

Liu, L., Xiao, Z., Liu, Y., Li, X., Yin, H., Volkov, A. and He, T. (2021) Understanding the fouling/scaling resistance of superhydrophobic/omniphobic membranes in membrane distillation. *Desalination*, 499, 114864. (doi: <u>10.1016/j.desal.2020.114864</u>)

There may be differences between this version and the published version. You are advised to consult the publisher's version if you wish to cite from it.

http://eprints.gla.ac.uk/226548/

Deposited on 27 November 2020

Enlighten – Research publications by members of the University of Glasgow <u>http://eprints.gla.ac.uk</u>

Highlights

- 1. New understanding of fouling/scaling resistance of superhydrophobic membranes was proposed.
- 2. Water-air-solid interface with suspended wetting incurs potential slippage.
- 3. Sustaining suspended wetting and slippage is critical for antifouling and antiscaling.
- 4. Conventional thermodynamic theories for fouling/scaling are special case of non-slip.

1	
2	
4	Understanding the fouling/scaling resistance of
5	superhydrophobic/omniphobic membranes in membrane distillation
6	
7 8 9	Li Liu ^{1,2,3+} , Zechun Xiao ¹⁺ , Yongjie Liu ¹ , Xuemei Li ¹ , Huabing Yin ⁴ , Alexey Volkov ⁵ , Tao He ^{1,3*}
10	¹ Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, China
11	² University of Chinese Academy of Sciences, Beijing 100049, China
12	³ School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China
13	⁴ School of Engineering, University of Glasgow, Glasgow, G12 8LT, UK
14	⁵ A.V.Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky pr. 29,
15	Moscow, Russia 119991
16	*Corresponding authors: <u>het@sari.ac.cn</u> .
17	+ The authors contribute to the work equally.
18	
19 20	

Abstract

Membrane distillation has shown great promises in desalinating various water streams. Significant 23 progresses have been made in the past decades owing to the development of advanced membrane 24 materials, such as superhydrophobic and omniphobic membranes. However, fouling and scaling 25 remains a critical issue for stable operation. This account summarizes contemporary theories in fouling 26 and scaling formation and their limitations in explaining the fouling resistance of superhydrophobic 27 and omniphobic membranes. A new understanding is proposed based on hydrodynamics where non-28 slip boundary conditions play a critical role. By distinguishing a pinned and suspended wetting state, 29 30 it is suggested that a superhydrophobic or omniphobic membrane correlated to a suspended wetting state, consequently a slip surface leading to scaling/fouling resistance. A new framework for analyzing 31 the fouling/scaling behavior of MD membrane is provided to identify the wetting and hydrodynamic 32 33 character of the membrane. A novel concept of treating the highly saline waste streams is suggested to cover membrane synthesis, module design and process optimization. The present work will be of 34 interest to scientists and engineers searching for solutions to the MD fouling issues. 35

Keywords: Superhydrophobic; Omniphobic; Fouling/scaling resistant; Slip; Membrane distillation

38

40 1. Introduction

Water scarcity is and will probably continue to be a critical issue around the world. Seawater 41 desalination has provided quite some relief on fresh water shortage. For many developing countries 42 and regions, reuse of wastewater is becoming important as unconventional water resources and 43 44 essential for environmental and ecological protection [1, 2]. Among various treatment solutions, 45 membrane processes have been very successful because of their high energy efficiency and small footprint. A normal wastewater management includes a series of unit operations, as shown in Fig. 1, 46 including pre-treatment, ultrafiltration, microfiltration, nanofiltration, reverse osmosis (RO), high 47 pressure RO [3] [4, 5]. However, significant amounts of saline brine is generated accompanied with 48 organic contaminants; although the absolute volume is small, the energy consumption is high to reach 49 near zero liquid discharge (nZLD), such as electrodialysis (ED) [6, 7], mechanical vapor compression 50 51 (MVC) [8-10], or the footprint is large as evaporation pond [10]. Integrated forward osmosis (FO) and membrane distillation (MD) was reported recently for treating shale-gas-flow-back water for reuse 52 purpose [11], although technically viable, cost of FO-MD remains prohibited high. 53

Most current desalination technologies for treating highly saline brine are energy intensive, especially relying on high grade electric power supply [10]. Only MD, although thermal-driven, can work at a rather low feed temperature and thus can be satisfied with low grade thermal or solar energy [12, 13] (Fig. 1). Hydrophobic porous membranes are utilized, which allows only vapor to diffuse across the porous structure. MD has demonstrated great potential in treating various streams including those containing high total dissolved solids with nearly complete rejection to non-volatile matters. However, MD has not gained large scale applications because of deleterious membrane performance





Fig. 1 Schematic of conceptual nZLD waste water management using various membrane-based treatment technologies. Pre-treatment includes chemical and biological digestion. Ultrafiltration and microfiltration are selective. High pressure RO may be utilized to reach high water recovery rate and reduce brine discharge. In the brine management step, various concentration technologies are listed including evaporation pond, MVC, ED and MD. MD is highlighted by utilization of solar or low grade heat. Crystallizer completely removes liquid and solids are obtained.

69

A hydrophobic membrane is characterized by a water contact angle (WCA) above 90° whereas a superhydrophobic membrane above 150° and a low contact angle hysteresis < 5° (CAH, the difference between the advancing and receding contact angles) [14, 15]. An omniphobic membrane has both a high WCA and low sliding angle and exhibits high repellence to low surface tension liquids; a hierarchical re-entrant structure combining with the layer of low surface energy generally contributes to omniphobicity [16-18]. Fouling and scaling of the hydrophobic MD membrane can cause deleterious performance as manifested by reduced permeate quality and flux. Recent advancement in the development of novel materials has attributed superhydrophobic membranes significant success in fouling mitigation [10, 13, 19, 20]. Understanding the fouling resistance for superhydrophobic (SH) and omniphobic (OM) membranes has been mainly based on thermodynamic theories, but frequently challenged by contradictory results.

Herein we will provide a brief account on the scaling and fouling phenomenon in MD, the 81 preparation and performance of superhydrophobic and omniphobic membranes, the main stream of 82 thermodynamic scaling and fouling models, and finally our understanding on the superhydrophobic 83 effects on the fouling formation and mitigation. A new concept is proposed by introducing a 84 hydrodynamic factor of slippage to fill in the gap. We further correlate quantitatively the wetting states 85 to the hydrodynamic slip with experimental results to verify the finding. Stability and sustainability of 86 the slip surface are critically analyzed and potential solutions are suggested. We expect that scientists 87 and engineers would take this new concept for future development of robust hydrophobic membranes, 88 modules as well as processes. 89

90 2. Scaling and fouling phenomena in membrane distillation

In general, fouling is a process of unwanted matters aggregate/deposit on a membrane surface followed by increased mass transfer resistance and reduced rejection; based on their chemical physical characteristics, foulants are can be categorized as inorganic, organic in nature (Table 1) [21, 22]. Inorganic fouling is commonly known as scaling, referring to crystals, colloidal particles, mineral scales which either precipitate/ grow directly on the membrane surface or form in bulk solution first before aggregating on the surface [23, 24]. The attachment of dissolved organic matters (humic acid,

protein, polysaccharides, oils, etc.) to the membrane surface is termed as organic fouling [21], and 97 the drivers for foulants adhesion can be van der Waals forces, electrostatic interaction and 98 hydrophobic-hydrophobic interaction, which is well described by the Extended Derjaguin-Landau-99 Verwey-Overbeek theory (xDLVO) theory. The fouling layers can be removed by chemical treatment, 100 but the performance restoration is poor and damage to the membrane surface and environment is the 101 potential disadvantage [21, 25]. Therefore, design of antifouling/scaling membranes are essential for 102 the membrane development, and understanding the mechanism of fouling and scaling has been one of 103 the main focuses in MD research [26]. The following sections will outline the major foulants often 104 105 encountered in MD applications.

106 2.1 Scaling

Scaling often occurs for various feed streams including RO concentrate, produced water from 107 oil/gas industry, underground or geothermal water [13, 20]. Sparingly soluble salts play critical roles 108 in inducing both homogeneous nucleation and impurity-induced (e.g., air, dust or other particles) 109 heterogeneous nucleation, ultimately aggregating to visible bulky crystals [26]. The hydrophobic 110 111 membrane surface readily incurs heterogeneous nucleation (Fig. 2a). Fig. 2 shows some typical examples of calcium carbonate (CaCO₃), calcium sulfate (CaSO₄) and silica scaling on different 112 hydrophobic membrane surfaces. Scaling is often featured by an induction time before formation of a 113 detectable scale phase either amorphous or in the form of "prenucleation" clusters of just a few atoms 114 [27]. This would lead to the growth and deposition of crystals into membrane pores and even covering 115 the membrane surface. Scaling leads to membrane wetting and consequently reduced permeate quality 116 and flux [28], and propagation of the wetting frontier causes membrane integrity damage followed by 117

transition from hydrophobic to hydrophilic matrix, and deteriorated permeate quality [28-32].

For concentrating high salinity brine, most commonly discussed sparingly soluble inorganic salts 119 120 were CaSO₄ and silica. Carbonate chemicals are sensitive to solution alkalinity and pH. For simplicity, we classify the scaling in MD into three main categories: (1) Alkaline scalant, such as CaCO₃ [33, 34] 121 [35] (Fig. 2b), is often observed in shale gas produced and flowback water [17, 26] and seawater 122 concentrate [36, 37] (Table 1). CaCO₃ scaling is solution pH sensitive [33, 38, 39] and temperature-123 dependent as its solubility is inversely related to temperature [25, 40-42]. The most effective chemicals 124 to remove CaCO3 scale are acids [25, 43]. (2) Non-alkaline, as represented by CaSO4, which is pH-125 126 independent [26]; CaSO₄ mainly forms rod-like structures, but needle-like and rosette-like ones have also been observed (Fig. 2c) [31, 44-51]. CaSO₄ scaling has three forms as a function of temperature 127 [44, 52]: dihydrate (gypsum, CaSO₄·2H₂O), hemihydrate (bassanite, CaSO₄·0.5H₂O) and anhydrite 128 129 (CaSO₄) [34]. The high adhesion strength and low solubility render CaSO₄ a high scaling tendency and difficult to remove [53-55]. (3) Nonionic scale, such as that of silica (Fig. 2d), is less soluble in 130 water and solvents than the ionic scale due to the absence of charges to break up and dissolve [22]. 131 132 Silica is practically ubiquitous in inland RO brine [56, 57], geothermal water and shale gas produced water [58]. Silica scale is amorphous and formed via polymerization of silicic acid (e.g., NaSiO₃, etc.) 133 [59] with robust resistance to anti-scalants [34, 60]. Silica scale was reported to block surface pores 134 without wetting [28], however, this result was challenged by other reports [61-63]. 135





