Wetting phenomena in membrane distillation: Mechanisms, reversal, and prevention

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Wetting phenomena in membrane distillation:

Mechanisms, reversal, and prevention

Mohammad Rezaei a,*, David M. Warsinger b, c, John H. Lienhard V c, Mikel C. Duke d, Takeshi Matsuura e, Wolfgang M. Samhaber a

a Institute of Process Engineering, Johannes Kepler University Linz, Altenberger Strasse 69, 4040 Linz, Austria
b Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06520-8286, the USA
c Rohsenow Kendall Heat Transfer Laboratory, Department of Mechanical Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge MA 02139-4307, USA
d Institute for Sustainability and Innovation, College of Engineering and Science, Victoria University, Melbourne, Victoria 8001, Australia
e Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

*Corresponding Author: Tel: +4373224689747, Email: mohammad.rezaei@jku.at

Membrane distillation (MD) is a rapidly emerging water treatment technology; however, membrane pore wetting is a primary barrier to widespread industrial use of MD. The primary causes of membrane wetting are exceedance of liquid entry pressure and membrane fouling. Developments in membrane design and the use of pretreatment have provided significant advancement toward wetting prevention in membrane distillation, but further progress is needed. In this study, a broad review is carried out on wetting incidence in membrane distillation processes. Based on this perspective, the study describes the wetting mechanisms, wetting causes, and wetting detection methods, as well as hydrophobicity measurements of MD membranes. This review discusses current understanding and areas for future investigation on the influence of operating conditions, MD configuration, and membrane non-wettability characteristics on wetting phenomena. Additionally, the review highlights mathematical wetting models and several approaches to wetting control, such as membrane fabrication and modification, as well as techniques for membrane restoration in MD. The literature shows that inorganic scaling and organic fouling are the main causes of membrane wetting. The regeneration of wetting MD membranes is found to be challenging and the obtained results are usually not favorable. Several pretreatment processes are found to inhibit membrane wetting by removing the wetting agents from the feed solution. Various advanced membrane designs are considered to bring membrane surface non-wettability to the states of superhydrophobicity and superomniphobicity; however, these methods commonly demand complex fabrication processes or high-specialized equipment. Recharging air in the feed to maintain protective air layers on the membrane surface has proven to be very effective to prevent wetting, but such techniques are immature and in need of significant research on design.

**Keywords:** Membrane distillation; Membrane wetting; Hydrophobicity; Pretreatment; Membrane modification; Review
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1. Introduction

Membrane distillation (MD) is a thermally driven membrane separation process, which utilizes a microporous hydrophobic membrane that allows vapor to pass through it but not liquid. MD’s driving force for the mass transfer is the transmembrane vapor pressure difference, which is induced by the transmembrane temperature difference or by reduction of vapor pressure on the permeate side by vacuum or dry gas (Carrero-Parreño et al., 2017; Lee et al., 2015). The volatile components present in the feed solution evaporate at the entrances of pores, and therefore the mass transfer through the membrane only takes place in the vapor phase (Kishor G Nayar et al., 2015; Politano et al., 2016; Swaminathan et al., 2016b).

MD offers several advantages and some potential applications based on the following benefits. MD operates at lower temperatures than the boiling point of the solvent, and therefore it can deal with temperature-sensitive solutions (e.g., in the food or pharmaceutical industries (El-Abbassi et al., 2013)). Since the vapor pressure is not highly dependent on the salt concentration, MD can be used in combination with reverse osmosis (RO) for the treatment of highly saline water (Warsinger et al., 2018). Although MD is potentially attractive for some applications, it still suffers from a few drawbacks and has gained little acceptance industrially. These disadvantages include high-energy consumption compared to alternative membrane processes, and wetting phenomenon. The energy needs for MD can be provided if it integrates with renewable energy or available “waste” heat (David M. Warsinger et al., 2015) or solar thermal (Guillén-Burrieza et al., 2011), and new configurations and operating conditions continue to improve the energy efficiency of MD (Chung et al., 2016; Summers and Lienhard, 2013; J. Swaminathan et al., 2018; Swaminathan et al., 2016a, 2016c; David E.M. Warsinger et al., 2015). However, the incidence of membrane pore wetting due to the loss of membrane hydrophobicity for the feeds containing wetting compounds (e.g., oils, surfactants) is still challenging its industrial potential (Banat and Simandl, 1994; El-Bourawi et al., 2006; Qtaishat and Banat, 2013).
Penetration of feed solution into the membrane pores occurs if solutions with organic or/and inorganic compounds adsorb/deposit to the membrane surface or if the transmembrane hydrostatic pressure surpasses the liquid entry pressure. Pore wetting leads to either permeate flux reduction or permeate quality deterioration depending on the type of pore wetting. The former is the result of partial pore wetting, and the latter is as the consequence of full wetting.

A literature search for “membrane distillation” revealed more than 2180 records (through July 2017, in Scopus), with an escalating growth in the number of publications during the past decade (Fig. 1). In 1963, the first patent on MD was filed by Bodell (Bodell, 1963); however, the unavailability of adequate membranes for MD led to a lack of interest in MD for some time. Subsequent to the fabrication of porous polytetrafluoroethylene (PTFE) membranes by W. L. Gore and Associates, during the 1980s MD regained the attention of researchers. Nevertheless, research addressing wetting incidence and control wetting in MD remained minimal until recently. The entire number of published papers on MD is more than eleven times greater than that of MD articles exploring the wetting phenomena (2180 articles for MD and 171 for wetting in MD).
Fig. 1: The growth of research activity on MD and wetting phenomena, 1963-2016 (data from Scopus).

Today, wetting incidence in MD has gained more attention and more publications on MD investigate these phenomena, moving the field toward practical implementation. To the best of authors’ knowledge, no comprehensive literature review has focused on the wetting phenomena in MD. This article provides an extensive literature review on the subject. The aim of this paper is to analyze the key wetting conditions, wetting types, harmful effects, and prevention techniques and to lay the groundwork for future technological advances.

2. Parameters for wetting

2.1. Liquid entry pressure

The primary metric for measuring membrane wettability is liquid entry pressure (LEP). The LEP of a solution (sometimes incorrectly called “wetting pressure”) is the pressure (Pa) that must be applied to the solution before it goes through a dry membrane pore (Smolders and Franken, 1989). The maximum capillary pressure for a hydrophobic membrane depends on liquid surface tension, surface free energy and maximum pore size of the membrane. Based on the Young-Laplace equation (Young, 1807), LEP is defined as:

\[
LEP = \frac{-B \gamma_l \cos \theta}{r_{\text{max}}} > P_f - P_p = \Delta P_{\text{interface}}
\]  

where \(P_f\) and \(P_p\) are the hydraulic pressure on the feed and permeate side, \(B\) is a pore geometry coefficient (Table 1), \(\gamma_l\) is the liquid surface tension, \(\theta\) is the contact angle (CA) measured on the liquid side, where the liquid-vapor interface meets the membrane surface and \(r_{\text{max}}\) is the maximum pore size of the membrane (David M. Warsinger et al., 2016). This simple model is visualized in Fig. 2a and 2b. The \(\theta\) for a water droplet on different surfaces is shown in Table 2.

Many membranes and process conditions can impact the LEP through the variables in Eq. (1), including operating temperature, solution composition, surface roughness, surface porosity, pore shape (i.e., pore radius and fiber radius (Ali et al., 2012; Guillen-Burrieza et al., 2015). For instance, Barbe et al. (Barbe et al., 2000) studied the effect of contact with a membrane with water and a CaCl\(_2\) solution for 72 h on...
membrane surface morphology. They found that the intrusion of water meniscus into large pores led to increase in the porosity, pore area, pore length and pore equivalent diameter, as well as pore spread factor of the membrane. As a result, the LEP of the membrane decreased.

Table 1: Pore geometry coefficient for different membrane pores

<table>
<thead>
<tr>
<th>Type of membrane pore</th>
<th>Pore geometry coefficient</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>cylindrical pores</td>
<td>1.0</td>
<td>(David M. Warsinger et al., 2016)</td>
</tr>
<tr>
<td>elliptical or irregularly shaped pores</td>
<td>less than 1.0</td>
<td>(David M. Warsinger et al., 2016)</td>
</tr>
<tr>
<td>stretched membranes (e.g., PTFE) with small curvature radius</td>
<td>0.4-0.6</td>
<td>(Saffarini et al., 2013)</td>
</tr>
</tbody>
</table>

Table 2: Water contact angle (WCA) for different surfaces

<table>
<thead>
<tr>
<th>Surface</th>
<th>WCA</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Teflon</td>
<td>108° - 115°</td>
<td>(Alkhudhiri et al., 2012)</td>
</tr>
<tr>
<td>polyvinylidene difluoride (PVDF)</td>
<td>107°</td>
<td>(Alkhudhiri et al., 2012)</td>
</tr>
<tr>
<td>polypropylene (PP)</td>
<td>93.5°±0.2°</td>
<td>(Gryta, 2005)</td>
</tr>
<tr>
<td>ceramic membrane grafted with fluoroalkylsilanes</td>
<td>177°</td>
<td>(Khemakhem and Amar, 2011)</td>
</tr>
<tr>
<td>ceramic zirconia and titania membranes</td>
<td>160°</td>
<td>(Cerneaux et al., 2009)</td>
</tr>
</tbody>
</table>

Moreover, the utility of Eq. (1) for calculating LEP is limited because the CA and surface tension of feed may not be known for the system of interest. Therefore, Eq. (1) can be only used to interpret the experimental data (Lawson and Lloyd, 1997). Because membranes do not have cylindrical pores, the Purcell model was developed to describe the location of the pinning point of the liquid in the pores, using more realistic geometry (see Fig. 2d and e) than cylindrical assumed in Equation (1). The equation for LEP based on the Purcell model (Purcell, 1950) is
\[
LEP = \frac{-2\gamma \cos(\theta + \alpha)}{r(1 + R/r(1 - \cos(\alpha)))}
\]

where \( R \) is the fiber radius and \( \alpha \) is the angle below horizontal at which the liquid meniscus pins prior to breakthrough (Fig. 2). The value of \( \alpha \) is calculated using the following equation:

\[
sin(\theta + \alpha) = \frac{\sin \theta}{1 + r/R}
\]

Fig. 2: (a) and (b) cylindrical pore (Young-Laplace model, Eq. (1)). (c) scanning electron microscopy (SEM) image of the nylon membrane (scale bar is 1 mm). (d) and (e) toroidal pore. Purcell model, Eq. (2) (Servi et al., 2016).

