dimensional graphene nanoparticles into the PVDF dope solution for electrospinning [120]. With an optimal graphene concentration of 5 wt.%, the nanofiber membranes obtained a very high contact angle of 163° with high LEP of 187 kPa due to protruding nanoparticles on electrospun nanofibers. However, further increase in nanoparticle concentrations caused aggregation issues, leading to decrease in porosity and mean pore size; thereby, reducing the MD flux. Other hydrophobic particles that are added into dope solutions include micro-size polymers (PTFE, PDMS), one-dimension nanomaterials (carbon nanotube), and three-dimensional nanomaterials (surface modified silica) [117-119, 122].

Another technique, apart from electrospinning the nanoparticle-blended dope solution, that can also result in favorable membrane surface property is simultaneous electrospraying of the nanocomposite dope solution while electrospinning nanofibrous membranes. Su et al. fabricated a membrane with low sliding angle of 3° and high LEP of 280 kPa by electrospraying surface modified silica while electrospinning PVDF membrane [114]. The nanofiber membrane also showed superoleophilicity (**Fig. 10**).

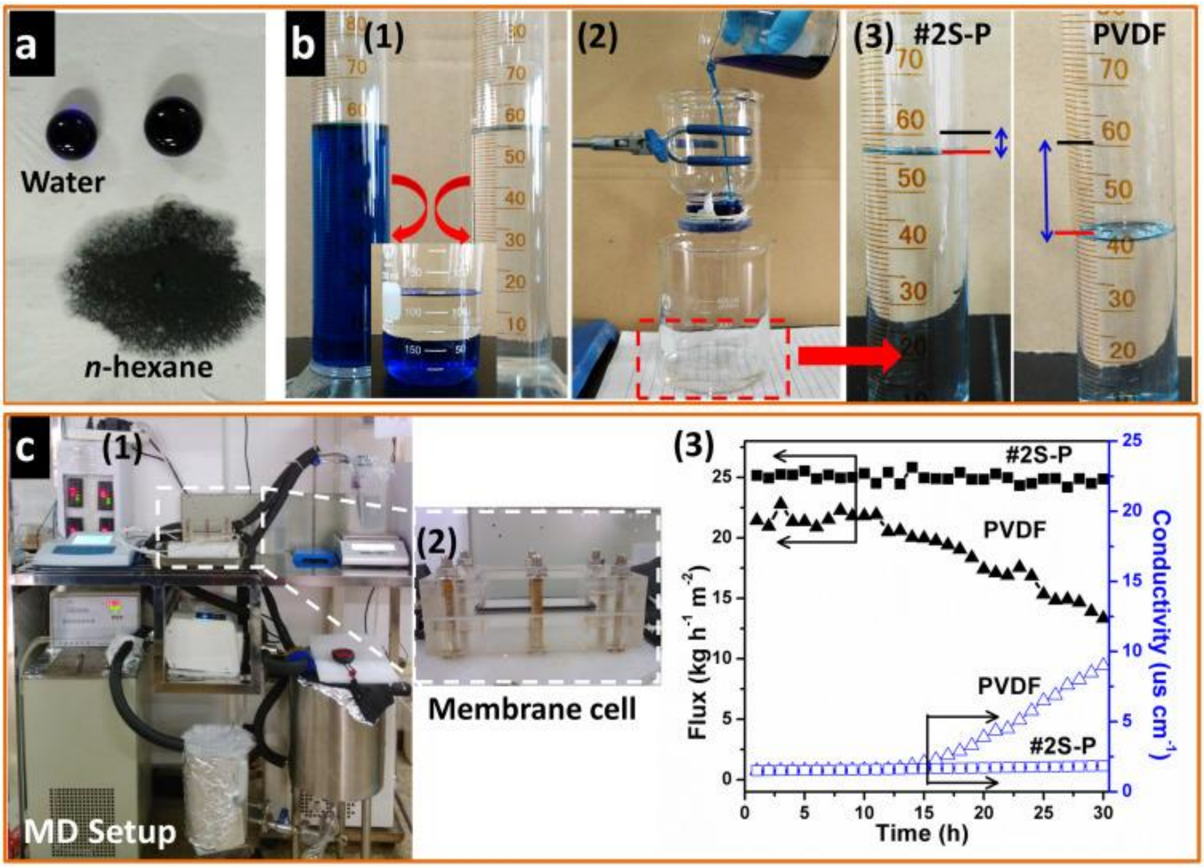


Fig. 10. a) resistance against water and n-hexane droplets; b) oil/water separation processes using neat nanofiber PVDF and superhydrophobic nanofiber membranes; c) DCMD configuration and permeation performance comparison. Image is reproduced with permission. Copyright 2016, Elsevier [114].

4.1.2 Applications

Nanocomposite membranes are usually superhydrophobic; illustrating excellent permeability with high selectivity and permeability. As such, they are highly suitable to be applied for seawater desalination and brine treatment. Upon surface modification, these nanocomposite membranes exhibit improved permeability [114, 121], as well as enhanced MD permeate fluxes compared with commercial PVDF membranes. Also, nanocomposite membranes achieve improved LEP and wetting resistance compared with commercial hydrophobic membranes in long-term operation [120, 122]. These surface-modified membranes illustrated stable performance for 60 h in the configuration of AGMD with a salt rejection of 99.99%. However, their applications are limited to desalination because of their inability to resist low surface tension liquids which can cause membrane fouling and wetting [117].

4.1.3 Challenges

The biggest issue for nanocomposite membranes is their relatively large maximum membrane and mean pore size compared with synthesized and surface-modified commercial membranes with special wettability characteristics, which greatly hinders long-term MD performance [117, 119]. Moreover, although nanocomposite membranes may have surface superhydrophobicity, the equilibrium of water droplets on these membranes are usually at Wenzel state, as the droplet cannot bounce or slide on membrane surfaces. As such, the hydrophobicity of these membranes is compromised, leading to lower wetting resistance than special wettability membranes from other categories. Most researchers have not addressed challenges of nanocomposite membranes in their papers as they only apply the membranes in MD for a very short duration (around 10 h). That means stability of these membranes in long-term MD operation are not guaranteed [114, 118, 121]. Another challenge is that nanocomposite membranes usually have lower mechanical strength than other types of membranes, so further treatment without affecting their superhydrophobicity is required to improve the strength [120, 122].

As nanocomposite membranes can only attain one special wettability feature, which is superhydrophobicity, their application is highly limited towards desalination. This is because, superhydrophobic membranes are prone to organic fouling (as mentioned in 3.1). As the minimal organic content in seawater does not affect the performance of nanocomposite membranes, they are suitable to treat sea water and its RO brine. Also, the superhydrophobicity of these membranes may be lost due to fouling in MD processes, so regeneration regimes in operation are required [123, 124].

The other major challenge is scaling up the electrospinning technique to the industrial level. Further research should be focused on the development and parameters optimization of electrospinning technique in pilot scale for the commercial realization [120, 125].

4.2 Surface-modified commercial membranes

This section covers discussions on surface-modified commercial membranes with special wettability for MD. Due to their low cost, constant quality, and wide availability, hydrophobic commercial membranes mostly made of PVDF with surface pore sizes ranging from 0.2 - 0.45 µm have been utilized for surface modification to enable improved properties and hence performance for MD.