136

Fig. 2 (Top) Schematic diagram of crystal formation in MD process (a). A certain induction period is 138 required prior to the formation of detectable crystalline phase. During the induction period, the solution 139 140 remains saturated or supersaturated in a metastable equilibrium without any occurrence of crystallization. Amorphous mineral "prenucleation clusters" form rapidly after the induction period, 141 for further growth and deposition. (Bottom) SEM images of typical mineral scaling in membrane 142 distillation: (b) CaCO₃ (vaterite) scaling; (c) CaSO₄ (gypsum) (Accurel PP polypropylene hollow 143 fibres with 0.20 µm pore size and external diameter of 1.8mm was used, Curcio et al. [43] (Copyright 144 2010 Elsevier B.V.)), and (d) silica scaling (PVDF membranes with a nominal pore diameter of 0.45 145 µm were purchased from GE Healthcare, Christie et al. [28] (Copyright 2019 American Chemistry 146 Society). 147

Typical	Water sources	Characteristics	Effect on MD performance*
contaminant			
CaCO ₃	Produced water,	Solubility susceptible to bicarbonate, carbon dioxide	Flux decline by pore blockage; negligible or detrimental effect on the distillate
	Industrial water,	concentration and pH [33, 38, 39]; Inverse solubility	quality [25, 33, 41, 43]; Co-precipitation with CaSO ₄ [52]; Precipitation
	Seawater brine	to temperature [21]	inhibited by humic acid [43]; Remove readily by acid [22, 26]
CaSO ₄	Industrial, Seawater	Inverse solubility to temperature [21]; Strong	Flux decline by pore blockage; negligible or detrimental effect on the distillate
	brine and groundwater	adhesion [22]	quality [28, 46-49, 52]; Hard to remove by chemical and physical cleaning [22,
			52]
Silica	Produced water;	Amorphous, resistance to anti-scalants; constant	Flux decline by pore blockage; negligible detrimental effect on the distillate
	Seawater brine	solubility at neutral or acidic pH, but increases above	quality [28, 59, 63, 65, 66]; scaling exacerbated by protein, alginate and humic
	Geothermal water	pH ~8 [26]; Precipitation at high pH with coexisting	acid [63]; Hard to remove by chemical and physical cleaning.
		metal ions (e.g., Al ³⁺ , Fe ³⁺ , Ca ²⁺ et al) [26, 61, 64]	
Humic acid	Surface, municipal	Hydrophobic [67]; solubility increases at high pH	Negligible detrimental effect on flux; no salt leakage [67-69, 73, 74]; diffusion
	wastewater	[68, 69]; complexation with the Ca^{2+} [68, 70, 71];	across the membrane; remove readily by caustic [68, 69]
		thermal disaggregation to LMW organics [72]	
Protein	Municipal, Dairy water	Hydrophobic [75]; Complexation with the Ca ²⁺ due	Negligible detrimental effect on flux; no salt leakage [47, 72, 73, 75-77]
		to negatively charged carboxyl groups at $pH > 4 \sim 5$	
		[75, 76]; Thermal irreversible denaturation (> 60 °C)	

148Table 1 Various persistent contaminants in membrane distillation

		[75]	
Alginate	surface water	Hydrophilic [67]	Negligible effect on flux; no fouling-induced salt leakage [67, 78]
Oil	Produced water;	Extremely hydrophobic [79]; stabilization by	Flux decline by pore blockage and pore wetting [67, 79]; higher proportions of
	industrial wastewater	surfactant	heavy hydrocarbons in the oil cause more severe fouling [80]
Surfactant	Municipal, produced	The higher the surfactant's HLB value, the more	Decrease in the surface tension of feed to wet pores; a surfactant with lower
	water	hydrophilic it is [81]; Above CMC, the surface	HLB value fouls hydrophobic membrane more readily and triggers earlier
		tension remains relatively constant [81]	onset of wetting.
Micropollutant	Secondary effluent	Low concentration; Pharmaceuticals and personal	DCMD achieved 86 to >99% removal; combined with persulfate, removal
		care products (PPCPs) and pesticides; molecular	was>99% for all micropollutants. Suspect fouling by micropollutant, but
		weight from 150-400 Da; various chemical structure	largely covered by other contaminants in the effluent.
		and charges [82]	

149 * Summary of MD scaling experiments using conventional hydrophobic membrane; LMW: low molecular weight; HLB: Hydrophilic lipophilic Balance. CMC: The

150 Critical Micelle Concentration.

Organic matter typically accounts for a sizable portion of contaminants in wastewater, such as 152 natural organic matter (NOM, i.e. humic substances, protein and polysaccharides), oil and surfactants 153 in seawater, surface water, municipal wastewater, underground water and shale gas produced water 154 (Table 1) [67, 72, 81, 83]. Organic fouling is relatively complex compared to scaling due to a wide 155 156 molecular weight distribution of NOM, temperature triggered degradation [21, 67], hydrophobichydrophobic interaction with hydrophobic MD membranes [47] and interaction with other solutes in 157 the feed [21, 22]. Humic acid is a heterogeneous mixture (i.e., aromatic groups and carboxyl groups) 158 and its hydrophobic part contributes fouling in MD [73, 84]. 159

Protein fouling represented by caseins and bovine serum albumin (BSA) has been mainly found in 160 dairy and municipal wastewater [85]. The intrinsically hydrophobic proline residue in the proteins [47] 161 162 tends to cause their deposition on a hydrophobic surface via hydrophobic-hydrophobic attraction [77]. Similarly, long chain hydrocarbon oil, often found in the shale oil and gas produced water [17], readily 163 fouls MD hydrophobic membranes because of the long-range hydrophobic-hydrophobic attraction [86, 164 165 87]. Surfactants' lyophobic tails show strong affinity to hydrophobic membrane [30, 80, 88, 89], but hydrophilic head-groups incur hydrophilic characteristics [81]. Once fouled by the surfactants, the 166 membranes are prone to wetting by the feed streams though some contradictory results have been 167 reported. For example, Wang et al [30, 90, 91] have shown that surfactant attachment to the membrane 168 surface intrinsically inhibits surfactant-induced wetting rather than facilitates it, and Liquid Entry 169 Pressure (LEP) of membranes is reduced. Literature also reveals that the combination of oil, surfactant 170 and NaCl drastically deteriorates MD performance, but when the feed solution contains oil or 171

172	surfactants or NaCl alone, the effect was not apparent [92]. Micropollutants present wide chemical
173	structures and charge variations (Table 1). Treatment of micropollutant containing wastewater may
174	suffer from fouling. However, due to the low concentration, the fouling by micropollutants were largely
175	covered by other organic contaminants [82].
176	
177	2.3 Biofouling
178	Biofouling of MD membranes has reported compromised the MD performance when treating a natural
179	surface water composed of organics and dead bacteria [93]. It is a very undesirable form of pollution,
180	bacteria cells and micro-colonies attached on membrane surface with growth, the formed biofilm was
181	hard to clean via physical or chemical methods [93]. High operational temperature and relatively high
182	salinity of the feed limit the impacts imposed by the microbial growth [94]. Nonetheless, once formed
183	on the membrane surface, the biofilms will enhance the concentration and temperature polarization,
184	leading to declined permeate flux and quality [21]. No explicit solution has been established on how
185	to avoid initial attachment of bacterial onto the membrane surface [22] [21] [95].
186	
187	3. From hydrophobic to superhydrophobic and omniphobic
188	3.1 Engineered superhydrophobic and omniphobic membranes with improved fouling

189 resistance

190 The failure of hydrophobic membranes in MD due to fouling/scaling has been widely known [43].

191 One of the most important solutions is to mimic a lotus leave by creating superhydrophobic surfaces.

192 Table 2 summarizes the state-of-the-art technologies for fabricating superhydrophobic membranes for

MD and their behavior observed in scaling and fouling tests. Many approaches have been attempted 193 to create superhydrophobic membranes using electrospinning, templating, soft lithography, sol-gel and 194 layer-by-layer deposition [94]. The main strategy to create a superhydrophobic membrane is to 195 physically increase surface roughness combined with chemical modification to endow a low surface 196 energy. The use of CF₄ plasma treatment increased the contact angle of a commercial PVDF 197 microfiltration membrane from 130° to 160°, which was ascribed to the combined effect of a rough 198 porous surface and fluorination [94]. One can also chemically modify the surface to increase the 199 contact angle of a nanofiber surface [95], or nanoparticles coated surfaces [69] [16]. Electrospun [96] 200 201 or electrospray [46] have been utilized to improve the surface roughness and the fluorination achieved by CF₄ [97, 98] or heptadecafluorotetrahydrodecyl trichlorosilane (denoted as 17-FAS) [99, 100]. All 202 superhydrophobic membranes demonstrate improved fouling and/or scaling resistance (Referring to 203 the description in Table 2). 204

Fig. 3a shows the simplified model for the location where the fouling/scaling occurs at the first instance. For a hydrophilic membrane, there exists a water-solid (membrane material) interface, but for a hydrophobic membrane, ideally a water-solid-air forms the interface. Myriads of evidence supports that superhydrophobic membranes are superior to the normal hydrophobic ones in scaling and fouling resistance[46, 48, 94, 101]. This implied that the water-solid-air interfaces for hydrophobic and superhydrophobic membranes are probably different, however frequently neglected.

When a water droplet is placed on a highly hydrophobic surface, two wetting states are usually identified, namely Wenzel and Cassie-Baxter states (Fig. 3b and c) [102]. In a Wenzel state, the liquid follows the structure and wets the textured surface, i.e., the liquid-membrane contact area is maximized. Due to the maximal contact between the liquid and the surface, the Wenzel state corresponds to a

pinned state with significant contact angle hysteresis (CAH) [14]. In Cassie-Baxter state, a composite 215 surface of air and the membrane solid allows the liquid droplet suspend atop the asperities (Fig. 3c). 216 217 Figs. 3d and e schematically show the surface morphology of some typical engineered omniphobic membranes, named as a re-entrant structure, featuring cylindrical or spherical morphology (e.g., 218 219 electrospun nanofibers and silica nanoparticles), forming ideal platforms for creating omniphobicity. Surface fluorination is important in contributing to the omniphobicity. Omniphobic membranes have 220 strong repellency towards a wide range of liquids demonstrating particularly stable performance when 221 treating wastewaters containing low surface tension substances [103]. Moreover, surface 222 223 omniphobicity can also delay or deter the onset of wetting when the feed solution contains low surface tension matters (e.g., ethanol, surfactants and oil molecules stabilized by excess of surfactants) [69, 224 225 104-106].