Unlike the Young-Laplace model, which predicts the LEP to be less than zero for all values of CA less than 90°, the Purcell model predicts positive values of LEP for all values of CA. However, this result is also in contradiction to the fact that many membranes wet at very low values of CA. Therefore, Servi et al. (Servi et al., 2016) developed a new model to predict the LEP for all values of CA considering the interactions between the liquid and the pores below the initially wetted surface by incorporating a “floor” below each pore into the model. This floor describes those fibers that may enable the liquid to penetrate further into the membrane. Therefore, LEP can be determined as the pressure at which the liquid separates from the pore or intercepts the floor, whichever takes place at the lower pressure. To calculate LEP using this new model, Eq. (2) is used along with Eq. (3) and the following equation.
\[
\frac{r + R(1 - \cos(\alpha))}{-\cos(\theta + \alpha)} (1 - \sin(\alpha + \theta)) = R (1 - \sin(\alpha)) + h
\]  

where \( h \) is defined as the floor height (nm) describing the fibers that may attract the liquid to enter further into the membrane (Fig. 3). The modified model could explain the observed LEP performance over CAs ranging from 63° to 129°.

Fig. 3: The pore configuration for the Servi model, Eq. (4), from (a) the side; and (b) in three dimensions. \( h \) is the length between the bottom of the fibers and the floor. \( h \) can be positive or negative (Servi et al., 2016).

2.2. Membrane surface free energy

Surface free energy of a membrane (\( \gamma_m \)) is defined as the energy difference between the bulk and surface of a membrane. It can be estimated by measuring the receding CA (\( \theta_r \)) and advancing CA (\( \theta_a \)) of two liquid on the membrane surface using the two following equations (Owens and Wendt, 1969)

\[
(1 + \frac{\cos \theta_a + \cos \theta_r}{2}) \gamma_I = 2(\gamma_m^d \gamma_I^d)^{0.5} + (\gamma_m^{nd} \gamma_I^{nd})^{0.5}
\]  

\[
\gamma_m = \gamma_m^d + \gamma_m^{nd}
\]

where the superscripts \( d \) and \( nd \) correspond to the dispersive and nondispersive contributions to the total surface energy, respectively.
2.3. Surface wettability

The surface wettability is highly dependent on the free energy of the surface and its CA. In its simplest form, the wettability of a liquid droplet on a flat, smooth surface is commonly determined by Young’s equation (Young, 1805):

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{Sl}}{\gamma_{lv}}$$  \hspace{1cm} (7)

where $\theta$ is the CA in the Young’s model, $\gamma_{lv}, \gamma_{SV}, \gamma_{Sl}$ are the interfacial tensions liquid/vapor, solid/vapor, and solid/liquid, respectively.

However, in reality, smooth surfaces are rare and some roughness is contained; therefore, the Wenzel’s theory (Wenzel, 1936) was proposed where the roughness of the surface was considered for wettability determination.

$$\cos \theta_w = \frac{r(\gamma_{SV} - \gamma_{Sl})}{\gamma_{lv}}$$  \hspace{1cm} (8)

where $\theta_w$ is the apparent CA in the Wenzel mode and $r$ is the surface roughness factor as the ratio of the actual solid/liquid contact area to its vertical projection. Based on Wenzel’s theory, the liquid enters the grooves of micro-nano composite structure, and therefore this leads to higher CA on a rough surface than CA on a true flat surface (Fig. 4).

In Cassie’s theory (Cassie and Baxter, 1944), the area fraction of solid and gas phase as a result of surface roughness contributes to the determination of wettability

$$\cos \theta_c = f_s \cos \theta_s + f_v \cos \theta_v = f_s(\cos \theta + 1) - 1$$  \hspace{1cm} (9)

where $\theta_c$ represents the apparent CA in the Cassie mode, taking into account that $f_s + f_v = 1$, $\theta_s = \theta$, and $\theta_v = 180^\circ$. The Wenzel state and the Cassie state can be coexisting and transition between them can also occur (Lu et al., 2009). Change of the hydrophobicity toward superhydrophobicity is induced by air pockets, so-called “pillars” (Fig. 4c), between liquid and the surface generated by hydrophobic forces (Dumée et al., 2013; David E.M. Warsinger et al., 2015), therefore increasing the CA greater than 150° (Cao et al., 2009), reducing sliding angle ($SA_{water} < 10^\circ$) (Tijing et al., 2014a) and the surface free energy. Superhydrophobic
membranes made based on combined micro, and nanoscale roughness behave in Cassie-Baxter state and water droplet is easy to roll off.

Fig. 4: Schematic representation of: (a) the Young model, Eq. (7); (b) the Wenzel model, Eq. 8; and (c) the Cassie-Baxter model, Eq. (9). The last of these best describes unwetted MD membranes (An et al., 2017).

3. Wetting mechanisms

Membrane pore wetting involves a complex of physical and chemical interactions (Alklaibi and Lior, 2005). The non-wetting liquid facing a hydrophobic membrane forming a fixed interface at the membrane pores was initially considered as one of the first principles of MD process by C. Gostoli et al. in 1987 [3]. They proposed that, based on capillary action, the non-wetting of a liquid is the result of its high surface tension forming a convex meniscus that impedes the liquid from entering the membrane pore. Therefore, the liquid feed in contact with membrane bulges in the pore until the pressure difference arising from the surface tension of the curved interface balances the pressure drop caused by the partial pressures of vapors and air across the membrane. The pressure caused by surface tension is called capillary pressure. When this pressure balance is overwhelmed, the liquid begins penetrating the pores. Once wetting takes place, the membrane starts to lose its hydrophobicity locally, leading to continuous water bridging.

Membrane wetting can be distinguished into four degrees (Fig. 5): non-wetted, surface-wetted, partially-wetted, and fully-wetted (Gryta, 2007a). Surface wetting shifts the interface of liquid/vapor inward of the membrane cross-section. Permeate flux may then decline gradually as a result of the associated increase in temperature polarization which lowers the temperature of the evaporating interface in the pore (Gryta, 2016a; Gryta et al., 1997). Although surface wetting even to a significant depth, e.g. 100–200 µm, still provides a liquid/vapor interface for separation, scaling as a result of solvent evaporation can take place
inside the pores in the vicinity of the meniscus (Gryta, 2007a). Moreover, crystal growth inside the pores accelerates scale formation rate by inhibiting diffusive transport of solutes and solvent between wetted pores and the feed bulk, raising solute concentrations locally. Conversely, under certain conditions, the intrusion of liquid into the pore has been observed to cause a temporary flux increase as a result of the shorter vapor diffusion path through the part of the pore that remains dry (Gilron et al., 2013). As feed solution penetrates deeper into the membrane pores, partial wetting can take place. In this case, the MD process can be continued if the majority of pores are dry. However, partial wetting under certain conditions can reduce the permeate flux due to a reduction of the active surface area for mass transport associated with partial wetting (blue solid line in Fig. 5) (Karakulski and Gryta, 2005) or it can cause an increase in the permeate flux due to wetting of some pores (i.e. vapor transport is overtaken by liquid transport) followed by a rapid decrease due to steady blockage of pores by the foulants depending on the experimental setup (blue dash line in Fig. 5) (Dow et al., 2017). The partial wetting also leads to deterioration of permeate quality. Interestingly, all the hydrophobic membranes used in MD, such as PP, PTFE, and PVDF, have shown partial wettability during a long-term use (Gryta, 2005). In the case of full wetting, the MD process no longer acts as a barrier, resulting in a viscous flow of liquid water through membrane pores, incapacitating the MD process (Rezaei et al., 2017a; Rezaei and Samhaber, 2016b). Fig. 5 shows qualitatively the permeate flux and rejection rate for an MD process based on the degree of wetting.
4. **Wetting detection**

Wetting is typically detected by evaluating the permeate quality. When membrane wetting occurs, the electrolyte solutes dissolved in the liquid feed penetrate into membrane pores, which leads to a significant increase of permeate electrical conductivity. This permeate quality change is frequently measured by permeate conductivity readings (Warsinger et al., 2017a). However as electrical conductivity increase also happens when volatile components such as ammonia and carbon dioxide pass through an intact membrane, wetting is detected occasionally by in-situ visual observation of the membrane (wetted membranes transition from opaque to transparent) (Dow et al., 2017), transmembrane pressure changes and membrane autopsy. Recently, Ahmed et al. (Ahmed et al., 2017) applied an electrically conductive layer to a direct contact membrane distillation (DCMD) combined with an electrochemical system to detect wetting (Fig. 6). The membrane acted as an electrode wherein the current through the system enabled Na⁺ and Cl⁻ ions
to complete the cell. A constant voltage of +1V was applied during the MD process, and a quick increase in current was noticed at the moment where wetting occurred.

Fig. 6: Wetting detection mechanisms. a) measuring pressure changes across the membrane, reduced by leaks, b) measuring permeate conductivity, or c) electrochemical cell, where black is the electrically conductive carbon cloth layer, and white is the active electrospun PVDF-HFP (Ahmed et al., 2017).