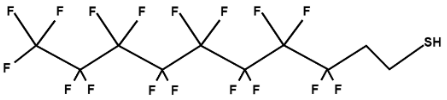
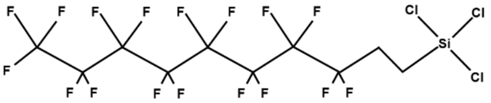
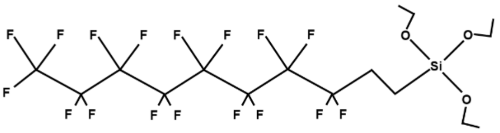
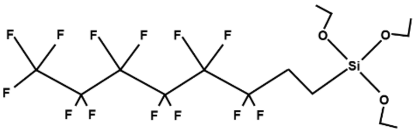
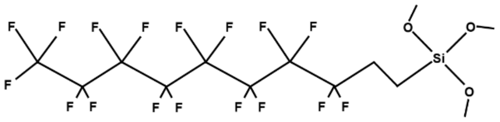
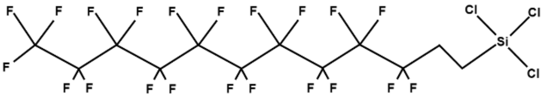
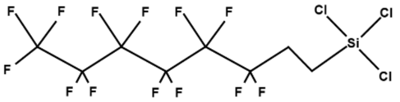
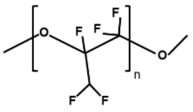
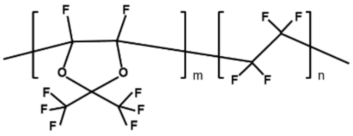
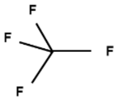
4.2.1 Modification methods

Commercial membranes can attain superhydrophobicity and omniphobicity by increasing the surface roughness and providing multi-level structures. A favorable manner to achieve these conditions is by incorporating nanoparticles (e.g. TiO_2, silica, etc.) on the surfaces of the commercial membrane surfaces. Nanoparticles can be incorporated onto a commercial membrane surface via dip-coating or by adhesive-deposition (such as using polydopamine (PDA) as adhesive). For example, Shan et al. deposited Ag nanoparticles (AgNPs) on commercial PVDF membrane using PDA as adhesive [126]. As a result, Error! Reference source not found.the roughness of the commercial membrane increased from 99.1 to 157.6 nm, and the CA increased from 126° to 136°. The deposition of composite particles with multiscale roughness on membrane surfaces has also been explored to obtain MD membranes with hierarchical structure. Zheng et al. firstly fabricated polystyrene (PS) microspheres with silica NPs deposited on their surfaces; then coated the composite particles onto commercial membranes using the adhesive polymer 3-methacryloxypropyltrimethoxysilane. The hierarchical membrane achieved a significantly increased surface roughness, R_a = 343 nm, while the silica-coated membrane and pristine membrane had a roughness of 142 and 99 nm, respectively [115]. With the aid of fluorination, the imparted re-entrant structure on the membrane surface maintained a Cassie-Baxter state of wettability. It had a very high water CA of 176.5° and low sliding angle of 7°, and water droplet could bounce back when falling on to the membrane surface. The modification approaches using NPs can also enhance the permeability of MD membranes due to the large surface areas of NPs, if well designed. Similarly, most of above-mentioned modification methods can be applied on to commercial hollow fiber membrane (e.g. in the module as a post treatment) [127].

Commonly, the nanoparticle-coated commercial membranes are then fluorinated to achieve superhydrophobicity or omniphobicity.

Table 3 shows various compounds used for fluorination, mostly long-chain fluoroalkylsilanes. Razmjou et al. fluorinated the TiO_2 coated membrane with 1H, 1H, 2H, 2H-perfluorododecyltrichlorosilane [39]. This new membrane illustrated self-cleaning property as indicated by the significantly decreased sliding angles. Fluorination of NPs coated membranes with re-entrant structures renders them omniphobic surfaces. The fluorinated multiscale membranes showed strong resistance against low surface tension liquids: 156˚ for oil emulsion, 133° for diiodomethane, and 138° for hexadecane (**Table 4**), making the membrane capable of treating feed water containing low surface tension components [115]. Generally, the fluorinated NPs coated commercial membranes have much improved wetting and fouling resistance due to the multi-scale roughness on the surface. The wettability is maintained at Cassie-Baxter state for all these membranes, which means they have very high contact angle and low sliding angles.

Table 3. Various chemical compounds for fluorination.

Chemical name	**CAS no.**	**Chemical structure***	**Ref.**
1H,1H,2H,2H-Perfluorodecanethiol (PFDT)	34143-74-3		[126, 128]
1H,1H,2H,2H-Perfluorodecyltrichlorosilane (FDTS)	78560-44-8		[92, 129-131]
1H, 1H, 2H, 2H-Perfluorodecyltriethoxysilane (PFTES)	101947-16-4		[132-136]
1H, 1H, 2H, 2H-Perfluorooctyltriethoxysilane (PFOTES)	51851-37-7		[137]
1H, 1H, 2H, 2H-Perfluorodecyltrimethoxysilane (FAS17)	83048-65-1		[115, 138, 139]
1H, 1H, 2H, 2H-Perfluorododecyltrichlorosilane (FTCS, FAS21, FDDTS)	102488-49-3		[39, 104, 140, 141]
1H, 1H, 2H, 2H-Perfluorooctyl-trichlorosilane (PFOTCS)	78560-45-9		[40, 99]
Perfluoropolyether (PFPE)	69991-67-9		[117, 142]
Poly[4,5-difluoro-2,2-bis(trifluoromethyl)-1,3-dioxole-co-tetrafluoroethylene] (PTFE AF 2400)	37626-13-4		[101]
Tetrafluoromethane (CF_4)	75-73-0		[116, 143]

*All the chemical structures of compounds in this table are adopted from relevant product documents on the website of Sigma-Aldrich except the chemical structure of CF_4 which is adopted from National Institute of Standards and Technology Chemistry WebBook, SRD 69

Apart from the use of nanoparticles coating and fluorination, other modification treatments have also been implemented to acquire superhydrophobicity on commercial membrane. Yang et al. obtained a superhydrophobic membrane by applying CF_4 plasma-modification, which had improved CA of 162° [116]. The membrane surface roughness and structures were not affected by plasma modification, so the surface wettability remained at the Wenzel state; low sliding angle of water droplets was not observed.

Table 4. Published reports in the literature about surface-modified commercial membranes with special wettability for MD.

Substrate	**Modification methods**	**Special wettability**	**Water contact angle (º)**	**Mean pore size (µm)**	**Application and configuration**	**Claimed benefits**	**Ref.**
PVDF	Plasma-modifying (CF_4)	superhydrophobic	162	0.25	DS by DCMD	HP	[116]
PVDF	Dip-coating (TiO2)/ f	superhydrophobic	163	0.39±0.03	DS by DCMD	AF	[39, 141]
PP (hf)	PDA-depositing (SiNPs)/ f	superhydrophobic	157	0.2	DS by VMD	AW	[132, 137]
PVDF	Dip-coating (SiNPs)/ f	omniphobic	167 141-MI	0.40±0.02	SF by DCMD	AW	[40, 92]
PVDF	P(A 174)-depositing (SiNPs@PS)/ f	omniphobic	177 156-oil emulsion 133-MI 138-HXD	0.26±0.05	SF by DCMD	AF/AW	[115]
PVDF	PDA-depositing (AgNPs)/ f	omniphobic	168 137-rapeseed oil	0.38	SF by DCMD	AF/AW	[126]
PVDF	Dip-coating (TiO_2)/ plasma modifying (He)	Janus (hydrophilic-on-hydrophobic)	25.2	0.18	OW by DCMD	AF/AW	[111]
PVDF	Spraying-coating (CTS-PFO/SiNPs)	Janus (hydrophilic-on-hydrophobic)	0 UW 150-crude oil	0.39±0.03	OW by DCMD	AF	[144]
PVDF	Spraying (SiNPs)/ PDA-depositing	Janus (hydrophilic-on-hydrophobic)	35 UW 163-crude oil	0.4	OW by DCMD	AF	[95]
PVDF	Dip-coating (PVA)	Janus (hydrophilic-on-hydrophobic)	0	-	SF by DCMD	AF/AW	[34]
PVDF	Filtration-coating (graphene oxide)	Janus (hydrophilic-on-hydrophobic)	125	0.69	SF by DCMD	AF	[145]
PTFE	Chemical-etching (PDA)	Janus (hydrophilic-on-hydrophobic)	-	0.34±0.02	OW by VMD	AF	[146]
PTFE	Electrospinning (PVA)	Janus (hydrophilic-on-hydrophobic)	36 UW 149-crude oil	0.28±0.04	OW by DCMD	AF	[147]