226

Fig. 3 (a) Distinct hydrodynamic condition between hydrophilic and hydrophobic surface: watersolid interface for hydrophilic membrane and water-solid-air interface for a hydrophobic membrane; (b) the Wenzel state: the textured surface is entirely wetted by the liquid droplet; (c) the Cassie-Baxter state: the liquid droplet is suspended by trapped air; (d) Trapezoid re-entrant architecture; (e) Reentrant structure imparted by spherical particles or cylindrical fibers. The water-air interface is enlarged

- as the liquid penetrates deep down into the surface, which is thermodynamically unfavorable. (adapted
- with permission from Huang et al. [86] (Copyright 2017 American Chemical Society).

235

Membrane*	Materials	Fabrication method/ modification technique	MD performance	Reference
SH	FAS/TiO ₂ /PVDF	Hydrothermal process/Fluorination	Feed: 150 mg/L HA and 3.77 mM $CaCl_2$, Flux	[69]
			decline by 48 % for 20 h, DCMD	
SH	FAS/PVDF	Imprinting/phase separation/Fluorination	Up to 0.4 mM SDS, no wetting for 8 h; Real	[99]
			seawater (42-49 mS/cm), no scaling and	
			wetting for 135 h, DCMD	
SH	PVDF	CF4 plasma	4 wt. % NaCl , ~ 30 % flux enhancement in	[97, 98]
			DCMD	
SH	PVDF	Nano-casting	35 g/L NaCl, 420 mg/L CaCl ₂ , 10 mg/L HA, 10	[101]
			mg/L BSA and 10 mg/L SA; No scaling,	
			fouling and wetting for 150 h in DCMD	
SH	PDMS/Silica /PVDF	Electrospinning/Electrospray	For 3 g/L CaSO ₄ ; 10 mg/L HA showed scaling	[74]
			resistance; for 10 mg/L TDAB showed fouling	

Table 2 Overview of recent advances in superhydrophobic or omniphobic surfaces in MD

			resistance; for 10 mg/L SDS showed rapid	
			fouling and wetting in DCMD	
SH	FAS/Silica/PVDF-HFP	Electrospinning/Electrospray/ Fluorination	For 25 wt. % NaCl; No scaling and wetting; for	[46]
			14 mM CaSO ₄ , scaled and wetted at high water	
			recovery in DCMD	
SH	CNTs/PVDF-HFP	Electrospinning	35 g/L NaCl; High flux performance and salt	[107]
			rejection > 99.99 % for 300 min in DCMD	
SH	FAS/SiO ₂ /PP	In-situ sol-gel process/Fluorination	15 wt. % NaCl and 0~9 wt. % MgCl ₂ ; stable	[108]
			permeate flux and anti-fouling property for 12 h	
			in VMD	
SH	PVDF	Solvent-thermal induced roughening	Up to 0.2 mM SDS; No wetting for pentanol-	[109]
			treated membrane in DCMD	
SH	iPP/PVDF	Coating/Phase separation	100 mg/L sunset yellow textile; No fouling and	[110]
			wetting for 50 h in DCMD	

SH	PTFE/PVA with POSS	Electrospinning, calcinate	3.5 wt. % NaCl; stable permeate flux for 200 h	[111]
			in DCMD	
ОМ	PVDF-HFP	Coating/Fluorination	Up to 0.4 mM SDS; No fouling and wetting for	[16]
	/FAS/Silica/glass fiber		9 h in DCMD	
ОМ	FAS/Silica/PVDF	Coating/Fluorination	For Up to 0.2 mM SDS and Up to 0.01 % v/v oil,	[17, 31, 59]
			no fouling and wetting for 6 h; For 20 mM	
			CaSO ₄ and 6 mM Na ₂ SiO ₃ • 5H ₂ O, 50 mM NaCl	
			and 1 mM NaHCO $_3$, saling resistance to 20 mM	
			CaSO ₄ but readily scaled by silica scaling,	
			DCMD	
ОМ	PVDF nanofiber	Phase separation /coating with Teflon AF 2400	Up to 0.6 mM SDS; No wetting for 7 h in VMD	[95]
		/Silica particles		
ОМ	PVDF nanofiber	Phase separation /heat-press treatment/ Teflon	For Up to 0.4 mM SDS, no fouling and wetting	[45]
		AF 2400 coating	for 9 h; For 20 mM CaSO ₄ , no scaling at water	

			recovery of 10 % in DCMD	
ОМ	PVDF	Sodium/naphthalene-based etching /vapor-phase	Up to 0.4 mM SDS, no fouling and wetting for 9	[100]
		silanization	h in DCMD	
ОМ	PVDF nanofiber	Electrospinning /CF4 plasma	Up to 0.7 mM SDS, no fouling and wetting for	[112]
			10 h in AGMD	
ОМ	PVDF-HFP nanofiber	Electrospinning	Up to 0.3 mM SDS, no fouling and wetting for 8	[113]
			h in DMCD	
ОМ	PVDF-HEP/FAS /ZnO/glass	Chemical bath deposition and coating	Up to 0.3 mM SDS, no fouling and wetting for 8	[18]
	fiber		h in DCMD	
ОМ	PVDF	Coating/Spraying/Silica@polystyrene particle	240 mg/L SDS, 2400 mg/L hexadecane and	[114]
		/Fluorination	1000 mg/L NaCl, no fouling and wetting for	
			1000 min in DCMD	
OM	PVDF nanofiber	Electrospinning/Self-roughening	Up to 0.1 mM SDS, no fouling and wetting for 6	[115]
			h in DCMD	

ОМ	PVD F-HFP	Self-roughening /Fluorination	Up to 0.5 mM SDS; Up to 480 mg/L oil	[116]
			solution , some fouling and wetting in high	
			concentration solutions in DCMD	
OM	PVDF-HFP	Electrospinning/Electrospray	Up to 0.3 mM SDS, Some wetting in high	[96]
			concentration solution in DCMD	
ОМ	PVDF, superomniphobic	Phase inversion, Coating SiNPs/Fluorination	Up to 0.3 mM SDS, no wetting for 11.5 h in	[117]
	membrane (SOM)		DCMD	
ОМ	PVDF	Electrospinning, STIR methods, Fluorination	Up to 0.4 mM SDS, no wetting for 5 h .Up to	[118]
			480 mg/L mineral oil solution, no wetting for 7h	
SH-OM	Polyimide nanofiber	Electrospinning, SiNPs adsorbion, 17-FAS	20 wt. % NaCl solution, stable permeate flux	[119]
		Fluorination	and anti-scaling property for 23 h in DCMD	

* SH means superhydrophobic; OM means omniphobic; SDS: Sodium Dodecyl Sulfate; FAS: Fluorinated Alkyl Silane; PDMS:

238 Polydimethylsiloxane; CNTs: Carbon nanotubes; VMD: Vacuum membrane distillation; iPP: isotactic polypropylene; F-POSS: Fluorinated-decyl

polyhedraloligomeric silsesquioxane; FTCS: fluorododecyltrichlorosilane; FOTS: Trichloro (1*H*,1*H*,2*H*,2*H*-tridecafluoro-*n*-octyl) silane. SOM:

240 superomniphobic membrane; PFTS: 1H,1H,2H,2H-perfluorooctyltrichlorosilane; STIR: solvent-thermal induced roughening; RSHO: robust

241 superhydrophobic-omniphobic.

243 3.2 Typical thermodynamic models for scaling and fouling

Classical nucleation theory is the mainstream mechanism for understanding scaling in MD. Nucleation falls into two categories: homogeneous nucleation, occurring in solutions without any foreign particles, and heterogeneous nucleation in solutions containing foreign substances that provide active sites for nucleation. For membrane scaling, the heterogeneous nucleation has been widely accepted [31, 45, 46, 51, 120-122] and the nucleation energy barrier is expressed as [43, 123]:

249
$$\frac{\Delta G_{heterogeneous}^*}{\Delta G_{homogeneous}^*} = \frac{1}{4} (2 + \cos\theta) (1 - \cos\theta)^2 \left[1 - \varepsilon \frac{(1 + \cos\theta)^2}{(1 - \cos\theta)^2} \right]^3 \tag{1}$$

where θ is membrane-crystal-liquid contact angle and ε is the membrane surface porosity. For a membrane with larger contact angle θ , and lower surface porosity ε , higher free energy is required for heterogeneous nucleation, thus has a lower scaling tendency.

Eq. 1 clearly indicates that a high surface porosity and a high contact angle (CA) are essential in reducing heterogeneous nucleation. The nucleation theory may be effective in explaining scaling formation, but when organic foulants are present, the situation becomes complicated.

256 The xDLVO theory describes the thermodynamic intermolecular interactions between the foulant and membrane [124]: three different non-covalent forces, i.e., (1) Lifshitz-van der Waals (LW) 257 interactions,; (2) electrical double layer (EL) interactions, and (3) Lewis acid-base (AB) or electron-258 acceptor/electron-donor interactions, and hydrophobic-hydrophobic interactions [125]. The interfacial 259 free energy between the membrane and foulant provides an indication of the attraction or repulsion 260 between two materials. xDLVO theory has often been utilized to interpret experimental results [67, 87, 261 89, 126-129] and severe organic fouling has been ascribed to hydrophobic-hydrophobic interactions 262 [67, 75, 77, 79, 87]. The theory implies that the electric interaction between the foulants and the 263

hydrophobic membrane surface is negligible comparing to the LW and AB interactions [87, 130]. This 264 is correct in that at high salinity, the electrical double layer is largely suppressed due to a shortened 265 266 Debye length [21], but LW and AB interactions remain unchanged [67, 131]. However, experimental results showed that a strongly negatively charged superhydrophobic membrane was not fouled by 267 negatively charged oil emulsions in a 1% NaCl solution [132] (Fig. 4) with dyes [133] present in the 268 feed. The fact that the superhydrophobic membrane has a higher surface charge than its hydrophobic 269 counterpart is considered as the main contributor to its superior performance. CF₄ plasma treatment 270 provides thorough fluorination for membrane materials and renders the membrane higher water 271 repellency. Consequently, stronger hydrophobic-hydrophobic interactions would have dictated that 272 CF4 plasma modified PVDF membranes be less fouling resistant. However, both logic scenarios have 273 been contradicted by the experimental observation. This contradiction may point to a gap between the 274 275 theories and the behavior of superhydrophobic membranes.