5. Causes of wetting

The numerous causes of wetting in MD are detailed in Table 3. The primary cause of the wetting of MD membranes is fouling, meaning material deposition on the membrane surface and in membrane pores (Camacho et al., 2013; Gryta, 2007a; Hausmann et al., 2011; Tijing et al., 2015). Other causes of wetting include surfactants which reduce the surface tension of the feed (Rezaei et al., 2017a), capillary condensation, and membrane damage (Ge et al., 2014; Lee et al., 2018). Different types of fouling in MD are distinguished by the deposited materials and include organic fouling (C. Liu et al., 2017; Mokhtar et al., 2016; Nguyen et al., 2017; Wu et al., 2016; Zarebska et al., 2014) such as biological fouling (or biofouling) (Wu et al., 2017; Zodrow et al., 2014) or fouling of organic compounds (Chew et al., 2014; Tan et al., 2016), and particulate or colloidal fouling (Ding et al., 2010; He et al., 2008; Qin et al., 2016; Zarebska et al., 2015), as well as scaling deposition (inorganic fouling). The deposits can reduce LEP as they are often hydrophilic, may damage the membrane (Guillen-Burrieza et al., 2013), and also clog the pores, which leads to a decline of permeate flux and permeate quality due to membrane wetting. Past studies have reviewed these foulants (D. M. Warsinger et al., 2015).
<table>
<thead>
<tr>
<th>Cause</th>
<th>Mechanism</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmembrane pressure</td>
<td>Higher than LEP</td>
<td>Pressure spikes, operating with low surface tension fluids or large pore size membrane</td>
</tr>
<tr>
<td>Capillary condensation</td>
<td>Loss of temperature gradient</td>
<td>Temporary shutdowns or variable operating temperatures: these reduce the saturation pressure for vapor, causing condensation</td>
</tr>
<tr>
<td>Scale deposition (inorganic fouling)</td>
<td>Reducing the hydrophobicity of membrane</td>
<td>Deposition on surface and crystallization inside membrane pores</td>
</tr>
<tr>
<td>Organic fouling</td>
<td>• Reducing the hydrophobicity of membrane</td>
<td>• Forming attractive forces between hydrophobic materials within an aqueous system</td>
</tr>
<tr>
<td></td>
<td>• Lowering the surface tension</td>
<td>• Increasing the affinity of solution and membrane</td>
</tr>
<tr>
<td>Surfactants</td>
<td>Reducing the liquid entry pressure of the feed into the pores</td>
<td>The liquid entry pressure is linearly proportional to surface tension.</td>
</tr>
<tr>
<td>Membrane degradation during long-term operation</td>
<td>Formation of hydrophilic groups on membrane surface</td>
<td>Oxidative chemical or mechanical degradation</td>
</tr>
</tbody>
</table>

Besides the fouling, pore wetting can also occur when the hydraulic transmembrane pressure exceeds the LEP. Chemical and mechanical degradation of the membrane are also considered to accelerate the membrane wetting during long-term MD process. Gryta et al. (Gryta et al., 2009) reported that hydrophilic groups on the membrane surface (e.g. hydroxyl (OH), carbonyl (C=O) and unsaturated (C=C) groups) formed by chemical oxidative degradation of membranes could reduce the CA from 90° to 61.4°. The
following section discusses the MD wetting caused by inorganic and organic compounds more in detail (El-Bourawi et al., 2006). Weakly hydrophobic membranes are also known to gradually wet over time.

5.1. Inorganic fouling

Crystal growth of inorganic compounds (usually primarily consisting of calcium carbonate, calcium sulfate, and halite) on the surface of the membrane can reduce membrane hydrophobicity and eventually cause water logging due to partial wetting (Banat and Simandl, 1994; Bouchrit et al., 2015; Dah Y. Cheng and Wiersma, 1983; Gilron et al., 2013; M. Gryta, 2002; McGaughey et al., 2017; K.G. Nayar et al., 2015). This phenomenon has only been observed for the treatment of saturated solutions (Cho et al., 2016; Feng et al., 2016; Naidu et al., 2017; Sakai et al., 1988; Sanmartino et al., 2016) and not for diluted solutions (Li and Sirkar, 2004; Mericq et al., 2010; Song et al., 2007).

Extreme temperature and concentration polarization within the feed boundary layer can also result in the growth of minerals or salt crystals on the membrane surface and subsequently membrane scaling and wetting (Martínez-Diez and Vázquez-González, 1999; Meng et al., 2015b; Ruiz Salmón et al., 2017; R.W. Schofield et al., 1990; Warsinger et al., 2017b). However, Gryta (M. Gryta, 2002) observed that only NaCl salt deposits with a higher depth of 10 µm from the pore inlet for a membrane with a wall thickness of 400 µm could cause the pore wetting (Fig. 7).

![SEM micrographs of a cross-section of Accurel PP S6/2 membrane demonstrating the pores on the feed side (inside the membrane capillary). a) pristine membrane, b) after 138 h of MD integrated with salt crystallization, c) membrane with salt crystals inside the membrane pore (M. Gryta, 2002).](image-url)
Importantly, MD membranes benefit from their hydrophobic surfaces, which have low surface energy and thus reduce crystal nucleation (David M. Warsinger et al., 2016).

### 5.2. Organic fouling

Organic compounds are particularly problematic for MD. When organic compounds are present in the feed solution, the surface tension of the solution decreases, and below a critical surface tension (i.e., surface free energy of the membrane), due to the high affinity of hydrophobic species such as oils to the hydrophobic membrane surface, wetting of the membrane may occur. In this respect, the chemical nature of the foulant (not the thickness) dictates the rate of wetting. For example, a thin layer of an amphiphilic fouling can reduce the CA of the membrane and result in wetting (Goh et al., 2013; Matheswaran and Kwon, 2007; Warsinger, 2015). Notably, while MD membranes are prone to wetting by organic compounds, they have been shown to experience less flux decline than RO or FO membranes undergoing biofouling (Jang et al., 2016).

Among different fouling types, growth of microorganisms can be significantly limited in MD due to high operating temperatures and feed salinity (e.g., in clean water production and desalination) (Marek Gryta, 2002a; Krivorot et al., 2011; D. M. Warsinger et al., 2015). However, organic foulants can contribute more to the wetting of hydrophobic membranes in MD (Naidu et al., 2015). Among organic foulants, surface-active compounds cause a major challenge in the technical implementation of MD (Soni et al., 2008). When a surfactant reaches a membrane surface, the hydrophobic membrane surface adsorbs the hydrophobic moiety while the hydrophilic part of the surfactant stays in the water phase (Chew et al., 2017a). Therefore, the hydrophobic surface is converted to a hydrophilic surface, resulting in a decreased CA and increased incidence of membrane wetting.

Notably, due to the hydrophobicity of MD membranes, solutes with lower surface tension can also cause wetting. For example, alcohols can cause membrane fouling and consequently pore wetting in MD due to the decrease of the surface tension of alcohol solutions, but their concentration plays an important role in the wetting occurrence. Table 4 summarizes the upper alcohol concentrations allowable in water for different membrane materials to avoid wetting.
Table 4: The upper alcohol concentrations in water for MD to avoid wetting

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Maximum allowable alcohol concentration in water</th>
<th>Membrane</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>butanol</td>
<td>1.0 wt. % at 63°C</td>
<td>PP</td>
<td>(Kujawska et al., 2016)</td>
</tr>
<tr>
<td></td>
<td>2.5 wt. % at 63°C</td>
<td>PTFE</td>
<td></td>
</tr>
<tr>
<td>ethanol</td>
<td>10.2 wt.%</td>
<td>PVDF</td>
<td>(Banat and Simandl, 1999)</td>
</tr>
<tr>
<td>ethanol</td>
<td>7 wt.% at 55°C</td>
<td>PTFE</td>
<td>(Shirazi et al., 2015)</td>
</tr>
<tr>
<td>ethanol</td>
<td>34 wt.%</td>
<td>PVDF with a mean pore size of 0.45 µm</td>
<td>(Treybal, 1980)</td>
</tr>
</tbody>
</table>

6. Wetting measurement

Hydrophobicity is determined by the interaction between the liquid and the membrane material. Immediate wetting in MD can be predicted by feed solution surface tension and water CA measurements (Lies Eykens et al., 2017). However, long-term performance tests are required to determine the non-wettability of the membrane with non-immediate wetting characteristics. The following section describes the common hydrophobicity measurements for membranes used in MD.

6.1. CA measurement

The conventional method to assess hydrophobicity of a membrane is CA measurement (Shaw, 1992). In this approach, the CA made by a liquid droplet on a membrane surface is measured by a goniometer, which determines relative wettability of membranes. The CA is obtained as the angle between the surface of the wetted membrane and a line tangent to the curved face of the drop at the point of three-phase contact (Onsekizoglu, 2012). The relative wettability of a membrane surface can be studied by measuring the receding and advancing angles of water on a membrane surface. The advancing water CA is associated with membrane hydrophobicity, and the receding angle is related the degree of molecular reorientation necessary to create a new equilibrium state with the aqueous solution (Khayet and Matsuura, 2004). The benefit of this approach is that the actual measurement is easy to perform (K. Y. Wang et al., 2008). However, CAs
can show hysteresis and are influenced by the surface structure (roughness) of the membrane (Adamson and Gast, 1997).

For CA determination, Neumann et al. (Kwok and Neumann, 1999) established an equation of state using Young-Laplace equation to relate the three interfacial tensions, which can predict the surface energy of a homogeneous dense polymer from surface tension and CA measurements for pure liquids

\[ \cos \theta = -1 + 2\sqrt{\gamma_{SV}/\gamma_{LV}} \exp[-\beta(\gamma_{SV} - \gamma_{LV})^2] \] (10)

where \( \beta \) is a parameter independent of the solid and the liquid. However, this model can just be applied for high values of surface tensions capable of generating obtuse CAs, thus implicitly excluding the critical zone where wetting occurs (Chibowski and Terpilowski, 2008). Courel et al. (Courel et al., 2001) modified Eq. (10) by introducing surface porosity of the membrane to improve the fitting quality of the model

\[ \cos \theta^* = y^2 \cos \theta - (1 - y)^2 - 2y(1 - y) \sqrt{\gamma_{SV}/\gamma_{LV}} - \cos \theta \] (11)

where \( \theta^* \) is the CA of a rough and hairy surface, \( 1 - y \) is the surface porosity.