PP	Electrospinning (PVA with Triton X-100)	Janus (hydrophilic-on-hydrophobic)	23	0.07	DS by DCMD	AW	[148]
PVDF (hf)	PDA-depositing (PEI)	Janus (hydrophilic-on-hydrophobic)	26,13	0.02	OW by DCMD	AF/AW	[127, 149]

Note: hf = hollow fiber, f = fluorination, DS = desalination, MI = diiodomethane, HXD = hexadecane, IW = industrial wastewater, SF = surfactants removal, OW = oil/water separation, AF = anti-fouling, AW = anti-wetting, HP = high permeability

Janus (hydrophilic-on-hydrophobic) membranes can be acquired by coating a layer of highly hydrophilic compounds (i.e. high surface tension) on the commercial membranes. Wang et al. successfully coated one layer of PVA on PTFE membrane using electrospinning. After crosslinking, the Janus membrane had a low in-air water CA of 35.5° and high underwater oil CA of 148.7°. However, its pore size significantly decreased from 0.45 to 0.28 μm (**Fig. 11Error! Reference source not found.**). Owing to the low roughness of commercial membranes, NPs have also been employed to impart multi-scale structures to the membrane surfaces. Wang et al. created a hierarchical structure on commercial PVDF membrane using silica NPs. As a result, the composite membrane had a very high underwater oil CA of 163°. **Fig. 12** shows that, unlike hydrophobic and superhydrophobic membrane surfaces, the composite Janus membrane had minimal interaction with oil droplets due to low attraction between them; therefore, there was no physical contact between the oil droplet and the membrane surface [144]. The surface charge of the Janus membranes must be taken into consideration as it affects the wettability of oil significantly. Wang et al. found that a negatively-charged Janus membrane could maintain high oil CA at 163° consistently while the positively-charged one failed. Also in DCMD experiments, only the negatively-charged composite membranes could maintain high flux stably when treating saline solution containing crude oil [95].

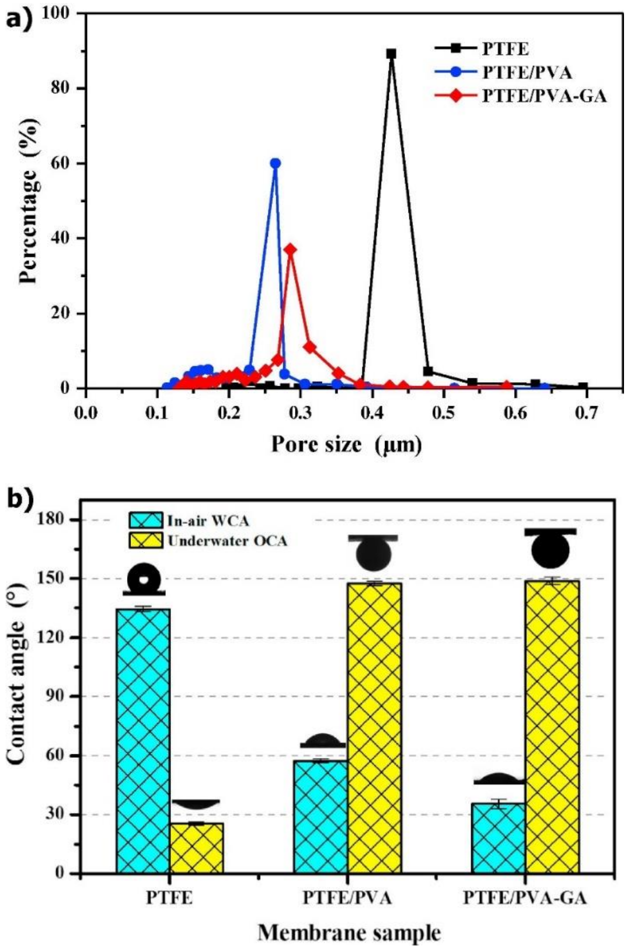


Fig. 11. a) Pore size distribution of virgin PTFE membrane, the PVA coated PTFE membrane, and cross-linked surface-modified membrane; b) in-air water contact angle and underwater oil contact angle of these membranes. Image is reproduced with permission. Copyright 2018, Elsevier [147].

After surface modification, nearly all the commercial membranes still maintain their high mechanical strength, making them viable in long-term operation. However, the pore size of these surface-modified commercial membranes becomes even smaller after the modification; therefore, they have relatively lower flux than superhydrophobic nanocomposite membranes.

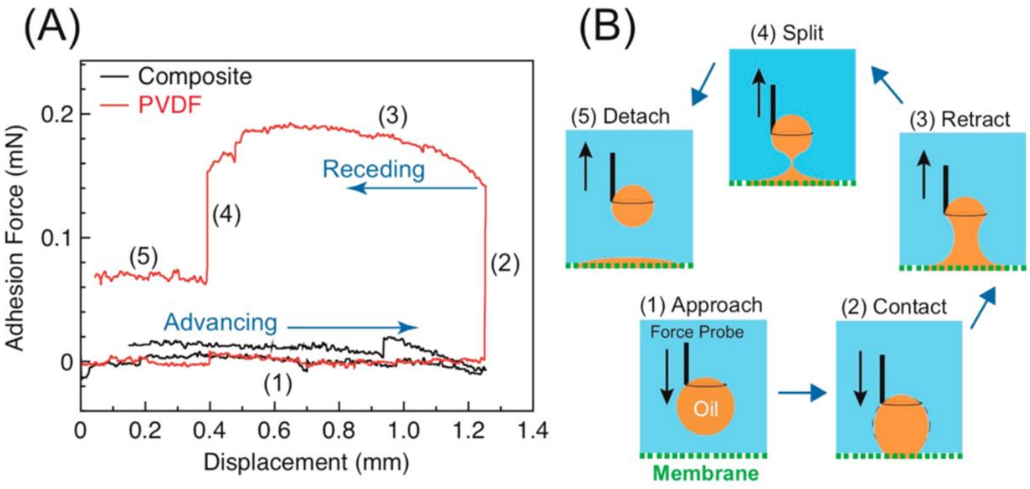


Fig. 12. a) Force-displacement curves showing the patterns where a mineral oil droplet interacted with the composite Janus membrane (black curve) and hydrophobic membrane (red curve); b) the five stages in the patterns. Image is reproduced with permission. Copyright 2016, American Chemical Society [144].