Fig. 4 (a) SEM images of the top surface of a CF₄ plasma modified PVDF membranes (PVDF-M, 0.22

276

 μ m) showing a contact angle of 163° and a sliding angle of 9.3-20.9°. (b) Zeta potential of the original 278 PVDF-V and PVDF-M membranes showed more negatively charges. (c) and (d) Optical images of 279 280 droplets of the negatively charged (E1) and positively charged (E2) emulsions. Oil droplets were prepared by dispersing hexadecane in 1% NaCl solution containing Sodium dodecyl sulfate (SDS), E1, 281 or Tetradecyl dimethyl benzyl ammonium chloride (TDBAC), E2. (e) Flux and salt rejection profiles 282 for PVDF-M membrane using E1 and E2 as feed solutions. Concentration factor refers to the ratio of 283 remaining liquid volume and the initial liquid volume in feed storage tank. [132] (Copyright 2017) 284 Elsevier B.V.) 285

286

Fig. 5 shows that similar superhydrophobic PVDF membranes with SiNP coating and FAS-17 287 fluorination from different literatures behaved different in scaling resistance during concentrating a 288 289 feed with supersaturated CaSO₄ [134-136]. We found that a superhydrophobic PVDF membrane with porous micropillars (MP-PVDF) showed nearly the same performance as that of the commercial PVDF 290 membranes (C-PVDF) in DCMD (Fig. 6c) [47]. However, the classical nucleation theory projected 291 that the MP-PVDF should have behaved differently from C-PVDF. Furthermore, the classical 292 nucleation model indicated that a superhydrophobic membrane after CF₄ treatment (CF₄-MP-PVDF) 293 would have showed similar scaling behavior to MP-PVDF (Fig. 5c, the map of Gibbs free energy for 294 the formation of CaSO₄). But the results demonstrated that CF₄-MP-PVDF membrane was much more 295 robust in resisting scaling (Fig. 5c, the SEM photos after experiment and Fig. 6c) [47]. These examples 296 illustrated that other factors beyond superhydrophobicity might play a critical role in determining the 297 scaling behavior. 298

For orgnaic fouling, superhydrophobic PVDF membrane coated with TiO₂ nanoparticles (FTCS-

300 TiO₂-PVDF) showed similar flux decline as that of commerical PVDF membranes (Referring to Fig. 5d) [69]. But in a different experiment, a superhydrophobic PVDF membrane with silica nanoparticles 301 coating showed improved MD performance (Referring to Fig. 5e) [137]. Clearly the scaling and 302 fouling behavior of superhydrophobic/omniphobic membranes cannot be understood in the framework 303 of conventional scaling and fouling theories. The correlation between the superhydrophobic or 304 omniphobic surface and anti-fouling property needs new explanation. A careful analysis of the physical 305 starting point of the fouling raises an alarm on the key assumption of utilizing the thermodynamic 306 models for hydrophobic membranes. The classical nucleation and xDLVO theories have found success 307 308 in analyzing the fouling and scaling phenomenon for a water-solid (polymeric materials) interface of hydrophilic membranes [134-136]; but for a hydrophobic membrane, an extra phase in the membrane 309 pores contributes to a triple-phase of water-solid-air interface which might show differences in 310 311 occurrence of fouling and scaling, thus invalidate both theories.





Fig. 5 (a) SEM and DCMD performance of commercial PVDF hydrophobic membrane and modified

membrane FAS-SiNPs-PVDF by Karanikola et.al [31] (Copyright 2018 American Chemical Society). 315 FAS-SiNPs-PVDF was prepared by coating the surface with Silica nanoparticles followed by 316 fluorination using 17-FAS). DCMD test was a supersaturated gypsum solution prepared by mixing 20 317 mM CaCl₂ and 20 mM Na₂SO₄. (b) Similar FAS-SiNPs-PVDF membrane showed insignificant 318 enhancement in CaSO₄ scaling resistance using a feed solution consisted of 14 mM CaCl₂ and 14 mM 319 Na₂SO₄, by Horseman et al.[51] (Copyright 2019 American Chemical Society). (c) Surface 320 morphology before and after DCMD experiment using superhydrophobic micropillared patterned 321 PVDF (MP-PVDF) membrane, CF4 plasma treated MP-PVDF membrane (left) and map of Gibbs free 322 323 energy for the formation of CaSO₄ scale as a function of contact angle (ranges from 100 to 180°) and surface porosity (50 to 100 %) [48]; Feed: 14.7 mM CaSO₄ and a synthetic casein solution (480 mg/L). 324 (Copyright 2019 Elsevier B.V.). (d) Comparing PVDF and superhydrophobic PVDF membranes with 325 326 TiO₂ nanoparticle coating (FTCS-TiO₂-PVDF) for humic acid fouling by Razmjou et al [69] (Copyright 2012 Elsevier B.V.). (e) Superhydrophobic PVDF membrane PVDF-M3 prepared by 327 coating with silica nanoparticles showed improved MD performance by Hou et.al [137] (Copyright 328 329 2020 Elsevier B.V.).

330 4. From thermodynamic to hydrodynamic: non-slip to slip

4.1 Understanding the onset of fouling/scaling upon a water-solid-air interface

Previous experimental results have not been coherently explained by present models. This raises concerns of the missing links between the theory and experimental observation. As in Fig. 3a, a superhydrophobic membrane ideally shows water-solid-air tri-phases possessing a wetting state different from a hydrophilic membrane. A more holistic view on the fouling and scaling is thus required to analyze the onset of the fouling and scaling for a hydrophobic surface. For a water-solid-air interface
(Fig. 3a), we propose two critical rationale statements for occurrence of fouling and scaling on a
hydrophobic surface:

- 339 (1) Probability of adsorption: foulants, organic or inorganic, can incur fouling or scaling when
 340 adsorbed on the solid part of the membrane; When the membrane surface porosity is increased,
 341 the probability for the foulants to attach onto the membrane surface is reduced;
- 342 (2) Time of interaction: a certain time is required for the foulants to attach to the solid membrane
 343 material and form a stable fouling layer. If the water-solid-air interface is not static, fouling is
 344 mitigated because of insufficient interaction time.

Above Statements do not consider any thermodynamic factors and are seemingly independent as 345 Statement 1 is related to probability and Statement 2 kinetics. However, both are intertwined as 346 increasing surface porosity would lead to enlarged air area thus affecting probability of adsorption 347 (Statement 1) and create hydrodynamic slippage to shorten the contact time (Statement 2) between the 348 foulants and membrane. In the following discussion, we will provide detailed experimental evidence 349 and support to unravelling the importance of the hydrodynamic factor to the scaling and fouling for 350 superhydrophobic/omniphobic membranes. Then by analysis of the wetting state (Section 4.2) and the 351 slip length (Section 4.3), we will show that a suspended wetting (Statement 1) corresponds to the 352 slippery surface. 353

A slip surface means that the water flow velocity next to the membrane surface is above zero. This leads to reduced time of interaction (Statement 2). Under this theoretic framework, we need to analyze first the wetting state and slip length of the membrane surface. If the membrane is at a suspended wetting state, thus slip condition, we would expect that fouling and scaling to be mitigated. If the membrane is at a pinned wetting state, thus non-slip, we would expect that the membrane is not fouling/scaling resistant. All classical theories, CNT and xDLVO would apply.

360 4.2 Fouling/scaling behavior on superhydrophobic/omniphobic surfaces

Current methods of using nanofiber or nanoparticle coated superhydrophobic membrane fall into 361 an approach of randomly controlled surface morphology. To explore the validity of the Statement 1 362 and 2, we designed a patterned surface with micropillars by micromolding phase separation [32, 47, 363 48, 101, 138] and further modified with CF₄ plasma to improve the surface hydrophobicity (CF₄-MP-364 PVDF) (Fig. 6 a). Fig. 6b shows an omniphobic pillared membrane coated with silica nanoparticles 365 (SiNP-MP-PVDF) followed by chemical fluorination by FAS with a dual-scale roughness. CF₄-MP-366 PVDF membrane outperformed the virgin pillared PVDF membrane with a stable MD flux using 367 supersaturated 14.7 mM CaSO₄ feed (Fig. 6c). This result was contradictory to the classical nucleation 368 theory which dictates that the Gibbs free energy of nucleation of both membranes would have been 369 similar as well as scaling propensity (Fig. 5c). Fig. 6d confirms that omniphobic SiNPs-MP-PVDF 370 membrane is also scaling resistant and Fig. 6e demonstrates that SiNPs-MP-PVDF is resistant to 371 372 fouling by Casein, a typical protein found in wastewater [139, 140]. These examples are based on the same base membranes. The CF4-MP-PVDF and SiNP-MP-PVDF membranes showing scaling and 373 fouling resistance is probably a result of the limited interaction time to allow the foulants to attach due 374 to the extra slip effect provided by both superhydrophobic and omniphobic surfaces [47, 48]. 375



376

Fig. 6 (a) Schematic for fabrication of micro pillared PVDF membrane (MP-PVDF) and physics 377 meanings of parameters used in the calculation of the wetting state factor developed by Grewal et 378 al.[141]: spacing factor S_f , aspect ratio a_r and interior angle φ ; (b) Preparation of micro pillared PVDF 379 membrane with dual-scale roughness (SiNPs-MP-PVDF) by coating silica nanoparticles (~640 nm). 380 (c) Superhydrophobic CF4 plasma treated MP-PVDF showed improved scaling performance 381 comparing to MP-PVDF and commercial PVDF. (d) Omniphobic SiNPs-MP-PVDF membranes 382 showed improved scaling resistance comparing to both MP-PVDF and commercial PVDF membranes. 383 For (c) and (d), the feed was: 14.7 mM CaSO₄ solution; (e) Omniphobic SiNPs-MP-PVDF membranes 384 showed antifouling performance comparing to both MP-PVDF and commercial PVDF membranes. 385 Feed: 14.7 mM CaSO₄ and a synthetic casein solution (480 mg/L). Normalized water vapor flux (J/J₀) 386 as a function of concentration factor (CF) (ratio of the feed salt concentration in process to the initial 387 concentration) [47] (Copyright 2020 Elsevier B.V.). 388

390 To further support the slippage theory, the wetting state of the membrane surface is evaluated. A

model developed by Grewal et al [141] is adopted here.

392 A wetting state factor ζ is given by:

393
$$\zeta = \frac{(\sqrt{2}S_f - 1)}{2a_r} tan(\theta_a - \varphi)$$
(2)

where S_f represents the spacing factor (ratio of pitch to diameter, Fig. 6a) and a_r the aspect ratio given by height and diameter of pillar on the membrane surface. θ_a is advancing angle of membrane surface and φ is the interior angle as a geometrical factor (e.g., = 90° for cylindrical pillars). A Cassie-Baxter (suspended) state to transition state occurs at $\xi < 0.5$, whereas a transition state to Wenzel (pinned) state occurs at $0.75 > \xi > 0.5$; a Wenzel (pinned) state is observed at $\xi > 0.75$.

For a pillared surface with a dual-scale roughness, Wu et al. [142, 143] proposed a different model to estimate the wetting states using the apparent contact angle, the primary roughness and the secondary roughness (Fig. 6b). Eq. 3-4 describe the criteria for determining whether the surface is at a Cassie-Baxter (suspended) (Eq. 3) or Wenzel (pinned) (Eq. 4) wetting state. [142, 143]

403
$$\cos\theta < f_1 f_2 \cos\theta_0 + f_1 f_2 - 1$$
 (3)

404
$$\cos \theta > f_1 r_2 \cos \theta_0 + f_1 - 1$$
 (4)

Where f_1 and f_2 : area fractions of microstructure and nanostructure, representing the solid fraction of a surface containing only one type of asperities. r_2 : roughness factor of nanostructure, defined as ratio between the total surface area and the projected surface area. Physics meaning of f and r is illustrated in Fig. 6b.