6.2. LEP measurement

The LEP depends on the interfacial tension of the feed, the CA of the membrane and the size, and structure of the membrane pores (Eq. (1)-(5)) (Franken et al., 1987; Rezaei and Samhaber, 2015, 2014). The LEP of a membrane can be measured by two approaches: static and dynamic method. The static LEP determination proposed by Smolder et al. is a variation of the bubble point method (ASTM International, 2014) (thoroughly described elsewhere (Smolders and Franken, 1989)). However, dynamic LEP measurement can be performed using a typical MD configuration (e.g., vacuum membrane distillation (VMD)). Similar to CA measurements, static LEP measurements have been considered to exhibit hysteresis (Bilad et al., 2015; Durham and Nguyen, 1994; Racz et al., 2015; Sarti et al., 1985). Moreover, this method has been abandoned because membrane compaction occurs during the test, which leads to higher LEP measurements (Durham and Nguyen, 1994). Notably, a recent study showed that this measurement could be improved by
measuring the rate of depressurization after stepwise pressure increase, rather than taking the maximum pressure value achieved (Warsinger et al., 2017a).

6.3. Penetrating drop concentration method

To determine the critical solute concentration in the penetrating drop method (Franken et al., 1987), a droplet with the particular concentration of organic material, which is on the verge of penetration into the membrane, is considered as the penetrating drop and the corresponding surface tension is the surface tension of penetrating droplet. The surface tension at which microporous membranes are wetted under process conditions can be calculated by the following equation:

\[ \gamma_L = \gamma_L^P + \frac{\Delta P r_{max}}{2B} \]  

where \( \gamma_L^P \) is the surface tension of penetrating liquid measured from penetrating drop method, \( \Delta P \) is the applied pressure difference and \( B \) is a dimensionless geometrical factor. However, this approach can be used for membranes with a surface tension greater than 23 mN/m (Durham and Nguyen, 1994) as the liquid with lower surface tensions wet the membrane instantaneously.

6.4. Sticking bubble technique

In this method, a piece of membrane is placed horizontally at the bottom of the beaker containing a liquid with defined surface tension (Keurentjes et al., 1989). The air bubbles are brought into contact with the top surface by a flat-ended needle. Hydrophobicity is expressed in terms of the surface tension of liquid at which an air bubble has a 50% chance of detaching from the membrane surface (\( \gamma_L = \gamma_d \)). In the case where radius of bubble (\( R \)) is equal to radius of curvature at the top of the bubble (\( b \)), the following expression provides the CA of a spherical and deformed air bubble (Fig. 8):

\[ \gamma_d = \frac{\Delta \rho g R^2 \left( \frac{2}{3} + \cos \theta_2 - \frac{1}{3} \cos^3 \theta_2 \right)}{2 \sin^2 \theta_2} \]  

\[ \sin \theta_1 = \frac{\Delta \rho g R^2 \left( \frac{2}{3} + \cos \theta_2 - \frac{1}{3} \cos^3 \theta_2 \right)}{2 \gamma_d \sin \theta_2} + \sin \theta_2 \]
Fig. 8: The air bubble-liquid-membrane system for spherical (a) and deformed air bubbles (b).

6.5. Penetration temperature method

Penetration temperature method was developed for membranes with a surface tension less than 23 mN/m (Durham and Nguyen, 1994). In this approach, either propan-1-ol (n-propanol) or propan-2-ol (isopropanol) is placed into a test tube (10 ml at 15° C) with the membrane and thermometer. The test tube is sealed with Parafilm® and placed in a 35° C water bath. The test tube is gradually heated until bubbles appeared on the membrane, then the test tube is lightly tapped, and then the temperature increased at 1° C intervals. The penetration temperature measurement (PT° C) was recorded, when the membrane was almost transparent. The surface tension of the membrane was evaluated using following relationships:

\[
\gamma_s = PT° C \times -0.0777 + 25.253 \quad \text{for Propan-1-ol} \tag{15}
\]

\[
\gamma_s = PT° C \times -0.0777 + 22.85 \quad \text{for Propan-2-ol} \tag{16}
\]

7. Membrane restoration

Wetted membranes must be entirely dried and cleaned before subsequent usage (Tomaszewska, 2000), which leads to process downtime and potential membrane degradation (Guillen-Burrieza et al., 2013). On one hand, membrane regeneration in the MD process is challenging, and because in many cases fouling is associated with the membrane wettability (Marek Gryta, 2002b), the acquired results are not favorable. On the other hand, reducing the hydrostatic pressure below the LEP will not guarantee the restoration of membrane pores back to unwetted condition. This phenomenon is explained by Lawson et al. (Lawson and Lloyd, 1997) and illustrated in Fig. 9. As \(\Delta P_{\text{interface}}\) is increased to LEP no liquid wets the membrane pores until LEP is reached (step 1). From this point on the liquid starts to penetrate into and flow through
the bigger pores as the pressure increases (step 2). Once all the pores become filled with the liquid, the flux is governed by the Darcy’s law ($J = K \Delta P$). Decreasing the pressure results in a linear decrease of flux (step 3). In order to restore the membrane to the initial conditions, the membrane needs to be dried. However, solutes in the feed can be left inside the pores of the membrane after the evaporation of the solvent. In this case, the membrane needs to be initially chemically cleaned and then dried in an oven.

Fig. 9: Liquid flux versus transmembrane pressure difference (Lawson and Lloyd, 1997) (LEP = $\Delta P_{\text{entry}}$) Periodic removal of fouling layer can also limit the gradual reduction of permeate flux in MD. Moreover, stabilizing a thinner scaling layer on membrane surface by shortening the interval between the cleaning operation is reported to reduce the risk of partial wetting due to the restriction of the degree of oversaturation inside the wetted pores (Fig. 10a and b) (Gryta, 2015). However, the dissolution of deposits can facilitate wetting as a result of internal scaling (Fig. 10c) (Chen et al., 2014a; Gryta, 2017, 2008).
Fig. 10: SEM image of the membrane surface with deposit formed after (a) 1 h of MD process duration (b) 5 h of MD process duration. Feed: tap water (c) SEM image of capillary membrane cross-section. The crystallite formed inside the membrane pores (Gryta, 2015).

7.1. Rinsing and drying

Regeneration of membranes wetted by chemical membrane degradation via rinsing and drying has proved to be ineffective because of the presence of the hydrophilic groups on membrane surface (Gryta et al., 2009). He et al. (He et al., 2008) reported that the effective regeneration of wetted membrane could not be achieved by the process of rinsing the membrane with distilled water, and drying in the oven. This was due to deposition of salt crystals inside the pores and consequently, an irreversible structural change induced by the liquid intrusion inside the pores. Another attempt was also performed to remove the iron dioxide precipitates from the surface and pores of PP membrane with concentrated HCl solutions (Gryta, 2007b). The results showed that the complete removal of iron oxides from the capillary membrane (also including that precipitated into the pores) by rinsing caused wetting of some membrane pores leading to a reduction of permeate flux by 21%. In this case, the acid solution filled the pores adjacent to the pores filled by the deposit, which resulted in an increase of the area of the wetted membrane.

7.2. Backwashing

Another approach for membrane cleaning is backwashing. For instance, air backwashing of the scaled membrane can help to remove crystals and scales. However, when applied to a dried membrane, the effectiveness of this method is limited only for removal of deposits on at the membrane pore mouth (Choi et al., 2017). Backwashing with air is best when a wetted membrane still contains liquid: air pressures exceeding the liquid entry pressure can force wetting liquid out, keeping the solutes from precipitating. (D. M. Warsinger et al., 2016; Warsinger et al., 2017a). Shin et al. (Shin et al., 2016, 2015) explored the dewetting efficiency of high-temperature air on a wetted PVDF membrane. They found that the optimal condition for the air temperature and exposure time ranged from 60-70 °C and 8-12.5 min, respectively. UV irradiation has also been reported to partially clean the PVDF/TiO₂ superhydrophobic membranes fouled by gallic acid (Hamzah and Leo, 2017). Their results showed that the gallic acid foulants were
decomposed under the irradiation of UV light due to photocatalytic activity of TiO$_2$ nanoparticles blended in the membrane.

Recently, Warsinger et al. (Warsinger et al., 2017a) studied the effectiveness of pressurized air backwashing (PAB) relative to the membrane dryout to reverse membrane wetting in MD. They found out that PAB restored the LEP to 75% of the pristine membrane for lower salinity feeds by removing the saline solution from the membrane without separating water and salts by vaporization. Notably, this method did not involve a dryout step or evaporation (the air was cool), and thus provided dewetting in ~10 seconds of treatment. However, there remains a possibility that air backwashing can cause partial tears in the membrane structure (Fig. 11).