4.2.2 Applications

The commercial membranes imparted with superhydrophobicity are used for desalination. Depending on the modification approaches, these membranes can have improved permeability, wetting resistance, or scaling resistance [39, 116, 141]. The commercial membranes designed with omniphobicity are used to treat highly saline oil-field produced water containing surfactants. The surface modified membranes have improved wetting and fouling resistance against sodium dodecyl sulfate (SDS) with concentration up to 0.5 mM in feed wastewater [40, 115, 126]. Also, the surface-modified commercial membranes with omniphobicity can deal with wastewater containing oil emulsion. More specifically, as oil emulsion can be prepared by surfactant or physical emulsification, the capacity of omniphobic MD membranes treating the oil emulsion varies. Oil-emulsion (prepared by surfactant) with the addition of oil up to 0.005 %v/v into the wastewater can be treated with stable MD permeation performance [92]. Wastewater containing oil emulsion that are prepared physically using high concentration of crude oil (1,000 ppm) can also be treated by the surface-modified membranes [144]. On the other hands, produced water or oil-emulsion wastewater can also be treated by Janus membranes (hydrophilic-on-hydrophobic) after surface-modifying commercial membranes. The membranes show improved fouling and wetting resistance against wastewater containing high crude oil (~ 1000 mg/L) and salinity (~ 35 g/L NaCl) [95, 144, 145].

4.2.3 Challenges

The approaches towards achieving surface-modified commercial membranes face several challenges. First, permeation of MD membrane may be decreased when polymers are used as adhesive to deposit NPs on the commercial membranes as the polymers can block membrane pores and hence reduce the mean pore size of the membranes. For these reasons, the thickness of NPs layers must be controlled precisely. Secondly, the strength of attachment between the NPs and the membrane substrates is compromised. Currently, PDA-depositing membranes have shown the highest stability; the membranes show high stability as they remain intact after undergoing ultrasonic tests. However, in real applications using membrane technology, chemical cleaning is a commonly applied practice [12]. Chemical cleaning reduces the strength of attachment of NPs on the surface modified membranes [150]. The detachment of nanoparticles into treated water could be a serious risk to human health, making NPs deposited membranes not viable for potable water treatment. Thirdly, most nanoparticles have low hydrophobicity, which means further modification approaches are required to reduce their surface tension. Fluorination is an effective technique for the development of MD membrane with desired wettability, but several issues hinder its potentials in industrial usage. The stability of the deposited fluorine compounds on membrane surface can be severely challenged by chemical cleaning during water-treatment cycles. Especially, in terms of fluorinated NPs coated membranes, the potential detachment of fluorinated NPs makes the membrane only viable for industrial usage. Also, most fluorine compounds have extremely poor degradability in the environment, and they can easily accumulate in living organisms and cause long-term harm. As stricter regulations on fluorine compounds are being imposed by many governments, it can further hinder their application in membrane modification. For these reasons, it is important to evaluate the potential of using chemicals with lower toxicity such as octamethylcyclotetrasiloxane as a substitute to fluorine compounds to reduce surface tension.

4.3 Synthesized membranes with special wettability

This section discusses developments in lab-synthesized membranes with special wettability for MD. Most of the published studies are directed towards developing new membranes that can address the challenges for long-term MD application. Two most commonly utilized techniques for substrates are by phase inversion (casting) and electrospinning. One of the key difference of membranes synthesized by these two techniques is that cast membranes have much smaller pore sizes compared to electrospun nanofiber membranes.

4.3.1 Modification methods

Various special wettability characteristics can be achieved on synthesized membranes via surface modification. As discussed in the last section, the common approaches of imparting superhydrophobicity or omniphobicity on commercial membranes are to coat nanoparticles onto the membrane surface followed by fluorination. This approach is also utilized for synthesized membranes. Moreover, templating has been applied to construct patterned/micropillared structures on membrane surfaces for the improvement of membrane surface roughness. Aside from fluorination, some other low surface tension chemicals had been deposited on the membrane surface to acquire superhydrophobicity (**Table 5**).

Table 5. Published reports in the literature about surface-modified synthesized membranes with special wettability for MD.

Substrate	**Substrate preparation method**	**Modification methods**	**Special wettability**	**Water contact angle (º)**	**Mean pore size (μm)**	**Application and configuration**	**Claimed benefits**	**Ref.**
PVDF	NIPS	Dip-coating (OTMS)	superhydrophobic	160	0.05	DS by DCMD	AW	[151]
PVDF	NIPS	Spraying (PDMS and hydrophobic SiNPs)	superhydrophobic	156	0.36±0.02	BT by DCMD	AF	[23]
PVDF (hf)	NIPS	Ultrafiltration-coating (etched PVDF particles)	superhydrophobic	164	n/a	SF by DCMD	AW	[100]
PVDF-HFP	Elec	Electrospraying (PDMS)	superhydrophobic	155 157	0.49, 0.40±0.05	IW by DCMD	AF/AW	[152, 153]
PVDF-HFP	Elec	Electrospraying (silica aerogel/PDMS)	superhydrophobic	170	0.47±0.05	SF by DCMD	AW	[154]
PVDF	Elec	Dip-coating (AgNPs)/ (1-Dodecanethiol)	superhydrophobic	153	0.34±0.01	DS by DCMD	HP	[155]
PVDF	Elec	Electrospinning (hydrophobic SiNPs)	superhydrophobic	156 152	0.69±0.02, 0.61	DS by DCMD	AW	[142, 156]
PVDF	Elec	Electrospinning (hydrophobic Al_2O_3NPs)	superhydrophobic	150 154	0.37 0.39	IW by AGMD	AF	[157, 158]
PVDF	NIPS	Templating/ f	superhydrophobic	176	0.20±0.01	BT by DCMD	AF	[159]
PVDF	NIPS	Templating	superhydrophobic	155	0.14	DS by DCMD		[160]
PVDF	NIPS	LBL (Si aerogel)/ f	omniphobic	177 163-mineral oil 160-methanol	0.09±0.01	SF by AGMD	AW	[134]
PVDF (hf)	NIPS	Chemical-modifying (SiNPs)/ f	omniphobic	142 100-cooking oil 75-ethanol	0.20±0.02	SF by VMD	AW	[101]
PVDF	Elec	Plasma-modifying (CF_4)	omniphobic	161 158-MI	0.80±0.02	SF by AGMD	AF/AW	[143]
PVDF-HFP	Elec	f	omniphobic	138 127-soybean oil	0.84	SF by DCMD	AW	[128, 133]
PVDF	Elec	Dip-coating (FTCS)/ f	omniphobic	160 130-mineral oil	0.26	SF by DCMD	AW	[140]
PVDF	Elec	Dip-coating (SiNPs)/ f	omniphobic	150 138-mineral oil	0.42	SF by DCMD	AW	[130]

PVDF-HFP	NIPS	Spraying (SiNPs-CTS/PFO)/ heat-treatment	Janus (hydrophilic-and-omniphobic)	15 UW 150-crude oil	n/a	OW by DCMD	AF/AW	[106]
PVA	Elec	f	Janus (superhydrophobic-on-hydrophilic)	158	0.46±0.01	DS by VMD	AF	[139]
PI	Elec	PDA-depositing (SiNPs)/ f	Janus (omniphobic -on-hydrophilic)	152	2.23	SF by DCMD	AF/AW	[135]
PVDF	Elec	Electrospraying (SiNPs@PAN)	Janus (hydrophilic-and-superhydrophobic)	0 UW 164-soybean oil	1.45	OW by DCMD	AF/AW	[161]

Note: NIPS = non-solvent induced phase separation, Elec = electrospinning, hf = hollow fiber, f = fluorination, DS = desalination, MI = diiodomethane, BT = brine treatment, IW = industrial wastewater, SF = surfactants removal, OW = oil/water separation, AF = anti-fouling, AW = anti-wetting, HP = high permeability

Besides inorganic nanoparticles, polymer particles have also been coated on synthesized membranes to create multi-scale morphology. Yan et al. deposited etched PVDF particles (average size of 300 nm) on hollow fiber membranes using ultrafiltration coating process to create lotus effect. The coating layer significantly increased its water CA to 164° , without blocking the membrane pores [100]. Some other researchers obtained superhydrophobic nanofiber membranes by electrospraying polydimethylsiloxane (PDMS) polymeric microspheres onto membrane surfaces [152, 153]. After the PDMS deposition, re-entrant hierarchical structures were created on the membrane surfaces, leading to increased water CA and significantly decreased sliding angle. The polymeric particles used in the modification are hydrophobic, so there is no requirement of reducing surface tension, which means the modification procedure is simpler.