Fig. 7 shows the modelled results for both pillared membranes and SiNP coated pillared membranes. Although both MP-PVDF and CF4-MP-PVDF incur similar Gibbs free energy of nucleation (Fig. 5), they fall into very different wetting states: a pinned wetting state for MP-PVDF and a suspended wetting state for CF4-MP-PVDF. For the SiNP-MP-PVDF membrane, a suspended state is predicted accordingly (Fig. 7b). Experimental verification of the wetting states is very important, but the progress in visualization of water-air-solid interface is limited. Very recently, a confocal microscopy was utilized to observe the wetting state of Gas-Entrapping Membrane (GEMs) surface [144]. If this technology is modified to suit the membrane morphology, we believe more solid fundamental support or proof for wetting state confirmation at static or process could be discovered.





Fig. 7 (a) Map of the wetting state for MP-PVDF and CF₄-MP-PVDF membranes using the model by
Grewal et al [48]; (Copyright 2019 Elsevier B.V.). (b) determination of the wetting state of SiNP-MPPVDF factor using the model by Wu et al. [47] for dual-scale roughness. (Copyright 2020 Elsevier
B.V.).

423 4.3 Quantification of slip by Navier's model

For a non-slip surface, a thin layer of water adjacent to the surface remains static, or of zero flow velocity, although the bulk moves at a certain flow rate. For a slip surface (Fig. 8a), the tangential velocity of the fluid at the solid-liquid interface is proportional to the velocity gradient of the fluid perpendicular to the solid-liquid interface [145]. A physical meaning of *b* is the distance where the tangential velocity of the fluid is extrapolated to 0 (within the solid part as shown in Fig. 8a). Therefore, b = 0 means non-slip, and b < 0 slip.

Although limited by analytical instruments at the times of Navier and Maxwell [146, 147], a
mathematic model of slip was derived to quantify the slip length *b* [146] as,

432
$$v_w = b \frac{\partial v}{\partial z}\Big|_{z=0}$$
 (5)

433 Where v_w is the flow velocity at the solid-liquid interface.

A rheometry is used to determine the slip length (Fig. 8b and c), in which the torque and the fluid viscosity are dependent on the adjacent surface (Fig. 8, top surface of the membrane in white). Using a known sample liquid, the difference in torque of a slip surface (adhered to the flat horizontal plate) and a stainless steel non-slip plate can quantify the slip length. Fig. 8b shows two parallel plate rotating at an angular velocity *w*; the relationship between the torque *M* and the slip length *b* is expressed as[48]:

$$b = \frac{1}{2M} \pi \mu \omega R^4 - h \tag{6}$$

Literature reports an maximal error of 3.5 % when experiments are properly implemented [148], however, the reproducibility of this indirect measurement is in dispute [148, 149]. Nonetheless, it is a simple and straightforward tool to scientifically explore the wetting, slip and fouling/scaling behavior in MD. Fig. 8c shows our experimental results for our various hydrophobic membranes and only superhydrophobic CF4-MP-PVDF membrane gives a positive slip length of a few tens of microns, corresponding to a suspended wetting state. Commercial C-PVDF and MP-PVDF membranes yielded negative slip lengths that correspond to a pinned wetting state [150].





Fig. 8 (a) Schematic of the non-slip and slip surfaces. A Newtonian fluid flows towards right. The arrows are proportional to the velocity. Non-slip means zero velocity v_w , slip means $v_w > 0$. The extent of slip is characterized by the slip length *b*. (b) Schematic of a rheometry measurement of slip length. The geometric parameters, shear rate (0-150 s⁻¹), and the diameter of the plate was 60 mm. peripheral components are detailed referring to literature [150]. (c) Experimental results for slip length of water as the probing liquid [48] (Copyright 2019 Elsevier B.V.)

455 4.4 Slip/wetting correlation to fouling/scaling

A strong connection seems to exit between the wetting state, slip length and fouling and scaling resistance. In the Wenzel state, i.e. pinned wetting, a static water-membrane materials interface is expected for hydrophobic or superhydrophobic membranes. In the Cassie-Baxter state, a suspended wetting occurs, corresponding to a slip surface. Slip occurs on a hydrophobic surface with suspended wetting or at a Cassie-Baxter state [150-152], but not at a pinned wetting state even though the surface 461 shows a rather high contact angle.

A pinned wetting state of a hydrophobic membrane is close to a hydrophilic membrane with a 462 463 water-solid interface as water penetrates into the surface pores and actual air fraction disappears from the surface. Thus, foulants or inorganic scalants in the feed can intimately contact the membrane 464 materials, and the thermodynamic xDLVO and nucleation theory thus prevail. This explains that 465 micropillared MP-PVDF membrane show similar scaling and fouling pattern to the commercial PVDF 466 membrane as both are in a pinned state. However, for a suspended wetting state, the water-solid-air 467 interface attribute large air fraction to reduce direct contact of foulants to membrane materials 468 469 (Statement 1); moreover, it is non-static as slippage does not allow prolonged time for interaction thus mitigating formation of fouling and scaling (Statement 2). 470

471 4.5 Experimental observation of wetting state transformation

Retrospectively, observation of the suspended wetting and slip has been a coincident. Very 472 recently, we demonstrated that even for a superhydrophobic membrane with suspended wetting, a 473 slight overpressure in feed altered the suspended wetting to a more pinned wetting state, thus forfeited 474 475 the membrane scaling resistance. Fig. 9 shows that at a steady feed flow, an over-pressure forces the water-gas interface to sag into the pillars, thus creating a non-slip condition for both MP-PVDF and 476 CF₄-MP-PVDF membranes, leading to severe scaling as demonstrated by a full coverage of both 477 membranes with CaSO₄ crystals [153]. However, when a pulse flow is applied, the suspended wetting 478 in CF₄-MP-PVDF membrane is enabled leading to a lift-up of the water-gas interface and consequent 479 scale mitigation effects. The SEM images showed that even after experiment termination, the 480 membrane surface appeared clean and nearly intact. Because the pulse creates perpendicular 481

fluctuation at the air-liquid interface, the effect is an actual dynamic non-static situation similar to a slip surface. The results demonstrate that a combination of superhydrophobic slip surface plus a pulse flow can lead to scaling resistance. Unfortunately, most of the researches on superhydrophobic membranes have failed to analyze the wetting state and understand the feed overpressure effects on the wetting state; it is therefore understandable that the very important slippage effect on fouling and scaling has been hidden for decades.



Fig. 9 Schematic of scaling behavior for CF₄-MP-PVDF at steady and pulse flow. Observation of the
MP-PVDF and CF₄-MP-PVDF surface with steady flow and pulse flow during MD [153]. Reproduced
with permission from Liu et al. [153] (Copyright 2020 Elsevier B.V.).

492

488



Previous accounts present a holistic, the first-principle-based view on the slippage effect to fouling
and scaling. However, the discussion focused on solely a model membrane with precisely designed
pillar morphology (Fig. 6); in this respect, the universality of this theory is subjected to scrutiny. It is

fortunate that the slip concept has been widely recognized by different research groups as a 497 fundamental basis for the fouling and scaling resistance of their tailor-made superhydrophobic or 498 omniphobic membrane in MD. Fig. 10 and Fig. 11 shows the recent tailor-made nanofiber-based 499 superhydrophobic [46, 74, 111] and omniphobic [45, 116, 118] membranes with superior fouling and 500 scaling resistance. The preparation of these membranes followed a similar concept: firstly adding 501 nanoparticles to the nanofibers or creating surface roughness by a hydrothermal technique[118, 119] 502 or growing metal oxides [116]; then chemically modify the surface via fluorination. Fig. 11 shows 503 slightly more complicated procedure to prepare hierarchical nanostructures membrane with 504 505 omniphobicity [46, 117]. Either incorporation of the silica nanoparticles to the nanofibers [46] or attached to the positively charged surface [117], the final membrane demonstrated fouling resistance 506 to SDS or scaling resistance, which was mainly attributed to the slippage surface. Because the irregular 507 508 surface pattern, the evaluation of the wetting state was difficult. Measurement of the slip length has not yet been reported. However, from the experimental results of the sliding angles [45, 46, 74, 117], 509 we could give a qualitative judgement that the membrane water interface indeed are slip. Evidence 510 511 further validates that the slippage theory is not limited to the specific surface. We expected more experimental proof to be discovered in the near future as more researchers are exposed to the slippage 512 theory. 513

514

515



Fig. 10 Superhydrophobic/omniphobic nanofibrous membranes based on nanofiber substrate. (A): 517 518 Robust superhydrophobic-omniphobic (RSHO) polyimide nanofiberous membrane prepared by coating polyimide nanofibers with Dopamine (DA) and polyethylenimine (PEI) plus negatively 519 charged silica nanoparticles and chemically modified by 17-FAS and PDMS precursor followed by 520 welding at 120 °C [119] (Copyright 2020 Elsevier B.V.). (B): Electrospun PVDF fibrous omniphobic 521 slippery membrane (OMNI-SLIP) by heat pressing the pristine PVDF membrane at a high temperature, 522 then coated by fluorinating chemicals Teflon AF 2400/HT-70 to reduce the surface energy [45] 523 (Copyright 2020 Elsevier B.V.). (C): Dual-layered superhydrophobic membrane fabricated by 524 525 electrospraying fumed silica (PDMS-3) on top of electrospun PVDF nanofiber substrate [74] (Copyright 2020 Elsevier B.V.). (D): Superhydrophobic POSS-2 membrane fabricated by electrospun 526 PTFE/PVA aqueous solution with various vinyl-POSS and then calcinated to PTFE/POSS nanofibrous 527







Fig. 11 SEM images and DCMD performance of hierarchical nanostructures membranes. (A):
Comparison of negatively charged macro-corrugated membrane (CM) prepared by molding phase
inversion method and SiNPs coated/fluorinated SiNPs-patterned superomniphobic membrane (SOM).
The SCM had no SiNPs deposition but fluorination only. Right panel shows superior fouling resistance

541	to SDS comparing to other membranes [117] (Copyright 2020 Elsevier B.V.). (B): Comparison of
542	nanofiber membrane with ES^2 membrane by depositing SiNPs/PVDF-HFP onto the PVDF-HFP
543	fibrous substrate via the electro-co-spinning/spraying (ES ²) technique and chemical welding using
544	DMF vapor, followed by 17-FAS fluorination. DCMD performance shows much better antiscaling
545	performance of ES^2 membrane than commercial and nanofiber membranes (C) and (C'): Feed water
546	was 25 wt.% NaCl solution. (D) and (D') Feed solution was composed of 14 mM L^{-1} CaCl ₂ and 14
547	mM L ⁻¹ of Na ₂ SO ₄ [46] (Copyright 2019 American Chemical Society).