![Diagram of wetting reversal methods](image)

Fig. 11: Methods for wetting reversal, adapted from (Warsinger et al., 2017a).
8. Mathematical modeling of wetting

One of the main drawbacks in describing the wetting phenomenon in MD is the lack of mathematical models (Babalou et al., 2015). Membrane wetting behavior is complex to simulate, as it is mainly influenced by the microstructural characterization of the membrane itself (Dong et al., 2017). Peña et al. (Peña et al., 1993) proposed a MD model, which evaluates the decrease of permeate flux and steady-state pressure difference due to the progressive membrane pore wetting by the following equation:

\[
J = \text{non isothermal flux} - \text{hydraulic flux} = (1 - \alpha_i)B' \Delta T_b - \alpha_i A \Delta P_i
\] (17)

\[
J_i = \frac{B' \Delta T_b}{B' \Delta T_b + A \Delta P_i^{st}}
\] (18)

\[
\alpha_i = \frac{B' \Delta T_b}{B' \Delta T_b + A \Delta P_i^{st}}
\] (19)

where \(J\) is the net volume flux, at the arbitrary time of \(t\), \(J_i\) is each of the measured fluxes (non-isothermal or hydraulic), \(B'\) is a measured or apparent non-isothermal phenomenological coefficient, \(\Delta T_b\) is the temperature difference in the bulk phases, \(A\) is a permeability coefficient, \(\Delta P_i^{st}\) is the steady-state measured pressure difference when the cold chamber is sealed, and \(\alpha_i\) is the percentage of liquid-filled pores. Coefficients \(A\) and \(B'\) can be calculated based on a two-parameter non-linear regression method from the experimental pairs \(J_i\) and \(\Delta P_i^{st}\) for a given value of \(\Delta T_b\). Following the model proposed by Peña, García-Payo et al. (García-Payo et al., 2000) proposed the following equations to calculate the LEP taking into account the axial irregularity of pores:

\[
\text{LEP} = -\frac{2 \gamma_L}{r_{max}} \cos \left( \arcsin(\xi) \right) \frac{\cos \left( \arcsin(\xi) \right)}{1 + \frac{2R}{r} \sin^2 \left( \frac{\theta_A}{2} - \arcsin(\xi) \right)}
\] (20)

where \(r\) is the mean pore radius, \(\theta_A\) is the advancing CA, \(R\) is the mean curvature radius of pore wall element and \(\xi = \frac{R \sin \theta_A}{1 + \frac{R}{r}}\) (Fig. 12).
Fig. 12: Interface in an irregular pore of the hydrophobic membrane. (1) Liquid phase and (2) gas phase.

When the geometry of the pore is axially irregular, a structure angle, $\alpha$, may be defined as the angle between a pore wall element and the normal to the membrane surface in the axial direction (García-Payo et al., 2000).

For polar or hydrogen bonding liquids on non-polar solids with low surface energy, the LEP can be calculated based on van der Waals dispersion components of the work of adhesion of a fluid to a solid surface (García-Payo et al., 2000):

$$LEP = \frac{2}{r_{\text{max}}} \left( \gamma_L - 2 \sqrt{\gamma_S^d \gamma_L^d} \right) = \frac{2}{r_{\text{max}}} (\gamma_L - \gamma_L^w)$$

where $\gamma_S^d, \gamma_L^d$ are the dispersion components of surface tension of the solid and the liquid and $\gamma_L^w$ is the wetting surface tension (i.e., LEP=0).

9. Membrane non-wetting characteristics

The main prerequisite to be satisfied by the membranes during MD operation is that solutions on both sides of the membrane do not wet the pores of the hydrophobic membrane (Zydney, 1995). The question of how to characterize the wettability of a MD membrane is a critical one, although few structural studies can be found in the literature.

The selection of membrane material and properties can assist to prevent membrane wetting. In MD, intrinsic hydrophobic microporous polymeric membranes such as PVDF, PP, polytetrafluoroethylene (PTFE) and polyethylene (PE) are used. However, these membranes are prone to wetting if LEP is exceeded.
As the first prerequisite for a proper membrane operation under fluctuating pressures and temperatures in the plant, the LEP of the membrane is recommended to be higher than 2.5 bar regardless of the MD configuration (Eykens et al., 2016; Schneider et al., 1988a). A more hydrophobic membrane can decrease the chances of reduction of the permeate flux due to partial wetting. PVDF is a less hydrophobic polymer relative to other polymeric MD membranes. PVDF has a surface free energy of 30.3 mN/m while PE, PP, and PTFE membranes have surface free energies of 20-25 mN/m, 30 mN/m, and 9-20 mN/m, respectively (Ashoor et al., 2016; Bonyadi and Chung, 2007; Cheng et al., 2010). Therefore, PVDF membranes might be more prone to the wetting. However, PVDF membranes have been wildly used due to easy processability.

Moreover, the intrinsic CA of nonporous PVDF material is less than 90°. However, it can be enhanced by increasing the surface roughness (Kang and Cao, 2014). Compared to the hydrophobicity of the membranes, the surface roughness is more crucial than low surface energy. The reason is that when two surfaces with different hydrophobicity are roughened, both can become superhydrophobic (Tijing et al., 2014a).

Wetting concentration (i.e., the lowest concentration of a solution that wets the membrane spontaneously (García-Payo et al., 2000)) is always considerably higher for PTFE membranes than the wetting concentration for PVDF membranes under identical experimental conditions (An et al., 2016a; Courel et al., 2000; García-Payo et al., 2000). However, the utilization of PTFE in large-scale industrial applications is restricted due to its various disadvantages, such as a high fabrication cost and environmental impacts (Gryta, 2016b).

PP has a relatively high surface energy (29 mN/m) and the smallest CA among other polymers used in MD. These traits have been found to result in partial wetting after few weeks of operation in an MD process (Gryta, 2005).

Using membranes with a small pore size (maximum micropore radius of less than 0.6 µm and LEP more than 100 kPa (L. Eykens et al., 2017; Rao et al., 2014; Thomas et al., 2014)) and high tortuosity (i.e., 50-80%) as well as the sponge-like structure can ensure that process pressure and temperature fluctuations do not lead to membrane wetting (Kezia et al., 2015; Schneider et al., 1988b). Higher membrane porosities
than 80% are usually accompanied by large pore sizes which are not suitable as they intensify the danger of membrane pore wetting (Banat and Simandl, 1998). The use of a nonporous membrane in MD similar to pervaporation has been proposed since the dense structure of the membrane inhibits wetting (Purwasasmita et al., 2015).

The thickness of the membrane also plays a major role in wettability of the membrane. A decrease in membrane wall thickness significantly improves the permeate flux. However, it increases the risk of membrane wetting.

10. Effect of operating conditions on wetting

The operating conditions for MD can be controlled such that membrane wetting is prevented. For instance, pressure spikes or absence of temperature gradient can result in wetting of some pores and consequent deterioration in the quality of distillate (Peng et al., 2017; Walton et al., 2004). Membrane temperature decline due to membrane dry-out as the result of temporary shutdowns can precipitate dissolved substances from the feed on the membrane surface and pores, accelerating membrane wetting (capillary condensation (Atchariyawut et al., 2006; Meng et al., 2015b)). Therefore, for instance, in the case of intermittent operation, the proper shutdown protocols are needed when storing used MD modules for the extended periods of time (Guillen-Burrieza et al., 2014).

On the contrary, the surface tension of solutions decreases with an increase in temperature, making the wetting a greater challenge at higher temperatures (Nayar et al., 2014). For pure water, the value of surface tension varies between 72-64 mN/m for temperatures between 25-70°C. Increasing feed temperature can also increase the scaling and membrane wetting due to oversaturation in the boundary layer for the saturated brine solutions (Edwie and Chung, 2013; Ge et al., 2014; Shirazi et al., 2014). The sustainability of a DCMD process for a hypersaline solution at a higher temperature difference of 40 °C was compromised due to membrane wetting (Hickenbottom and Cath, 2014).

Lowering the applied pressure in the feed and the permeate through adjusting the feed and permeate flow rates reduces the pressure difference across the membrane, hence reducing the tendency for the membrane wetting due to operating below LEP (Luo and Lior, 2017; R W Schofield et al., 1990). Moreover, permeate
quality deterioration can be avoided if the permeate pressure is kept higher than the feed pressure. Therefore, the feed cannot directly flow through the wet pores to the permeate side. In this case, MD process may be continued; however, after a wetting incident, the permeate flux decreases due to the reduction of active pores. In DCMD, a slightly higher pressure on the permeate side than the feed side has been used to reduce the risk of wetting (Zakrzewska-Trznadel et al., 1999).

Although high cross-flow velocity minimizes the boundary layer resistances and leads to higher permeate flux, it increases the pressure difference across the membrane (e.g., 10-20 kPa) and enhances the risk of pore wetting. Thus, the recirculation rate should be high enough to reduce the polarization effect, and sufficiently low to operate below LEP (Lawal and Khalifa, 2015; Naidu et al., 2014; Srisurichan et al., 2006; Y. Zhang et al., 2015). In this case, the feed flow rate must be varied with due precautions as the transmembrane hydrostatic pressure which needs to be always lower than LEP is a function of the second power of the feed velocity.

Recently, Guillen-Burrieza et al. (Guillen-Burrieza et al., 2016) conducted DCMD experiments to understand the effect of operational parameters on the wetting phenomenon and concluded that when parameters are adjusted in a way that increases permeate flux, both the wetting time and rate are reduced.

Notably, feed and permeate temperatures are more associated with the wetting time (e.g., high ΔT increases the wetting time), while feed and permeate flow rates are more influencing the wetting rate (the lower one decreases the wetting rate).

Additionally, it is important to note that numerous operating factors that increase fouling also may increase wetting. These factors imply the need for avoidance of stagnation zones from spacers or piping that give time for crystal nucleation, avoidance of high-energy surfaces (e.g. metals) which may induce nucleation, and implementation of proper pretreatment for fouling particles (Warsinger et al., 2017b).

11. Effect of MD configurations on wetting

As the feed conditions can vary independently of configuration, in most cases the configuration impacts wetting little. Particular attention must be noted in VMD to avoid membrane wetting because in this configuration vacuum is applied to the permeate side and therefore ΔP_{interface} is usually higher in VMD.
than in the other MD systems (Hassan et al., 2015; Lawson and Lloyd, 1997; Mohammadi and Akbarabadi, 2005). Therefore, the VMD has been used just for removal of volatile organic compounds from dilute aqueous solution and, unlike other membrane processes such as pervaporation, not for separation of organic/organic or organic/water mixtures. Notably, process conditions influenced by configuration choice can have an impact on wetting, such as temperature differences at the membrane surface (which impacts foulants and also surface tension), and concentration polarization caused by greater flux. In a study conducted by Meng et al. (Meng et al., 2015a), membranes in submerged VMD (with no agitation) were wetted quickly within the first 8 h of inland desalination operation, whereas membranes in cross-flow VMD maintained rather low permeate conductivity for 50 h.