As nanofiber membranes have advantages of high surface roughness with multi-scale structures, it is possible for these membranes to achieve omniphobicity with single-step surface modification. An et al. obtained omniphobic membranes by fluorinating electrospun PVDF-HFP nanofiber membranes, and the membranes gained the ability to repel soybean oil with a contact angle of 127°. Woo et al. obtained an omniphobic electrospun nanofiber membrane by CF_4 modifying. The surface-modified nanofiber membrane could repeal low surface tension liquids including ethanol and diiodomethane. Comparatively the same surface modified technique with commercial PVDF membranes failed to perform. The difference is attributed to air trapping on the hierarchical structures of the nanofiber membrane surfaces. Also, the CF_4 plasma modified nanofiber membranes had much higher mean pore size than the commercial membranes (0.80 vs. 0.25 μm). Aside from fluorination, some other low surface tension chemical had been deposited on the membrane surface to acquire superhydrophobicity. Ray et al. coated synthesized NIPS membranes with octadecyltrimethoxysilane (OTMS), resulting in the acquirement of superhydrophobicity with much improved wetting resistance [151].

In contrast, more complicated approaches have been developed to impart omniphobicity on polymeric substrates. Woo et al. developed a layer-by-layer (LBL) assembly technique to create hierarchical structures with reduced surface tension on NIPS membranes. Via electrostatic interaction, layers of poly(diallyldimethylammonium chloride), silica aerogel, and FTCS were coated on the membrane surface in sequence [134]. Although the deposited multiple layers on the membrane reduced its pore size from 0.20 to 0.09 μm, the LBL membrane achieved a very high water CA of 177° and oil CA of 163°.

In addition to omniphobic membrane, two special types of Janus membrane: hydrophilic-on-superhydrophobic, and hydrophilic-on-omniphobic designs have also been developed based on synthesized membranes to deal with low surface tension foulants in wastewater. The customized substrates offer additional benefits which cannot be achieved by Janus (hydrophilic-on-hydrophobic) membranes based on commercial membranes. Huang et al. developed omniphobic nanofiber substrates by fluorinating silica-coated electrospun membranes; then a hydrophilic layer of silica chitosan with perfluorooctanoate was sprayed on the omniphobic substrates to obtain the Janus membrane (hydrophilic-on-omniphobic) [106].

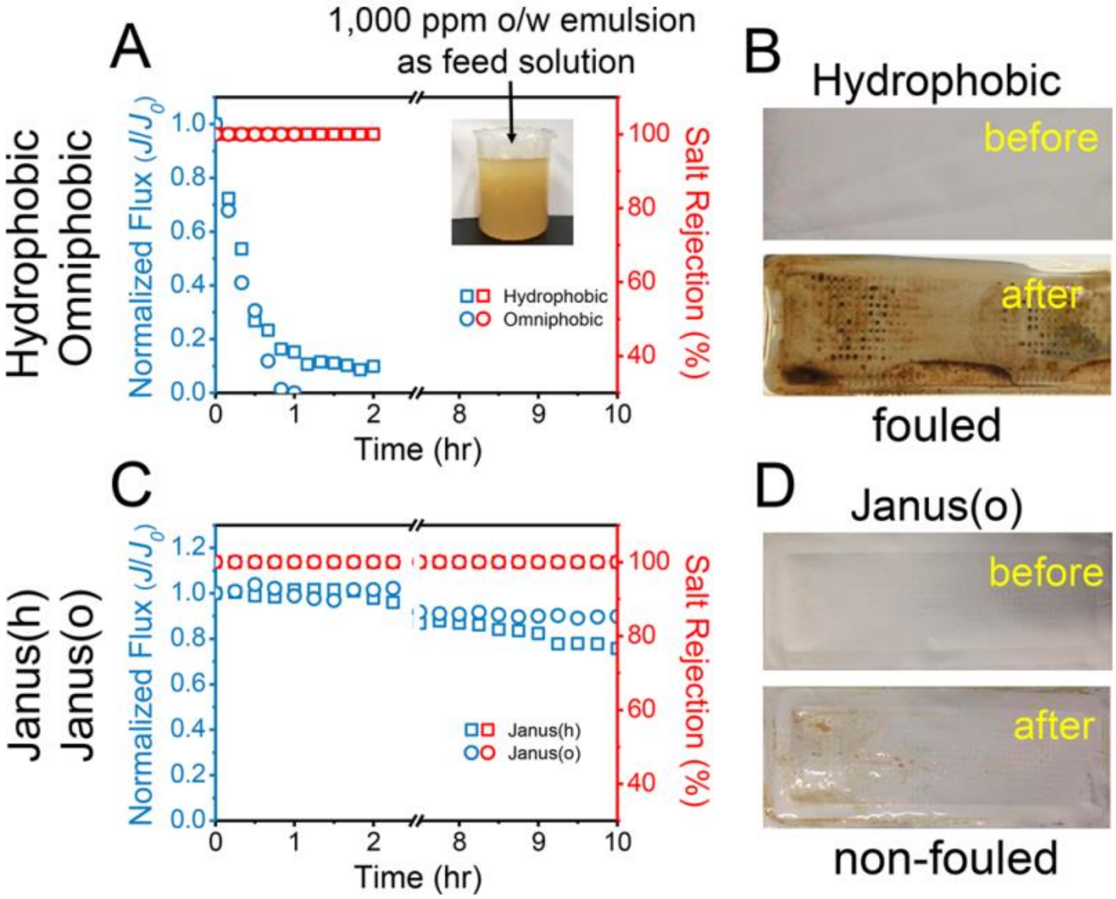


Fig. 13 shows that the omniphobic membrane had strong wetting resistance against oil/water emulsion but was still prone to organic fouling, and the coated hydrophilic layer on the top could improve its fouling resistance with minimal impact on flux performance.