549 5. Means to sustaining the fouling/scaling resistance

Experimental evidence has demonstrated that a slip condition holds the key for a hydrophobic membrane demonstrating antifouling/antiscaling characters. A slip surface is characterized by suspended wetting and positive slip length (Rationale 2). To achieve slippage, a high surface porosity with a low surface energy is a prerequisite. Under slip conditions, the classical CNT and xDLVO theories are not valid, but at a non-slip condition, represented as a pinned wetting, both CNT and xDLVO theories are applicable. The slip model does not cover the stability issue. In the following, we will outline means to create slip conditions to maintain MD process performance stability.

Literature reported stable MD performance for superhydrophobic or omniphobic membranes is often limited to a couple of days. This short working time is far from sufficient to demonstrating stable antifouling/antiscaling performance of these membranes. The over pressure experiments seem to infer that the loss of air trapped in the pores leads to the transition from the suspended into pinned wetting state. If this is true, then maintaining the suspended wetting can lead to membranes with sustained antifouling/scaling properties. Physically implementing a hydrodynamic control at the membrane interface has been practiced, such as introduction of air-bubble or turbulence [154], increase the feed flow velocity with flow variation [155] and ultrasonication.

Air bubbles can be created by air recharging or injection [154, 156-160] and electrolysis gas 565 production via embedded electrodes [161, 162] [163]. Turbulence can be generated via implementing 566 specially designed spacers [164-167]. Microbubble aeration reinforces the surface shear to reduce 567 polarization, but also alleviates scale precipitation due to aggregation of counter-ions at the gas-liquid 568 interface of microbubbles [168]. Two 3D printed spacers based on triply periodic minimal surfaces 569 570 (TPMS) architectures achieved 50 % higher flux and reduced crystal deposition than commercial spacers [164]. Ultrasonic irradiation can create cavitation, acoustic streaming [169], and hydraulic 571 pressure impulses; the hydrodynamic effect can reduce temperature polarization and mitigate the 572 573 fouling and scaling as well [76, 170-173]. However, external hydrodynamic turbulence is not fully controlled. For example, the created local over- or under-pressure varies at rather short time scale. The 574 effect of such hydrodynamic turbulence would be lost in a long timescale. This is one of the key factors 575 576 that cause normal hydrophobic membranes to fail within a shorter time than superhydrophobic or omniphobic membranes. 577

Many aspects have still to be systematically analyzed to reach a holistic solution to the fouling and scaling issue in MD. Besides membranes, other engineering approaches are also important. Pretreatment of the feed is necessary, such as flocculation [174], water softening [175], micro- or nanofiltration [176, 177] and pH control [22] to remove both suspended and dissolved fouling matters. pH adjustment is important and economic to avoid alkaline scale [33], silica scale [66] and humic acid fouling [68]. Dosing anti-scalants and magnetic treatment to delay the onset of nucleation [13] has also been adopted. However, the chemical consumption associated cost is of major concern; additional
fouling due to addition of chemicals also takes place [13, 26].

For an industrial scale module, the circulation pump induces a certain over-pressure to cause 586 sagging at the water-air interface and eventually a pinned wetting of the membrane. This generates a 587 nonslip condition, followed by fouling. In vacuum membrane distillation (VMD), under-pressure in 588 the permeate side incurs a "over-pressure" at the feed side, thus press the water-air interface into the 589 membrane pore and original slippage effect of a superhydrophobic membrane is lost. This indicates 590 that a fouling and scaling resistant superhydrophobic membrane would eventually fail in a VMD 591 592 operation. The effects of the membrane chemistry and morphology to attribute surface slip have yet to be integrated with the state-of-the-art process design. We believe that a proper membrane design plus 593 careful controlling operation process parameters, spacers cleaning protocols would significantly 594 595 improve MD process stability.

Engineering solutions have been reported by using appropriate fluid mechanical factors and 596 hydrophobic polypropylene hollow fiber membranes with a highly porous light plasma polymerized 597 598 fluorosiloxane coating. This membrane has a surface contact angle of 140°, thus not superhydrophobic. Seawater was concentrated to around 18-19% salt with scaling salt precipitates floating all around with 599 no flux reduction over 5 days of continuous operation at much higher values than SI. This demonstrated 600 that the "Slip" effect can be achieved without superhydrophobic membrane. The geometrical design 601 of the hollow fiber module and cross flow of hot brine created numerous spontaneous secondary flows 602 preventing accumulation of scaling salt crystals/nuclei on the membrane surface by continuously 603 scrubbing the surface of the hollow fibers [178, 179]. 604

605

42

A complete solution for treating the highly saline waste streams has yet to come from many aspects, 606 covering membrane synthesis, module design and process optimization. By proposing the slippage 607 608 effect and the consequent engineering implications, this perspective provides a higher dimension for researchers and engineers to bring about the success of MD in practice. The first priority to sustain the 609 MD performance is to maintain the slippage effect of the membranes. Design superhydrophobic or 610 omniphobic membranes would delay the fouling/scaling of MD membranes and will remain an 611 important direction from the materials development side. Systematic research to control or simulate 612 the slippage effect is very important as well. If process parameters could create equivalent slip water-613 614 air interface, commercial hydrophobic membranes could be utilized and cost for MD membranes will be significantly reduced, which will enable the commercialization of MD technologies. Module 615 development to create mechanical flow turbulence adjacent to a membrane surface could prevent or 616 617 reduce the nucleation of scalants and deposition of organic foulants. Certain pre-treatment to reduce a significant amount of sparingly soluble ions and organics is certainly desirable for maintain stable MD 618 Most importantly, engineering solutions beyond development of disruptive operations. 619 antiscaling/antifouling membranes would allow usage of commercial hydrophobic membranes at 620 lower cost. 621

622 6. Conclusions

The development and performance of superhydrophobic membranes for treatment of highly saline water streams is summarized in terms of fouling and scaling resistance. A water-solid-air triple phase interface has been introduced to replace the conventional water-solid interface for a hydrophobic membrane to be fouling/scaling resistant. A surface with high porosity is a pre-requisite as the

probability of direct contact between foulants and membrane materials is largely reduced. We further 627 propose suspended wetting and correlated slippage as an important hydrodynamic factor, minimizing 628 629 contact time for interaction of the foulants and the membrane. By defining slip length and evaluating the wetting states, the underlining mechanisms are elucidated and uncovered to explain the fouling and 630 scaling resistance of superhydrophobic and omniphobic membranes. The present theory encompasses 631 the xDLVO and classical nucleation models as a special case of pinned wetting, thus conforms to the 632 thermodynamic understanding of fouling and scaling. In practice, sustaining a suspended wetting with 633 a slip surface is critical to achieve a stable MD process for treating complicated waste streams, which 634 may help guide the design of suitable membranes, modules and processes for large-scale applications 635

636 of MD.

637 Acknowledgements

The research was partially supported by National Natural Science Foundation of China (No.
21978315, 52011530031), Royal Society Newton Advanced Fellowship (No. NA170113) and CAS
International Collaboration (No. GJHZ2080). We also thank the frame work research consortium for
partial financial support (RFBR No. 18-58-80031, NSFC No. 51861145313, DST IPN/7864, NRT
No.116020, CNPq/BRICS-STI-2-442229/2017-8).

643 **References**

- 6441.Goh, P.S., et al., Modification of membrane hydrophobicity in membrane contactors for environmental645remediation. Sep. Purif. Technol., 2019. 227: p. 115721.
- 2. Tao, T. and K. Xin, *Public health: A sustainable plan for China's drinking water.* Nature, 2014. **511**(7511): p. 527.
- Bavenport, D.M., et al., *High-Pressure Reverse Osmosis for Energy-Efficient Hypersaline Brine Desalination: Current Status, Design Considerations, and Research Needs*. Environ. Sci. Technol. Letters, 2018. 5(8): p. 467-475.
- 649 4. Kamali, M., et al., *Sustainability considerations in membrane-based technologies for industrial effluents* 650 *treatment.* Chem. Eng. J., 2019. **368**: p. 474-494.
- 6515.Ciofalo, M., et al., Turbulent heat transfer in spacer-filled channels: Experimental and computational study and652selection of turbulence models. International Journal of Thermal Sciences, 2019. 145: p. 106040.
- 6. Strathmann, H., *Electrodialysis, a mature technology with a multitude of new applications.* Desalination, 2010.
 264(3): p. 268-288.