12. Approaches to control wetting

Different approaches to control wetting in MD have been proposed by several researchers. Most of the emphasis has been on advancement in membrane fabrication in such a way to ensure a low affinity between the liquid and the polymeric material. This has been mainly done through modifying the membrane surface geometrical structure and surface chemistry. Several studies also investigated the integration of filtration processes with MD as pretreatment steps. The following section reviews these approaches in more detail.

12.1. Pretreatment/Hybrid MD processes

Wetting of the hydrophobic membrane can be avoided by the use of a robust pretreatment of the feed liquid. Many of these processes effectively removed membrane wetting agents before they reached the membrane. However, one should note that the capital and operating costs of the process will increase due to the addition of a pretreatment step.

Several methods are proposed to be integrated with MD for different applications (Table 5). Integration of filtration processes with MD can remove most contaminants and foulants from the feed solution, thus mitigating the wetting problem. In the case of protein as a fouling agent, either the feed solution can be boiled followed by filtration to reduce the precipitation of proteins on the membrane surface (Gryta, 2008), or ultrasonic waves can be introduced to mitigate protein fouling (i.e., the deposition of bovine serum albumin aggregates) and consequently wetting incidence (Hou et al., 2017). Nanofiltration can also be used
to remove less soluble compounds including divalent salts (Roy et al., 2017): this has been integrated into membrane distillation (Kumar et al., 2017). Ultrasonic treatment in a hybrid process with MD can also mitigate membrane CaSO₄ scaling and thus reducing the risk of membrane wetting (Hou et al., 2015). Additionally, coagulation pretreatment to form bigger crystals than the membrane pores can considerably minimize the risk of scale formation inside the membrane pores. Accelerated precipitation softening including pH adjustment with sodium hydroxide along with calcite seeding, followed by microfiltration to avoid clogging by the seeds was integrated before DCMD to desalinate a primary RO concentrate (Qu et al., 2009). Membrane distillation bioreactors (MDBR) couple thermophilic bioprocess, which results in the biological removal of high concentrations of organics and nutrients. This pretreatment expands the application of MD to the reclamation of industrial wastewater containing a low volatile solute content. Another way to reduce scaling incidence in MD is chemical conditioning of the feed using antiscalants (e.g., polyacrylic acid). The use of antiscalant could prolong the induction period for the nucleation of gypsum and calcite, respectively; and slow down the precipitation rate of crystals (He et al., 2009; Peng et al., 2015; P. Zhang et al., 2015). However, high dosing of antiscalant can also increase the risk of membrane wetting because of organic nature of antiscalants. Most recently, Dow et al. (Dow et al., 2017) demonstrated that the MD testing on a textile mill effluent that was first treated by flocculation and anaerobic/aerobic digestions eliminated the wetting issue.

Table 5: Pretreatment process applied for MD to control wetting occurrence

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Process</th>
<th>Application</th>
<th>Impact</th>
<th>Results</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical</td>
<td>Ultrafiltration</td>
<td>concentration of grape juice</td>
<td>protein removal</td>
<td>max ~7% increase in juice surface tension</td>
<td>(Bailey et al., 2000)</td>
</tr>
<tr>
<td></td>
<td>Microfiltration</td>
<td>ammonia stripping from pig manure</td>
<td>protein removal</td>
<td>2-4 times increase in ammonia mass</td>
<td>(Zarebska et al., 2015)</td>
</tr>
<tr>
<td>Method</td>
<td>Parameter</td>
<td>Transfer Coefficient</td>
<td>Efficiency of Contaminants</td>
<td></td>
<td></td>
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<tr>
<td>--------------------------------</td>
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<td>----------------------</td>
<td>-----------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Forward osmosis wastewater reuse</td>
<td>ammonium, COD, arsenic removal</td>
<td>&gt;99% removal</td>
<td>&gt;99% removal efficiency of volatile contaminants (Husnain et al., 2015)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Real domestic wastewater treatment</td>
<td>removal of most high molecular weight contaminants</td>
<td>&gt;90% removal efficiency of organic matters, calcium salts, magnesium salts, sodium salts, silicates (Li et al., 2018)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Integrated crystallization shale gas produced water treatment</td>
<td>reducing scalant loading of multivalent ions, such as barium and calcium</td>
<td>increasing the total water recovery from 20% to 62.5% (Kim et al., 2016)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Multi-stage flash distillation desalination of rejected brine</td>
<td>reducing concentration of different organic and inorganic contaminants</td>
<td>4-12% less reduction in permeate flux (Kayvani Fard et al., 2016)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method</td>
<td>Description</td>
<td>Efficiency</td>
<td>Reference</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Activated carbon</td>
<td>seawater and concentrated brine treatment</td>
<td>remove particulates and organic contaminants 21% and 23% removal of the antiscalant and antifoam agent</td>
<td>(Minier-Matar et al., 2014)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Foam fractionation</td>
<td>concentrating textile mill effluent</td>
<td>capturing surface-active materials increase of concentration factor from 27 to 34-fold</td>
<td>(Dow et al., 2017)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
<td>Coagulation desalination of recirculating cooling water</td>
<td>elimination of total organic carbon, total phosphorus substances 23% increase in permeate flux</td>
<td>(J. Wang et al., 2008)</td>
<td></td>
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<tr>
<td>Chemical conditioning</td>
<td>treatment of RO brine</td>
<td>removing calcium hardness and sulfate ions increase of final rejection factor form 58.6% to 97.9%</td>
<td>(Sanmartino et al., 2017)</td>
<td></td>
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<tr>
<td>Biological</td>
<td>Integrated bioreactors reclamation of industrial wastewater</td>
<td>biological removal of organics and nutrients delaying wetting by 1.7–3.6 times</td>
<td>(Goh et al., 2013)</td>
<td></td>
<td></td>
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<tr>
<td>Biological treatments</td>
<td>textile wastewater treatment</td>
<td>digesting surfactants reduction of TOC from 100 to 26 mg/L</td>
<td>(Dow et al., 2017)</td>
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</table>
Other Microwave-assisted photocatalysis treating the coal gasification wastewater preventing organic fouling by photodegrade the organic matters increase of normalized permeate flux from 79.8% to 98.5% (J. Wang et al., 2016)

12.2. Advances in membrane fabrication

Preventing and controlling membrane wetting via appropriate membrane design is of significant interest. Nevertheless, at present, most of the developed membranes still undergo some level of wetting. The current MD membrane design process relies heavily on commercial MF membrane fabrication methods, i.e., conventional thermal or dry/wet phase inversion techniques (Tijing et al., 2014a). These manufacturing methods lead to a non-homogeneous pore size distribution, which increases the risk of wetting for larger pores.

The primary goal of advancement in membrane fabrication is to obtain a surface with special non-wettability (Z. Wang et al., 2016a). These surfaces are categorized to superhydrophobic surfaces repellent to water, superoleophobic surfaces repellent to oil and omniphobic surfaces repellent to both water and oil. However, these methods commonly demand complex fabrication processes or high-specialized equipment, making them unacceptable inefficient production (Yang et al., 2016). Finally, the durability and long-term stability of these membranes are also questionable and require systematic research especially against high salinity feeds and different organic foulants (El-Bourawi et al., 2006; Yang et al., 2014; Zhang et al., 2005, 2013a).

Based on the goal of excellent liquid repellency, different strategies are developed to fabricate membranes with special non-wettability. Some of the methods developed to change not only the surface of the membrane but also the membrane matrix characteristics, while others are based on the physical and chemical modifications of surface morphology and microstructure of the fabricated membrane. The main disadvantages of the surface modification techniques are to change the membrane surface wettability
without affecting the bulk wetting properties. Superhydrophobic surface coating of the hydrophobic membranes increases the surface roughness and consequently the CA, $\theta$ as the contact angle in Eq. (1), but it can have less effect in increasing the LEP. The reason is that CA is a surface property only, while the LEP is affected not only by surface wettability of the membrane but also by the wettability inside of the pores. For example, according to Eq. (4), LEP is affected not only by the surface property but also “$h$”, the floor height describing the interactions between the liquid and the pores below the initially wetted surface (Fig. 3). (Franco et al., 2008; Liao et al., 2013; Prince et al., 2013; Yan et al., 2017). As by surface coating in case of membrane surface wetting, fewer resistances exist inside the pores, and the liquid penetrates more easily throughout the membrane thickness (Jin et al., 2008). Therefore, both surface and bulk modifications are necessary to create the membrane in a designed way, and this cannot be accomplished solely by the structuring of the surface or only by chemical functionalization (D.Y. Cheng and Wiersma, 1983; Kujawa et al., 2017). Table 6 summarizes the applied methods for advancement in membrane non-wettability to increase the membrane hydrophobicity or providing anti-sticking/self-cleaning surfaces.