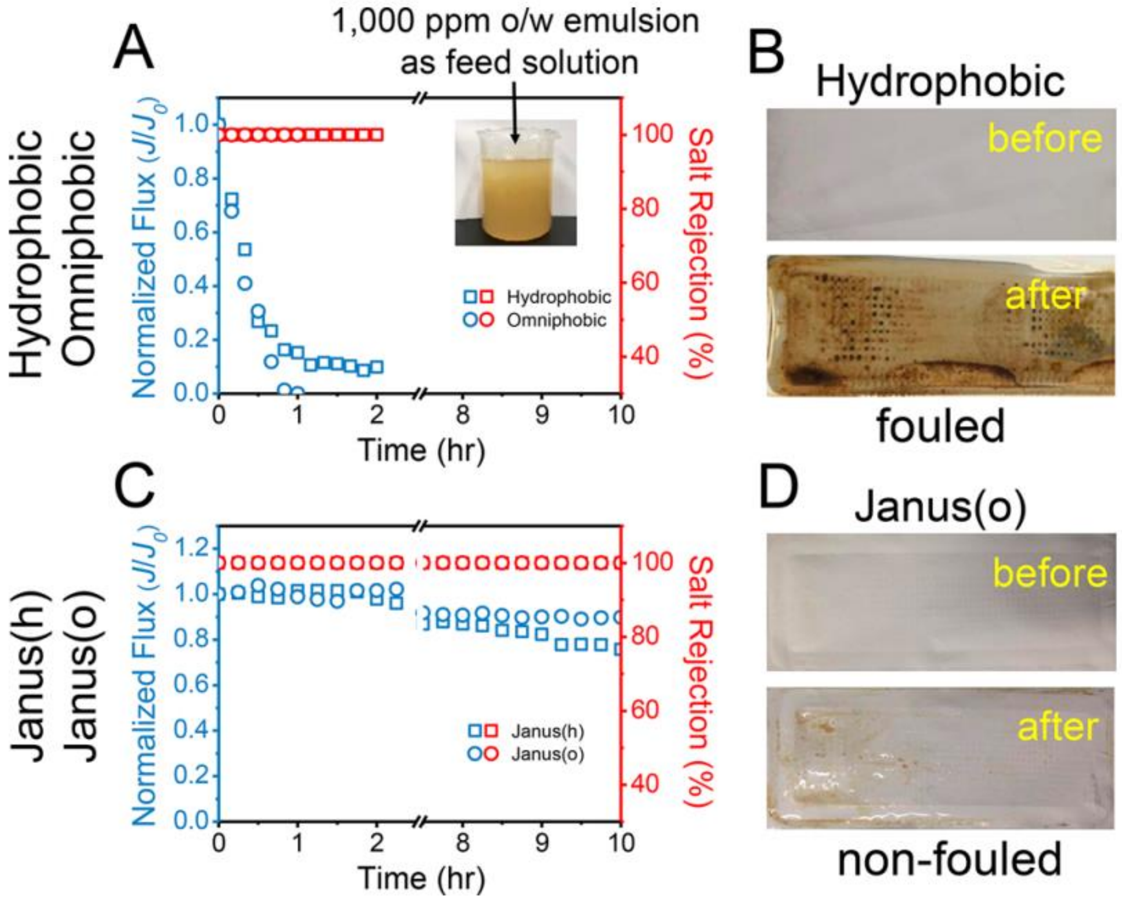


Fig. 13. a) Normalized MD flux and salt rejection rate or treating impaired solution (containing 1,000 ppm o/w emulsion) using a) hydrophobic-and-omniphobic and c) Janus (hydrophilic-on-hydrophobic) and Janus (hydrophilic-on-omniphobic) membranes; before and after MD test for b) hydrophobic membranes and d) Janus (hydrophilic-on-omniphobic) membranes. Image is reproduced with permission. Copyright 2017, American Chemical Society [106].

4.3.2 Applications

The superhydrophobic synthesized membranes offer a wide range of applications for the field for desalination, treatment of brine water and industrial wastewater. The membranes exhibit stable permeation flux and high salt rejection for 180 h in treating highly concentrated brine water (25 wt.%). It had significant anti-scaling properties as the post-tested membranes hardly showed any sign of foulants on the SEM images of the relative samples [23]. Superhydrophobic synthesized membranes can also be used to treat industrial wastewater. The PDMS coated membranes showed high flux recovery with water flushing in the treatment of single dye (crystal violet) in the configuration of DCMD with much mitigated fouling issues. Also, their permeability was higher than commercial membranes due to the large mean pore size and porosity of the synthesized electrospun substrates [152]. Industrial wastewater containing heavy metals (Pb, Cd, Zn, etc.) with concentrations up to 600 ppm can also be treated [157, 158].

On the other hand, omniphobic and Janus (hydrophilic-on-hydrophobic) synthesized membranes can be used to treat wastewater water containing low surface tension chemicals such as surfactants and oil emulsion. Usually, these membranes have higher permeability than surface-modified commercial membranes due to their large mean pore size and porosity [132, 143]. The omniphobic synthesized membranes achieved a high flux around 20 LMH with a feed solution temperature of 65°C when treating synthetic wastewater containing 0.1 mM SDS [133]. By sacrificing the permeation performance, even higher fouling and wetting resistance against low surface tensions feeds can be achieved. The hierarchical composite membranes had much improved wetting resistance as it can treat feed water containing SDS of concentration up to 0.5 mM without performance deterioration; also, these membranes could treat RO brine from coal seam gas produced water stably for 72 h.

4.3.3 Challenges

Development of synthesized membranes with special wettability is still a major challenge. Most of the preparations in literature have complex processing methods which require the use of multiple-steps with precise control, making it unpractical for large scale applications [23, 158]. Generally, construction of hierarchical structures and coating of nanoparticles/microspheres are two necessary steps to obtain special wettability characteristics on membrane substrates, and each of the steps need to be optimized and well controlled. A specific case involving multiple steps are LBL membranes [134]. These membranes are robust with high wetting and fouling resistance. However, they have relatively low permeation performance due to small pore sizes, making them limited to niche applications. Therefore, further optimization should be investigated to develop LBL membranes with large mean pore size without trading the omniphobic property.

Another major challenge is that many synthesized membrane surfaces with special wettability characteristics lack long-term durability due to their loose bonding between coating layers and substrates [101]. Dip-coating and spray-coating are widely utilized for both morphology construction and fluorination [130, 140]. The bonding between surface layers and substrates are relatively weak because it is based on physical entanglement only.

Regarding synthesized membranes with special wettability characteristics in MD applications, superhydrophobic and omniphobic membranes are susceptible to fouling by wastewater containing low surface tension liquids (e.g. oil) due to hydrophobic-hydrophobic interaction [153]. Therefore, these membranes are generally applied for desalination as nature organic matter is the main organic pollutants in seawater and its RO brine.

Fabrication of appropriate substrate is also a major challenge. Polymeric membranes may suffer swelling issue at high working temperatures [162]. Electrospun nanofiber membranes are highly favored for synthesized substrates as they offer high roughness, large mean pore size and porosity, and they are convenient for customization [143, 152, 153]. However, the mechanical strength of nanofiber substrate-based membranes needs improvement for larger scale applications; Moreover, there is still some challenges in the upscaling of electrospinning due to device limitation [135, 161].

4.4 Surface-modified ceramic membranes

Ceramic membranes have also been extensively developed for use in MD.

Table 6 summarises various studies using modified ceramic membranes with special wettability. In terms of characteristics, ceramic membranes generally exhibit high chemical, thermal, and mechanical stability. These characteristics make them especially suitable for applications in harsh environments such as corrosive and high temperature conditions.

4.4.1 Modification methods

Typically, inorganic materials such as glass, silica, alumina, titanium oxide, etc. are used to make ceramic membranes for MD. Surface modification should be applied onto the ceramic membranes to prevent membrane wetting as they are naturally hydrophilic. A superhydrophobic or omniphobic layer can be coated on these membranes, to form either (superhydrophobic-on-hydrophilic) or (omniphobic-on-hydrophilic) Janus membranes, respectively. Fluorination is the most common approach adopted to attain superhydrophobicity on ceramic membranes. In its natural condition, the surface of inorganic ceramic membrane contains hierarchical structures. As such, superhydrophobicity (high water CA of 160°) can be easily achieved in ceramic membrane with fluorination alone. Hubadillah mimicked the lotus effect by simply fluorinating silica membrane with PFTES; the surface modified membrane had high water CA of 161°, and a significantly reduced pore size from 1.43 to 0.54 µm, exhibiting high arsenic rejection of 99.6% in DCMD [136]. Also, other hydrophobic compounds can be deposited on the surface of ceramic membranes to achieve Janus structure (superhydrophobic-on-hydrophilic). Dong et al. developed Janus (superhydrophobic-on-hydrophilic) ceramic membranes by depositing carbon nanotubes (CNT) on nickel aluminate substrates via chemical vapour decomposition (CVD) [163]. The superhydrophobic membranes illustrate improved fouling resistance. **Fig. 14** shows that the organic fouling resistance could be further improved by changing the surface charge of the CNT-coated superhydrophobic membranes: the whole surface-modified membranes working as cathode led to stable permeation for the treatment of brine solution containing 30 mg L^{-1} humic acid.