- Sun, B., et al., *Performance evaluation on regeneration of high-salt solutions used in air conditioning systems by electrodialysis.* J. Membr. Sci., 2019. 582: p. 224-235.
- Elsayed, M.L., et al., *Transient and thermo-economic analysis of MED-MVC desalination system*. Energy, 2019. **167**: p. 283-296.
- 6599.Onishi, V.C., et al., Shale gas flowback water desalination: Single vs multiple-effect evaporation with vapor660recompression cycle and thermal integration. Desalination, 2017. 404: p. 230-248.
- Tong, T. and M. Elimelech, *The Global Rise of Zero Liquid Discharge for Wastewater Management: Drivers, Technologies, and Future Directions.* Environ. Sci. Technol., 2016. **50**(13): p. 6846-55.
- Bonnivard, M., A.L. Dalibard, and D. Gerard-Varet, *Computation of the effective slip of rough hydrophobic surfaces via homogenization.* Mathematical Models & Methods in Applied Sciences, 2014. 24(11): p. 2259-2285.
- Yang, X., A.G. Fane, and R. Wang, *Membrane distillation: Now and future*, in *Desalination : Water from water*,
 Wiley, London, Eng., pp.399-427, doi: 10.1002/9781119407874.ch8., J.e. Kucera, Editor. 2014.
- 13. Deshmukh, A., et al., *Membrane distillation at the water-energy nexus: limits, opportunities, and challenges.*Energy Environ. Sci., 2018. **11**(5): p. 1177-1196.
- Kota, A.K., et al., *Hierarchically structured superoleophobic surfaces with ultralow contact angle hysteresis.* Adv
 Mater, 2012. 24(43): p. 5838-43.
- Li, X.-M., et al., *Conversion of a Metastable Superhydrophobic Surface to an Ultraphobic Surface*. Langmuir, 2008.
 24(15): p. 8008-8012.
- Lin, S., et al., Omniphobic Membrane for Robust Membrane Distillation. Environ. Sci. Technol. Letters, 2014. 1(11):
 p. 443-447.
- Boo, C., J. Lee, and M. Elimelech, *Omniphobic polyvinylidene fluoride (PVDF) membrane for desalination of shale gas produced water by membrane distillation*. Environ. Sci. Technol., 2016. **50**(22): p. 12275-12282.
- 677 18. Chen, L.-H., et al., *Omniphobic membranes for direct contact membrane distillation: Effective deposition of zinc*678 *oxide nanoparticles.* Desalination, 2018. **428**: p. 255-263.
- 67919.Christie, K.S.S., T. Horseman, and S. Lin, Energy efficiency of membrane distillation: Simplified analysis, heat680recovery, and the use of waste-heat. Environment International, 2020. 138: p. 105588.
- Choi, Y., et al., *Membrane distillation crystallization for brine mining and zero liquid discharge: opportunities, challenges, and recent progress.* Environ. Sci.: Water Res. Technol., 2019. 5(7): p. 1202-1221.
- Tijing, L.D., et al., *Fouling and its control in membrane distillation-A review*. J. Membr. Sci., 2015. **475**: p. 215-244.
- Warsinger, D.M., et al., *Scaling and fouling in membrane distillation for desalination applications: a review.*Desalination, 2015. **356**: p. 294-313.
- Benecke, J., J. Rozova, and M. Ernst, *Anti-scale effects of select organic macromolecules on gypsum bulk and surface crystallization during reverse osmosis desalination*. Separation and Purification Technology, 2018. 198: p.
 688
 68-78.
- Shih, W.-Y., et al., *Morphometric characterization of calcium sulfate dihydrate (gypsum) scale on reverse osmosis membranes.* J. Membr. Sci., 2005. 252(1): p. 253-263.
- 691 25. Gryta, M., Fouling in direct contact membrane distillation process. J. Membr. Sci., 2008. **325**(1): p. 383-394.
- Tong, T.Z., et al., *Mineral scaling in membrane desalination: Mechanisms, mitigation strategies, and feasibility of*scaling-resistant membranes. J. Membr. Sci., 2019. **579**: p. 52-69.
- 694 27. Pouget, E.M., et al., *The initial stages of template-controlled CaCO3 formation revealed by cryo-TEM*. Science,
 695 2009. 323(5920): p. 1455-8.
- 696 28. Christie, K.S.S., et al., *Distinct Behaviors between Gypsum and Silica Scaling in Membrane Distillation*. Environ.
 697 Sci. Technol., 2020. 54(1): p. 568-576.
- 698 29. Chen, Y., et al., Probing pore wetting in membrane distillation using impedance: early detection and mechanism

- 699 of surfactant-induced wetting. Environ. Sci. Technol. Letters, 2017. 4(11): p. 505-510.
- Wang, Z.X., et al., *Mechanism of pore wetting in membrane distillation with alcohol vs. surfactant*. J. Membr. Sci.,
 2018. 559: p. 183-195.
- 70231.Karanikola, V., et al., Engineered Slippery Surface to Mitigate Gypsum Scaling in Membrane Distillation for703Treatment of Hypersaline Industrial Wastewaters. Environ. Sci. Technol., 2018. 52(24): p. 14362-14370.
- 70432.Xiao, Z., et al., Slippery for scaling resistance in membrane distillation: A novel porous micropillared705superhydrophobic surface. Water Research, 2019. 155: p. 152-161.
- 33. Gryta, M., Alkaline scaling in the membrane distillation process. Desalination, 2008. 228(1-3): p. 128-134.
- Antony, A., et al., *Scale formation and control in high pressure membrane water treatment systems: A review.* J.
 Membr. Sci., 2011. **383**(1-2): p. 1-16.
- 35. Drioli, E., et al., *Integrated system for recovery of CaCO3, NaCl and MgSO4· 7H2O from nanofiltration retentate.*J. Membr. Sci., 2004. 239(1): p. 27-38.
- 71136.Junghyun Kim, J.K., Seungkwan Hong, Recovery of water and minerals from shale gas produced water by712membrane distillation crystallization. Water Research, 2018. 129: p. 447-459.
- Waly, T., et al., *Will calcium carbonate really scale in seawater reverse osmosis?* Desal. Water Treatment, 2009.
 5(1-3): p. 146-152.
- Al-Anezi, K. and N. Hilal, *Scale formation in desalination plants: effect of carbon dioxide solubility*. Desalination,
 2007. 204(1-3): p. 385-402.
- 39. Sheikholeslami, R., Scaling potential index (SPI) for CaCO3 based on Gibbs free energies. AIChE J., 2005. 51(6): p.
 1782-1789.
- 40. Beck, R. and J.-P. Andreassen, *The onset of spherulitic growth in crystallization of calcium carbonate*. Journal of
 Crystal Growth, 2010. **312**(15): p. 2226-2238.
- He, F., K.K. Sirkar, and J. Gilron, Studies on scaling of membranes in desalination by direct contact membrane
 distillation: CaCO3 and mixed CaCO3/CaSO4 systems. Chem. Eng. J., 2009. 64(8): p. 1844-1859.
- Naidu, G., et al., *A review on fouling of membrane distillation*. Desalination and Water Treatment, 2016. 57(22):
 p. 10052-10076.
- 43. Curcio, E., et al., *Membrane distillation operated at high seawater concentration factors: Role of the membrane on CaCO3 scaling in presence of humic acid.* J. Membr. Sci., 2010. **346**(2): p. 263-269.
- 44. Shih, W.Y., et al., Morphometric characterization of calcium sulfate dihydrate (gypsum) scale on reverse osmosis
 membranes. J. Membr. Sci., 2005. 252(1-2): p. 253-263.
- 45. Chen, Y., K.J. Lu, and T.-S. Chung, *An omniphobic slippery membrane with simultaneous anti-wetting and anti-*730 scaling properties for robust membrane distillation. J. Membr. Sci., 2020. 595: p. 117572.
- 46. Su, C., et al., *Robust Superhydrophobic Membrane for Membrane Distillation with Excellent Scaling Resistance.*Finitron. Sci. Technol., 2019. 53(20): p. 11801-11809.
- Xiao, Z., et al., Unprecedented scaling/fouling resistance of omniphobic polyvinylidene fluoride membrane with
 silica nanoparticle coated micropillars in direct contact membrane distillation. J. Membr. Sci., 2020. 599: p.
 117819.
- 48. Xiao, Z., et al., *Scaling mitigation in membrane distillation: From superhydrophobic to slippery.* Desalination, 2019.
 466: p. 36-43.
- Zou, T., et al., Fouling behavior and scaling mitigation strategy of CaSO4 in submerged vacuum membrane
 distillation. Desalination, 2018. 425: p. 86-93.
- 74050.Lee, J.G., et al., An advanced online monitoring approach to study the scaling behavior in direct contact741membrane distillation. J. Membr. Sci., 2018. 546: p. 50-60.
- 742 51. Horseman, T., et al., Highly Effective-Scaling Mitigation in Membrane Distillation Using a Superhydrophobic

- 743 *Membrane with Gas Purging.* Environ. Sci. Technol. Letters, 2019. **6**(7): p. 423-429.
- 52. Gryta, M., *Calcium sulphate scaling in membrane distillation process*. Chemical Papers, 2009. **63**(2): p. 146-151.
- For the second second
- 54. Long, D.N.T.C., A scaling mitigation approach during direct contact membrane distillation. Sep. Purif. Technol.,
 2011. 80(2): p. 315-322.
- 55. Dan, Q., et al., Study on concentrating primary reverse osmosis retentate by direct contact membrane distillation.
 Desalination, 2009. 247(1-3): p. 540-550.
- Martinetti, C.R., A.E. Childress, and T.Y. Cath, *High recovery of concentrated RO brines using forward osmosis and membrane distillation.* J. Membr. Sci., 2009. **331**(1-2): p. 31-39.
- 75357.Mike, M., Overview of Global Inland Desalination Concentrate Management: Solutions, Challenges, and754Technologies. Ida Journal of Desalination & Water Reuse, 2010. 2(3): p. 48-52.
- 58. Du, X.W., et al., *Membrane fouling and reusability in membrane distillation of shale oil and gas produced water: Effects of membrane surface wettability.* J. Membr. Sci., 2018. 567: p. 199-208.
- Yin, Y.M., et al., *Elucidating mechanisms of silica scaling in membrane distillation: effects of membrane surface wettability.* Environ. Sci.: Water Res. Technol., 2019. 5(11): p. 2004-2014.
- Neofotistou, E. and K.D. Demadis, Use of antiscalants for mitigation of silica (SiO2) fouling and deposition:
 fundamentals and applications in desalination systems. Desalination, 2004. 167: p. 257-272.
- 61. Chen, G., et al., *Membrane distillation of a silver leaching solution: Role of the coexisting aluminum ions on silica scaling.* J. Membr. Sci., 2020. 603: p. 118021.
- Qin, W., et al., Comparison of colloidal silica involved fouling behavior in three membrane distillation
 configurations using PTFE membrane. Water Research, 2018. 130: p. 343-352.
- Qin, W., et al., Synergistic effect of combined colloidal and organic fouling in membrane distillation:
 Measurements and mechanisms. Environ. Sci.: Water Res. Technol., 2017. 3(1): p. 119-127.
- 767 64. Rao, U., et al., *Mineral Scale Prevention on Electrically Conducting Membrane Distillation Membranes Using*768 *Induced Electrophoretic Mixing.* Environ. Sci. Technol., 2020. 54(6): p. 3678-3690.
- 65. Gilron, J., Y. Ladizansky, and E. Korin, *Silica Fouling in Direct Contact Membrane Distillation*. Industrial &
 770 Engineering Chemistry Research, 2013. 52(31): p. 10521-10529.
- Bush, J.A., et al., *Prevention and management of silica scaling in membrane distillation using pH adjustment*. J.
 Membr. Sci., 2018. 554: p. 366-377.
- 67. Boo, C., S. Hong, and M. Elimelech, *Relating Organic Fouling in Membrane Distillation to Intermolecular Adhesion*774 *Forces and Interfacial Surface Energies.* Environ. Sci. Technol., 2018. **52**(24): p. 14198-14207.
- 5. Srisurichan, S., R. Jiraratananon, and A.G. Fane, *Humic acid fouling in the membrane distillation process*.
 Desalination, 2005. **174**(1): p. 63-72.
- Razmjou, A., et al., Superhydrophobic modification of TiO2 nanocomposite PVDF membranes for applications in
 membrane distillation. J. Membr. Sci., 2012. 415: p. 850-863.
- 779 70. Khayet, M. and J.I. Mengual, *Effect of salt concentration during the treatment of humic acid solutions by* 780 *membrane distillation.* Desalination, 2004. **168**: p. 373-381.
- 781 71. Khayet, M., A. Velazquez, and J.I. Mengual, *Direct contact membrane distillation of humic acid solutions*. J. Membr.
 782 Sci., 2004. 240(1-2): p. 123-128.
- 783 72. Naidu, G., et al., Organic fouling behavior in direct contact membrane distillation. Desalination, 2014. 347: p.
 784 230-239.
- 785 73. Naidu, G., S. Jeong, and S. Vigneswaran, *Interaction of humic substances on fouling in membrane distillation for* 786 *seawater desalination.* Chem. Eng. J., 2015. 262: p. 946-957.