<table>
<thead>
<tr>
<th>Approach</th>
<th>Method</th>
<th>Inference</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Membrane fabrication</td>
<td>incorporation of hydrophilic nonporous layers</td>
<td>to inhibit a transport of amphipathic molecules, however, includes more resistance than a porous hydrophobic coating</td>
<td>ethylene glycol (Chong et al., 2016; Majidi Salehi et al., 2016) polyvinyl alcohol (Z.-Q. Q. Dong et al., 2015; Mansouri and Fane, 1999; N.M. Mokhtar et al., 2014; Ray et al., 2017) polyethylene glycol (Feng and Jiang, 2006; Zuo and Wang, 2013) alginate (Xu et al., 2004)</td>
</tr>
<tr>
<td>Loading of perfluorinated polymers</td>
<td>to increase membrane hydrophobicity by reducing surface free energy (Chen et al., 2015; Edwie et al., 2012; Figoli et al., 2016; Guo et al., 2015; Kujawa et al., 2016; Lalia et al., 2013; Prince et al., 2014b; Tong et al., 2016; Xu et al., 2017; Y. Zhang et al., 2017; Zhao et al., 2017)</td>
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</table>
| Loading of functionalized hydrophobic nanoparticles/nanofibers | to maximize membrane hydrophobicity by increasing the membrane CA and minimize the surface pores size (Baghbanzadeh et al., 2015; Boo et al., 2016; Z.-Q. Dong et al., 2015; Dong et al., 2014; Efome et al., 2016; Fan et al., 2017; Gonzalez-Benito et al., 2017; Hammami et al., 2016; Hamzah and Leo, 2017; Lalia et al., 2014; E.-J. Lee et al., 2017; Li et al., 2014a, 2014b, X. Li et al., 2016, 2015; T. Liu et al., 2016; K.-J. Lu et al., 2017; X. Lu et al., 2017, 2016; Ma et al., 2009; Moradi et al., 2015; Qing et al., 2017; Rezaei and Samhaber, 2017) | alginic acid-silica (Xu et al., 2005b)
alginate-carrageenan (Xu et al., 2005a)
chitosan (Chanachai et al., 2010) |
| Membrane modification | Physical modification | to increase membrane surface roughness | plasma treatment (Chul Woo et al., 2017; Dumée et al., 2016; Fane et al., 2012; Li and Sirkar, 2005; L. Liu et al., 2016; Sirkar and Qin, 2001; Tian et al., 2015; Xu et al., 2015; Yang et al., 2014, 2015; X. Yang et al., 2011) layer-by-layer assembly (Arafat et al., 2015; N. M. Mokhtar et al., 2014; Prince et al., 2014b; Rezaei and Samhaber, 2016a; Tijing et al., 2014b; Woo et al., 2015; W. F. Zhang et al., 2016b; Yan et al., 2017; W. Zhang et al., 2017) | carbon nanotubes (CNTs) (Fan et al., 2016; J.-G. Lee et al., 2017; Y. Li et al., 2015; Mapunda et al., 2017; Okiel et al., 2015; Silva et al., 2015; Tijing et al., 2016; Woo et al., 2016a, 2016b) graphene (An et al., 2017; Moradi et al., 2015; Y. Wang et al., 2017; Woo et al., 2016a) | loading of carbon-based micro- and nanomaterials to enhance the membrane surface roughness Su et al., 2017; Tijing et al., 2014b; Z. Wang et al., 2016b; Yan et al., 2017; W. Zhang et al., 2017; Zhong et al., 2017) |
| Chemical modification | to reduce surface free energy | incorporation of surface-modifying molecules or low surface tension functional groups (Chua et al., 2015; Huang et al., 2016; Kujawa and Kujawski, 2016; Kujawski et al., 2016; Kyoungjin An et al., 2017; E.-J. J. Lee et al., 2016; K. J. Lu et al., 2016; Prince et al., 2012; Y. Wang et al., 2017; Wang and Lin, 2017; Xiaoxing et al., 2011; Yin et al., 2017; Zhang et al., 2013b; Zuo and Chung, 2016) | Yang et al., 2011; Zhu et al., 2015; Zuo et al., 2017) template replication (Peng et al., 2013) phase separation (Thomas et al., 2014; Xiao et al., 2015) electrospinning (An et al., 2016b; Huang et al., 2017) double re-entrant cavities (Domingues et al., 2017) thermal treatment (Shaulsky et al., 2017; Wang et al., 2014; Yao et al., 2017) |
Some of these techniques have disadvantages. Generally, adding layers to a membrane surface reduces permeability. Ideal MD membranes are highly porous with low conductivity, so denser regions may impair system-level performance (Swaminathan et al., 2018). Added cost in fabrication is also another concern, especially in steps that require long durations or expensive precursors. Importantly, many of the most hydrophobic compounds ideal for MD membrane anti-wetting have environmental toxicity concerns (e.g. fluoropolymers). Some processes (e.g., plasma coating) may damage some substrates, and so should be chosen carefully. Finally, while increasing surface roughness can increase hydrophobicity, surface roughness can have complex interactions with certain foulants, with increased adherence in some situations.

The following part of this section reviews some of the new aspects of advancement in membrane fabrication methods for higher wetting resistance in MD.

12.2.1. Membrane surface modifications

As mentioned, the surface chemistry and geometrical structures determine the wetting property of membrane. Surface chemistry adjusts the surface tension at the microscopic level, but geometrical structure controls how these forces act upon the liquid (McHale et al., 2004). Thus, varying one of these two parameters can regulate the surface non-wettability. The functionalization with low surface energy materials particularly fluorosilanes (Fig. 13) can decrease the surface free energy. Alternatively, generating a hierarchical nanostructure surface morphology with multi-level surface roughness can tune the surface wettability (Razmjou et al., 2012). Moreover, increasing the surface roughness via nano-coating not only contributes in engineering the hierarchical structure but also provides sites (OH functional groups) for the hydrolyzed silane coupling agent to be anchored forming a robust uniform water-repellent film (Meng et al., 2014a).
Fig. 13: The scheme of membranes functionalization by perfluoroalkylsilanes molecules (Kujawa et al., 2017).

Although the achievement of superhydrophobic membranes with these strategies is successful, most of the superhydrophobic surfaces are prone to wetting by organic solutions, and very few attempts are made to fabricate omniphobic membranes that provide enhanced repellency to different liquids such as oils and alcohols. Omniphobic membranes with a re-entrant structure provide a local kinetic barrier for shifting from the meta-stable Cassie-Baxter state to the completely wetting Wenzel state for low surface tension liquids. However, the main difficulties in fabricating stable omniphobic membranes for MD applications are the control of faultless and tedious surface topography and complicated fabrication procedures which are too expensive to be implemented in the large scales (Wei et al., 2016). On the other hand, applications of these membranes for the treatment of oily wastewater with all main components and the interaction between these elements via simulations tools are not deeply studied (Han et al., 2017). Until now, only a few reports studied the omniphobicity for non-polar liquids by developing specially designed patterns such as overhang structures, re-entrant curvatures, silicone nanofilaments and candle soots or by using inherently textured substrates (Brown and Bhushan, 2016; Darmanin and Guittard, 2013; Grynyov et al., 2016; Joly and Biben, 2009; Kota et al., 2013; Kota and Tuteja, 2012; L. Li et al., 2016; Song et al., 2013; Tuteja et al., 2007, 2008). Among these works, Lin et al. (Lin et al., 2014) developed the omniphobic microporous membrane
for MD that repels both water and low surface tension liquids by coating a hydrophilic glass fiber membrane with silica nanoparticles, followed by subsequent surface fluorination and polymer coating (Fig. 14). The 9 h course of DCMD experiments for the feed solution containing 1.0 M NaCl and 0.4 mM SDS at 60 °C no wetting occurred for the omniphobic membrane, while for the PTFE membrane wetting became progressively more severe as water flux increased more than fivefold and salt rejection dropped to 40% at 0.4 mM SDS. However, it is worth noting that the fluorinated chemicals are potentially dangerous and they are regarded as persistent and global contaminants. New non-chemical methods such as pretreatment methods or other physical water treatment techniques to prevent wetting are required to be evaluated. In another study, Lee et al. (J. Lee et al., 2016) fabricated omniphobic nanofiber membranes by preparing positively charged nanofiber mats and grafting negatively charged silica nanoparticles and fluoroalkylsilane to achieve multi-level re-entrant structures. Their fabricated membrane showed wetting resistance to various liquids, including ethanol with a surface tension of 22.1 mN/m and exhibited a stable desalination performance for eight-hour operation.

Fig. 14: SEM images featuring the local morphology of (A) a glass fiber (GF) membrane and (B) an omniphobic membrane after the five-step modification procedure. The inset image in B shows the morphology of a large piece of the omniphobic membrane (Lin et al., 2014).

12.2.2. Membrane bulk modifications

Membrane morphology and crystalline composition have a high impact on the wetting action of a membrane. Formation of finger-like macro-voids in the polymeric membrane matrix due to the type of solvent used in the fabrication process can reduce the LEP and therefore increase the risk of membrane
wetting (Fig. 15). In the wet/dry spinning technique for fabrication of PVDF membranes, faster solvent/nonsolvent exchange rate is responsible for the formation of finger-like structure or even macro-voids (García-Fernández et al., 2014). Blending PVDF and PTFE to form a sponge-like membrane structure is proved to be an effective way to increase membrane hydrophobicity (i.e., CA) (Gryta and Barancewicz, 2010). Fabrication of dual-layer membrane comprising finger-like and sponge-like layers can reduce the wetting risk while enhancing the membrane performance in regard to permeability. Wang et al. (Wang et al., 2011) demonstrated that the PVDF dual-layer hollow fiber with a fully finger-like inner layer and an entirely sponge-like outer-layer resulted in 98.6 L m⁻² h⁻¹ permeation flux and LEP of 0.7 bar.

Fig. 15: SEM images of the cross-section morphology of the PVDF-HFP hollow fiber membranes prepared with different solvents (García-Fernández et al., 2014). All the membranes exhibit a sponge-like structure in the middle layer and a finger-like structure in the internal and external layers of the hollow fiber membranes.