Table 6. Published reports in the literature about surface-modified inorganic membrane with special wettability for MD.

Substrate	Modification methods	Special wettability	Water contact angle (º)	Mean pore size (μm)	Application and configuration	Claimed benefits	Ref.
Glass	Glass fiber drawing/ f	Janus (superhydrophobic-on-hydrophilic)	165	3.4	DS by AGMD	AF/HP	[99]
Glass	Chemical-modifying (SiNPs)/ f	Janus (omniphobic-on-hydrophilic)	140 108-mineral oil 80-ethanol	0.7	SF by DCMD	AW	[104]
Glass	CBD depositing (ZnONPs)/ f	Janus (omniphobic-on-hydrophilic)	153 110-ethanol	0.4	SF by DCMD	AW	[138]
TiO_2	f	Janus (superhydrophobic-on-hydrophilic)	147	0.2	IW by VMD	AF/AW	[129]
Alumina	Sol-gelling (fluorinated Al_2O_3NPs)	Janus (superhydrophobic-on-hydrophilic)	158	0.4	DS by VMD	HP	[162]
Nickel aluminate (hf)	CVD (CNT)	Janus (superhydrophobic-on-hydrophilic)	170	0.15	BT by DCMD	AF/AW	[163]
Silica (hf)	f	Janus (superhydrophobic-on-hydrophilic)	161	0.54	IW by DCMD	AW	[136]
Anodized alumina	f	Janus (superhydrophobic-on-hydrophilic)	162	0.08	DS by DCMD	HP	[131]
Alumina	Dip-coating (C_6Cl_3)	Janus (superhydrophobic-on-hydrophilic)	154	0.81	DS by AGMD	AW	[164]

Note: hf = hollow fiber, f = fluorination, DS = desalination, BT = brine treatment, IW = industrial wastewater, AF = anti-fouling, AW = anti-wetting, HP = high permeability

To obtain even higher wetting resistance, the achievement of Cassie-Baxter wetting state is required. Therefore, re-entrant structures should be created on the membrane surfaces before being fluorinated. Directly changing the morphology of ceramic substrate is also an option that can be explored. For instance, Ma et al. developed superhydrophobic glass membranes with ordered arrays of nanospiked microchannel using a process involving multiple chemical and physical techniques, and the surface-modified membrane has high water CA of 165° [99]. Alternatively, NPs can be deposited onto ceramic membranes, which is a common technique used on polymeric membranes as discussed in previous sections. ZnO NPs was successfully deposited on glass membranes using chemical bath method to create hierarchical re-entrant structures, then FAS17 was applied on the NP-coated membrane to achieve omniphobic surface [138]. When treating saline water containing 0.3 mM SDS using this omniphobic membrane, a stable water flux was maintained for 8 h, while superhydrophobic glass membranes failed at the same operation conditions. Both approaches for improving surface roughness are complex, involving multiple chemical or physical techniques. Considering that the attachment of the deposited layer on ceramic substrates are less stable, the first approach is more attractive for the creation of re-entrant structures.

Ceramic membrane with special wettability can be very promising for MD due to their appropriate pore sizes. Also, they demonstrate strong robustness in harsh working environments.

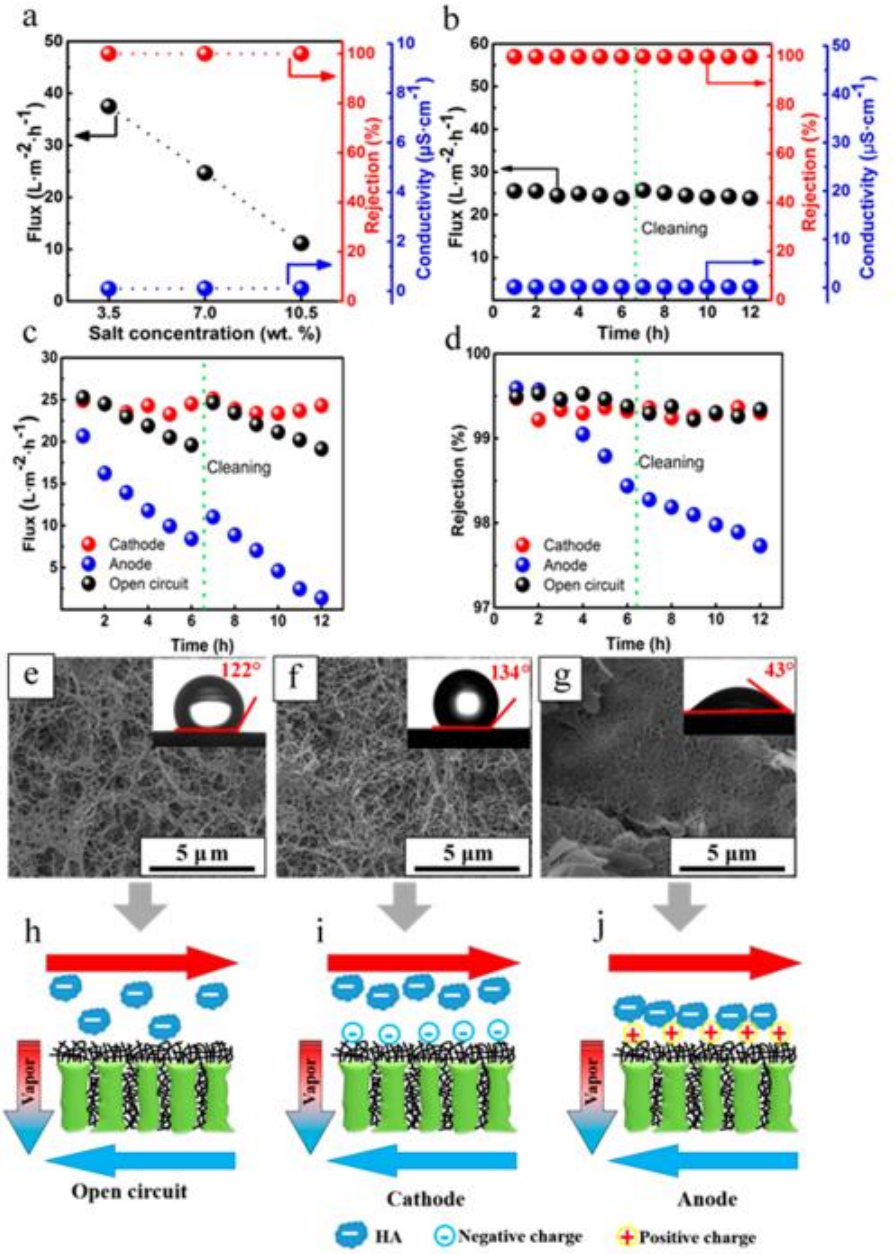


Fig. 14. Performance of DCMD in the treatment of high salinity water (70 g·L^{-1} NaCl) using carbon nanotube coated membranes as a function of a) salt concentration and b) time ; the flux of DCMD treating feed solution containing humic acid and sodium chloride when the membrane work as open-circuit, cathode, or anode regarding c) flux and d) salt rejection; e-g) the surface morphology and water contact angle of the coated membranes used as various electrodes after 12 h DCMD operation; h-j) schematic figures of electrostatic interaction between organic foulants and the surface modified membranes at various modes. Image is reproduced with permission. Copyright 2018, American Chemical Society [163].

4.4.2 Applications

Janus ceramic membranes (superhydrophobic-on-hydrophilic) are versatile and can be used for desalination, brine treatment and industrial wastewater treatment. When used for desalination, high water flux around 30 LMH and salt rejection of 99.9% can be achieved due to the large pore size of the membranes (0.4 μm) [162]. A Janus membrane based on nickel aluminate could treat highly saline wastewater with NaCl concentration up to 105 $g \cdot L^{-1}$. The membrane exhibited high flux performance of 24 LMH and salt rejection of 99.6% in 12 h DCMD operation [163]. Another application is the removal of volatile organic compounds (butanol, methyl-tert-butyl ether, and ethyl acetate) from binary aqueous solutions. A silica based Janus membrane (superhydrophobic-on-hydrophilic) showed much improved removal efficiency [129].

Janus ceramic membranes (omniphobic-on-hydrophilic) can be used to treat produced water having low surface tension. Wastewater containing 1 M NaCl and 0.3 mM SDS can be treated in DCMD with stable permeation and salt rejection using omniphobic glass fiber membranes based on ZnO nanoparticles modification [138].

4.4.3 Challenges

A variety of challenges should be addressed before surface-modified ceramic can achieve full commercialization. The process of ceramic membrane substrate fabrication is energy-intensive as it requires high temperature (>800°C) treatment for several hours [164]. Therefore, they are significantly more costly than polymer membranes. Moreover, as ceramic membrane is hydrophilic in nature, surface modification is necessary before it can be used as a MD membrane. If sintering is involved, it will be difficult to impart superhydrophobicity or omniphobicity on membranes simultaneously with good pore-size control [162]. Another challenge is that ceramic materials have much higher thermal conductivities than polymers, leading to lower energy efficiency in MD process [131]. Modification approaches for thermal efficiency improvement should be developed.

Generally, MD ceramic membranes with special wettability characteristics suffer significant lower flux performance as they generally have much higher thickness (>500 μm) than polymeric membranes due to technique limitation [99, 104, 129]. Some hydrophobic and omniphobic ceramic membranes suffer structure and performance deterioration such as fouling, wetting, and flux and rejection decline during long-term operation due to weak bonding between fluorination molecules and membrane surfaces [163].

Processes that render ceramics hydrophobic require specialized resources and skills as chemicals used for surface modification may block membrane pores if not properly applied. Therefore, more optimization on fabrication and modification approaches (simpler chemical or physical methods) is required before ceramic membranes with special wettability can be practically applicable for MD applications [138].

5. Conclusions and future perspectives

5.1 Conclusions

Membrane distillation (MD) is a promising thermally-driven membrane separation technology. The heart of the MD system is the porous membrane, where at least one layer of membrane should have the required hydrophobicity. The hydrophobic property of the membrane plays an important role in inhibiting wetting phenomena during MD operation. However, commercial hydrophobic microfiltration membranes, though deemed suitable for MD operation, suffer considerably from low flux and wetting issues. Hence, improving the characteristics of commercial membranes, or developing new membranes with special wettability features is highly pertinent to improve MD operation. Recent significant advances in the field of special wettability open new possibilities to improve MD membranes design and their performance in various applications. Promising results with long term MD tests have established the suitability of these special surface wettability membranes for the treatment of challenging water sources, such as highly saline brine and wastewater containing oils or low surface tension components. The present review article has compiled and analyzed various studies related to membranes with special surface wettability for MD, particularly referring to superhydrophobic, omniphobic, and Janus-type membranes for desalination. The fundamental concepts regarding surface wettability have been thoroughly discussed to aid in the membrane design. Individual special wettability is also defined in association with the fundamental concepts, and the insights of their benefits and issues are offered. Approaches to achieve special wettability have been summarized based on membrane substrates, which are classified for detailed comparison and analysis.

Membranes with various special wettability have been developed to deal with highly saline water, which includes oil-field produced water, industrial wastewater, seawater, and brine from desalination. Some conclusions regarding MD membranes with special wettability are highlighted below:

(1) Superhydrophobic membranes have been mainly designed to improve wetting and inorganic scaling resistance against brine, and Janus membranes (superhydrophobic-on-hydrophilic) have been to improve the permeate flux with the addition of a hydrophilic layer on the permeate side of the membranes. However, these membranes become more prone to organic fouling due to hydrophobic interaction with foulants in wastewater. Therefore, superhydrophobic membranes are not recommended to be used in the treatment of wastewater containing large amounts of organic foulants.

(2) Omniphobic and Janus membranes have been developed to deal with highly-saline produced water which usually contains surfactants and low surface tension liquids (e.g. oil water emulsion). These surface-modified membranes have significantly increased organic fouling resistance. However, the omniphobic property relies greatly on the hierarchical

morphology (especially re-entrant structures). The air trapped on the surface structures plays a crucial role in omniphobic membranes. As the trapped air may escape from air pockets during continuous MD operations, the membrane could gradually lose its omniphobicity. Therefore, new morphology design such as repulsive spring structures need to be developed for MD membranes to maintain omniphobicity in long-term operation. Another issue is the wide use of fluorination during surface modification to reduce surface tension. Alternatively, environment-friendly chemicals should be developed for the achievement of omniphobic membranes;

(3) Janus membranes have been developed to target low surface tension saline water. The hydrophilic layer exhibits high underwater oil resistance. Some researchers have found such membranes have higher oil resistance than omniphobic membranes as they completely prevent hydrophobic interaction. However, the surface charge of the Janus membrane should be carefully controlled based on the charge of organic compounds in water for electrostatic repulsion, so that the Janus membranes can maintain underwater oleophobicity for longer time. It is concluded that, in MD experiments, both omniphobic or Janus membranes can only mitigate the impacts of surfactants at low concentration for a limited time, suggesting that they can only delay the inevitable wetting. Therefore, novel designs should be evaluated for improved surfactant resistance.

(4) There are shared challenges for the surface-modified membranes with various special wettability. The attachment between substrates and coating layers need to be strong enough against routine water flush and chemical cleaning in real operational scenarios. However, few studies have investigated the robustness of the surface-modified membranes, which should be one of the main areas for research in future study. Another issue is the limitation of substrates. The mean pore size of substrates should not be too small as it will significantly decrease after surface modification, so electrospun and inorganic membranes are preferred. However, the energy consumption of these two fabrication techniques is intensive.

5.2 Recommendations

Nevertheless, membranes with special wettability have a promising future for MD applications if the challenges mentioned above are well addressed. Some potential technical advances and novel approaches, which will contribute to this emerging technology are highlighted below:

- The re-entrant structures on membrane surfaces are crucial for the achievement of superhydrophobic and omniphobic surfaces. Currently, its achievement is mainly dependent on depositing micro/nano particles on/in the surface. Novel top-down techniques (e.g., templating) or bottom-up techniques (e.g., carbon quantum dots) can be candidates for the construction of more stable re-entrant structures;
- Nanotechnology plays a strong role in material science supporting membrane fabrication. Its advance can bring novel nanomaterials with unprecedented benefits as an additive in either substrates or coating layers for special wettability with improved permeability or fouling resistance;

- Conventional surface modification methods such as lithography and templating can be implemented for hierarchical surface structures. A few researchers have developed superhydrophobic surfaces by casting dope solutions on prepared PDMS substrates. These top-down one-step methods can prevent the bonding issues between coating layers and substrates;
- Novel fabrication techniques (e.g. 3D printing) open possibilities of one-step fabrication of membranes with special wettability, solving weak bonding issues between coating layers and substrates;
- As membrane wetting and fouling is inevitable in MD, membranes with high flux recovery after cyclical water flush and chemical cleaning are practically necessary. Membrane designs with the capacity to withstand routine cleaning procedures must be considered;
- MD in conjunction with other technologies to form hybrid water treatment systems could mitigate the negative impacts of challenging feed solutions applied directly to membranes and may potentially reduce the requirement for special wettability on membrane surfaces.

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