A number of theoretical and experimental works have considered the composite hydrophilic/hydrophobic membranes for MD, but few have studied the wetting behavior of these membranes (Bilad et al., 2015; Feng et al., 2017; Gryta and Barancewicz, 2010; Jeong et al., 2014; X. Lu et al., 2016; Meng et al., 2014b; N. M. Mokhtar et al., 2014; Mostafa et al., 2017; Prince et al., 2013; Rezaei and Samhaber, 2016a; Tong et al., 2016; Zhu et al., 2015). Among these works, Peng et al. (Peng et al., 2005) developed a composite
membrane with a hydrophilic layer of polyvinyl alcohol (PVA) blended with polyethylene glycol (PEG) on a hydrophobic PVDF substrate for desalination. The composite membrane showed no wetting incident compared to hydrophobic membranes even after adding 25% ethanol to the brine feed. Later, Edwie et al. (Edwie and Chung, 2012) found out that membrane pore size and morphology beneath the membrane surface is more crucial to mitigate membrane wetting as compared to membrane wall thickness for a supersaturated NaCl feed solution. They fabricated three types of membranes including single-layer PVDF, dual-layer hydrophobic–hydrophobic PVDF and dual-layer hydrophobic–hydrophilic PVDF/polyacrylonitrile (PVDF/PAN) membranes. They found that the single-layer membrane possessing a smaller pore size and a cellular mixed-matrix structure outperformed the dual-layer membranes with a globular morphology with a superior wetting resistance. Triple layer nanofiber/hydrophobic/hydrophilic membranes have also been shown to increase in water CA and LEP. For this type of membranes (Fig. 16), the intermediate hydrophobic layer increases the LEP of the membrane by narrowing the pore size, while the bottom surface-modifying macromolecules (hydrophilic) layer draws water vapor from the intermediate layer by absorption (Prince et al., 2014a).

Fig. 16: The configuration of the triple layer membrane (Prince et al., 2014a).

Lin et al. (Lin et al., 2015) proposed a novel approach, hydrogel-covered membrane distillation (HcMD), by attaching an agarose hydrogel layer of a solid content of 6 wt.% with a thickness of 200 µm on the
surface of a PTFE membrane to reduce the risk of membrane wetting against various surfactants. The result showed no wetting during 24 h period when the concentration of surfactants was below critical micelle concentration (CMC) due to the repellency of hydrophobic moiety of the surfactant by the hydrogel phase. The agarose hydrogel with high water content acts as a static water layer by adsorbing the hydrophilic moiety and leaving the hydrophobic part outside of the surface, and preventing the surfactant from diffusing further into the hydrogel layer due to Donnan exclusion of ions (Bell, 2016) (Fig. 17a). This causes the buildup of the surfactant molecules on the interface. Above the CMCs the wetting occurred due to diffusion of the absorbed hydrophilic moiety of micelles into the hydrogel phase, but to a lower extent and at a slower pace compared to bare membranes (Fig. 17b). Attachment of hydrogel layer also decreased the permeate flux to about 71% of the flux using a bare membrane.

Fig. 17: The mechanism of hydrogel layer (a) against surfactant wetting (b) for the penetration of micelles through hydrogel layer.

12.3. Flow effects of buoyancy

Certain foulants have significant buoyancy differences from the bulk solution. MD systems can be designed to use this benefit to reduce surface adherence. For instance, in a study by Tan et al. (2017), inclined modules were used, with the membrane below the bulk fluid. The more buoyant oils in the seawater floated to the surface, and thus the inclination angle reduced fouling. This design works for flat plate modules (Warsinger et al., 2014), but the curved modules seen in the spiral wound and hollow fiber systems may be
more complex, as there will always be a surface above the foulant unless these modules are vertical (Tan et al., 2017).

### 12.4. Operating conditions

Flow operating conditions can be chosen to avoid fouling. Such systems can use saturation conditions, biocidal flow conditions, flow rates, and temperatures to minimize fouling. Past studies have developed a framework for operating MD systems at supersaturated salinities of inorganic foulants, by designing module geometry and saturation conditions so that the maximum residence time of potential salt particles is less than the nucleation induction time (Warsinger et al., 2017b). This control of timescales can inhibit inorganic deposition on the membrane, a major cause of wetting. Additionally, numerous studies have shown that temperatures in excess of ~60°C have biocidal effects in desalination systems. Operating conditions for avoiding wetting heavily overlap with conditions for preventing membrane fouling (D. M. Warsinger et al., 2015).

### 12.5. Membrane surface barrier protection

Partial or complete removal of dissolved air from the feed water before MD causes a decrease in partial pressure of air in the membrane due to equilibrium considerations. This is proved to lead to an increase in pressure difference across the liquid/gas interface, thus increasing the tendency for membrane wetting (R W Schofield et al., 1990). The use of gas bubbling has been considered for scaling and fouling control in MD (Chen et al., 2014b, 2013; Ding et al., 2011). These studies have shown bubbling of air in the MD feed could control fouling due to the reduced concentration polarization by increased mixing. Recently, a new approach to control membrane wetting has been studied for MD systems by preventing adsorption equilibrium at the liquid/solid interface through displacing the liquid which partly tends to penetrate the macroporous membrane structure with gas bubbles (D. M. Warsinger et al., 2016; Rezaei et al., 2017b; Rezaei and Samhaber, 2017a, 2017b). Therefore, based on the surface renewal theory (Danckwerts, 1951), the wetting agents do not have enough time to accumulate on the macroporous structures, because the interface is displaced or swept from the system by the gas bubbles. Recently, Rezaei et al. (Rezaei et al.,
2017a) examined the effect of recharging air bubbles on the membrane surfaces for the wetting incidence in a DCMD setup when a surfactant (sodium dodecyl sulfate, SDS) exists in a concentrated NaCl aqueous solution. The results showed that the in-situ air bubbles on the surface of the superhydrophobic membrane prevented the incident of wetting (~100% salt rejection) even for high concentrations of the surface-active species (up to 0.8mM SDS) in the feed solution. They concluded that introducing air into the feed side of the membrane displaces the liquid which partly tends to penetrate the macroporous structure with air bubbles and thus enhances the LEP, and also, the simultaneous use of a superhydrophobic membrane increases the solution CA (Fig. 18). In the other studies (Chen et al., 2014c, 2013; Wu et al., 2015), the air bubbling in MD has also shown to improve the permeate flux due to the reduction of boundary layer effects and enhancement of heat and mass transfer. Therefore, the research on air bubbling in MD should be a future focus and its capability to achieve multiple improvements needs to be further investigated.

Fig. 18: Wetting prevention mechanism by maintaining an air layer on the surface of a superhydrophobic membrane (Rezaei et al., 2017a).

13. Conclusions and perspective

Wetting is a key challenge limiting the application of MD into a wider number of industrial applications. In such cases where wetting is a risk, membrane design and prevention methods have been shown to be effective in controlling wetting. Three degrees of wetting have been recognized in MD: surface wetting, partial wetting, and full wetting. Surface wetting is considered to lead to scaling as a result of solvent
evaporation inside the membrane pores but does not deteriorate permeate quality. Partial wetting takes place when solutions penetrate deeper into the larger pores leading to reduced permeate quality, while full wetting can incapacitate the process of MD. The literature shows that inorganic scaling and organic fouling are the main causes of membrane wetting, and different prevention methods are discussed. Several pretreatment processes are found to inhibit membrane wetting by removing the wetting agents from the feed solution. Various advanced membrane designs are evaluated to bring the surface non-wettability to the states of superhydrophobicity and superomniphobicity through altering not only the surface chemistry and surface geometrical structure, but also modifying the membrane wall properties. In summary, the following needs are proposed for further assessment of wetting phenomenon in MD.

- The possibility of wetting occurrence for long-term performance and large-scale plant operations of MD needs to be further studied to obtain an entire outlook of the applicability of MD process for the treatment of solutions with low surface tension. When wetting has occurred, the possibility of its prevention should be investigated.
- Commercial hydrophobic membranes still suffer wetting due to capillary condensation. Therefore, development of a straight-forward and efficient approach for the fabrication of super-hydrophobic and superoleophobic surface for MD process is highly needed (Chew et al., 2017b; Z. Wang et al., 2017).
- Despite the promising prospect of MD with omniphobic membranes, additional investigations are required to examine other fabrication techniques and to optimize membrane performance. It is also crucial to assess the omniphobic membrane with a broad spectrum of surface-active agents and with feeds of more complex organic compositions (Liu (H. Liu et al., 2017).
- Potentially dangerous additives such as fluorinated chemicals are regarded as the persistent and global contaminants. New non-chemical methods such as pretreatment methods or other physical water treatment techniques to prevent wetting are should be evaluated.
- The impact of salinity and different organic foulants on the stability of the membrane with special wettability requires systematic research. Application of MD for the treatment of oily wastewater
with all main components should be more deeply studied, and more insight of the interaction between these elements via molecular dynamics simulations would be essential (Han et al., 2017).

- Further research is needed on the impact of air backwashing and air layer recharging for preventing fouling and wetting incidence in MD, especially at pilot scale.
- Due to lack of an appropriate model, mathematical models describing physics and thermodynamics of wetting phenomena for different wetting stages (i.e., surface, partial and full wetting) in MD need to be developed. To do so, a better mechanistic understanding of wetting as caused by different foulants is required
- More studies need to be focused on the design of large-scale MD modules, as regards the impact of module design on wetting and wetting reversal.
- Studies on improving membrane lifetime while avoiding wetting need to be conducted, and novel membrane material scale-up and testing for wetting should be established.

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None.

**Nomenclature**

- BSA: Bovine serum albumin
- CA: Contact angle
CMC Critical micelle concentration

DCMD Direct contact membrane distillation

GF Glass fiber

HA Humic acid

HcMD Hydrogel-covered membrane distillation

HLB Hydrophilic-lipophilic balance

LEP Liquid entry pressure

LTH Low temperature hydrothermal

MD Membrane distillation

NTIPS Non-solvent thermally induced phase separation

PAB Pressurized air backwashing

PP Polypropylene

RO Reverse osmosis

SEM Scanning electron microscopy

VMD Vacuum membrane distillation

WCA Water contact angle

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Distillation, Pervaporation, Vapour Permeation and Membrane Distillation.

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Highlights

- This review offers an extensive literature survey on the wetting phenomenon in MD.
- Describes wetting fundamentals, equations, parameters, and measurement techniques
- Analyzes wetting conditions, effects, prevention, and reversal techniques
- This review lays the groundwork for future technological advances in MD.

Graphical Abstract