- 787 74. Liao, Y., et al., Development of robust and superhydrophobic membranes to mitigate membrane scaling and
 788 fouling in membrane distillation. J. Membr. Sci., 2020. 601: p. 117962.
- 789 75. Hausmann, A., et al., Fouling of dairy components on hydrophobic polytetrafluoroethylene (PTFE) membranes for
 790 membrane distillation. J. Membr. Sci., 2013. 442: p. 149-159.
- 791 76. Hou, D.Y., et al., *Control of protein (BSA) fouling by ultrasonic irradiation during membrane distillation process.*792 Sep. Purif. Technol., 2017. **175**: p. 287-297.
- 77. Xie, M., W. Luo, and S.R. Gray, Surface pattern by nanoimprint for membrane fouling mitigation: Design,
 794 performance and mechanisms. Water Research, 2017. 124: p. 238-243.
- 795 78. Tow, E.W., et al., *Comparison of fouling propensity between reverse osmosis, forward osmosis, and membrane*796 *distillation.* J. Membr. Sci., 2018. 556: p. 352-364.
- 797 79. Wang, Z.X., D. Hou, and S. Lin, *Composite Membrane with Underwater-Oleophobic Surface for Anti-Oil-Fouling*798 *Membrane Distillation*. Environ. Sci. Technol., 2016. 50(7): p. 3866-74.
- 79980.Chew, N.G.P., et al., Surfactant effects on water recovery from produced water via direct-contact membrane800distillation. J. Membr. Sci., 2017. **528**: p. 126-134.
- 81. Chew, N.G.P., S. Zhao, and R. Wang, *Recent advances in membrane development for treating surfactant- and oil-* 802 *containing feed streams via membrane distillation.* Advances in Colloid and Interface Science, 2019. 273: p.
 803 102022.
- 804 82. Asif, M.B., et al., *Persulfate oxidation-assisted membrane distillation process for micropollutant degradation and* 805 *membrane fouling control.* Separation and Purification Technology, 2019. 222: p. 321-331.
- 83. Jermann, D., et al., Interplay of different NOM fouling mechanisms during ultrafiltration for drinking water
 production. Water Research, 2007. 41(8): p. 1713-22.
- 808 84. Meng, S., et al., Fouling and crystallisation behaviour of superhydrophobic nano-composite PVDF membranes in
 809 direct contact membrane distillation. J. Membr. Sci., 2014. 463: p. 102-112.
- 85. Wang, J., et al., 3-[[3-(Triethoxysilyl)-propyl] amino] propane-1-sulfonic acid zwitterion grafted polyvinylidene
 fluoride antifouling membranes for concentrating greywater in direct contact membrane distillation. Desalination,
 2019. 455: p. 71-78.
- 813 86. Huang, Y.-X., et al., *Novel janus membrane for membrane distillation with simultaneous fouling and wetting*814 *resistance.* Environ. Sci. Technol., 2017. 51(22): p. 13304-13310.
- 815 87. Wang, Z.X., et al., *Tailoring surface charge and wetting property for robust oil-fouling mitigation in membrane*816 *distillation.* J. Membr. Sci., 2016. **516**: p. 113-122.
- 817 88. Tan, Y.Z., et al., *Effect of surfactant hydrophobicity and charge type on membrane distillation performance*. J.
 818 Membr. Sci., 2019. 587: p. 117168.
- 89. Hou, D.Y., et al., *Effect and mechanism of an anionic surfactant on membrane performance during direct contact membrane distillation.* J. Membr. Sci., 2020. 595: p. 117495.
- Wang, Z.X., Y.M.L. Chen, and S.H. Lin, *Kinetic model for surfactant-induced pore wetting in membrane distillation*.
 J. Membr. Sci., 2018. 564: p. 275-288.
- Wang, Z.X., et al., Significance of surface excess concentration in the kinetics of surfactant-induced pore wetting
 in membrane distillation. Desalination, 2019. 450: p. 46-53.
- 825 92. Han, L, et al., Understanding oily wastewater treatment via membrane distillation. J. Membr. Sci., 2017. 539: p.
 826 284-294.
- 827 93. Bogler, A., S. Lin, and E. Bar-Zeev, *Biofouling of membrane distillation, forward osmosis and pressure retarded*828 *osmosis: Principles, impacts and future directions.* J. Membr. Sci., 2017. 542: p. 378-398.
- Li, X.-M., D. Reinhoudt, and M. Crego-Calama, *What do we need for a superhydrophobic surface? A review on the recent progress in the preparation of superhydrophobic surfaces.* Chem. Soc. Rev., 2007. **36**(8): p. 1350-1368.

- 831 95. Lu, K.J., et al., Omniphobic Hollow-Fiber Membranes for Vacuum Membrane Distillation. Environ. Sci. Technol.,
 832 2018. 52(7): p. 4472-4480.
- 433 96. Lee, E.J., et al., Engineering the Re-Entrant Hierarchy and Surface Energy of PDMS-PVDF Membrane for
 Membrane Distillation Using a Facile and Benign Microsphere Coating. Environ. Sci. Technol., 2017. 51(17): p.
 10117-10126.
- Yang, C., et al., *Effective evaporation of CF4 plasma modified PVDF membranes in direct contact membrane distillation.* J. Membr. Sci., 2015. 482: p. 25-32.
- Yang, C., et al., *CF4 plasma-modified superhydrophobic PVDF membranes for direct contact membrane distillation.*J. Membr. Sci., 2014. **456**: p. 155-161.
- 840 99. Kharraz, J.A. and A.K. An, *Patterned superhydrophobic polyvinylidene fluoride (PVDF) membranes for membrane*841 *distillation: Enhanced flux with improved fouling and wetting resistance.* J. Membr. Sci., 2020. 595: p. 117596.
- Wang, W., et al., *Trade-off in membrane distillation with monolithic omniphobic membranes*. Nature
 Communications, 2019. **10**(1): p. 3220.
- 844101.Zhao, F., et al., Hierarchically textured superhydrophobic polyvinylidene fluoride membrane fabricated via845nanocasting for enhanced membrane distillation performance. Desalination, 2018. 443: p. 228-236.
- 846102.Yao, M., et al., A review of membrane wettability for the treatment of saline water deploying membrane847distillation. Desalination, 2020. 479.
- Kang Jia Lu, Y.C., Tai-Shung Chung, *Design of omniphobic interfaces for membrane distillation A review*. Water
 Research, 2019. **162**: p. 64-77.
- 850104.Boo, C., J. Lee, and M. Elimelech, Engineering Surface Energy and Nanostructure of Microporous Films for851Expanded Membrane Distillation Applications. Environ. Sci. Technol., 2016. 50(15): p. 8112-9.
- Wang, Z.X. and S. Lin, *Membrane fouling and wetting in membrane distillation and their mitigation by novel* membranes with special wettability. Water Research, 2017. **112**: p. 38-47.
- Rezaei, M., et al., *Wetting phenomena in membrane distillation: mechanisms, reversal, and prevention.* Water
 Research, 2018. **139**: p. 329-352.
- Tijing, L.D., et al., Superhydrophobic nanofiber membrane containing carbon nanotubes for high-performance
 direct contact membrane distillation. J. Membr. Sci., 2016. 502: p. 158-170.
- Shao, Y., et al., Superhydrophobic polypropylene membrane with fabricated antifouling interface for vacuum
 membrane distillation treating high concentration sodium/magnesium saline water. J. Membr. Sci., 2019. 579: p.
 240-252.
- 109. Qing, W., et al., One-step tailoring surface roughness and surface chemistry to prepare superhydrophobic
 polyvinylidene fluoride (PVDF) membranes for enhanced membrane distillation performances. Journal of Colloid
 and Interface Science, 2019. 553: p. 99-107.
- 864110.Deng, L., et al., Engineering construction of robust superhydrophobic two-tier composite membrane with865interlocked structure for membrane distillation. J. Membr. Sci., 2020. 598: p. 117813.
- I11. Ju, J.G., et al., Engineering hierarchically structured superhydrophobic PTFE/POSS nanofibrous membranes for
 membrane distillation. Desalination, 2020. 486: p. 11.
- Kyong Shon, H., *CF4 plasma-modified omniphobic electrospun nanofiber membrane for produced water brine treatment by membrane distillation.* J. Membr. Sci., 2017. **529**: p. 234-242.
- 870 113. Lu, C., et al., *F-POSS based Omniphobic Membrane for Robust Membrane Distillation*. Materials Letters, 2018.
 871 228: p. 85-88.
- 872 114. Zheng, R., et al., *Preparation of omniphobic PVDF membrane with hierarchical structure for treating saline oily*873 *wastewater using direct contact membrane distillation.* J. Membr. Sci., 2018. 555: p. 197-205.
- 874 115. Deng, L., et al., Self-roughened omniphobic coatings on nanofibrous membrane for membrane distillation. Sep.

875 Purif. Technol., 2018. **206**: p. 14-25.

- Li, X., et al., Omniphobic Nanofibrous Membrane with Pine-Needle-Like Hierarchical Nanostructures: Toward
 Enhanced Performance for Membrane Distillation. Appl. Materials & Interfaces, 2019. 11(51): p. 47963-47971.
- Kharraz, J.A., et al., *Macro-corrugated and nano-patterned hierarchically structured superomniphobic membrane for treatment of low surface tension oily wastewater by membrane distillation.* Water Research, 2020. **174**: p. 15.
- Qing, W.H., et al., Omniphobic PVDF nanofibrous membrane for superior anti -wetting performance in direct
 contact membrane distillation. J. Membr. Sci., 2020. 608: p. 7.
- 882 119. Zhu, Z., et al., Superhydrophobic-omniphobic membrane with anti-deformable pores for membrane distillation
 883 with excellent wetting resistance. J. Membr. Sci., 2020: p. 118768.
- Jiang, X.B., et al., Interface-based crystal particle autoselection via membrane crystallization: From scaling to
 process control. AIChE J., 2019. 65(2): p. 723-733.
- Warsinger, D.M., E.W. Tow, and J. Swaminathan, *Theoretical framework for predicting inorganic fouling in membrane distillation and experimental validation with calcium sulfate*. J. Membr. Sci., 2017. 528: p. 381-390.
- Rice, D., et al., *Scaling Resistance in Nanophotonics-Enabled Solar Membrane Distillation*. Environ. Sci. Technol.,
 2020. 54(4): p. 2548-2555.
- Curcio, E., et al., Influence of the Structural Properties of Poly(vinylidene fluoride) Membranes on the
 Heterogeneous Nucleation Rate of Protein Crystals. The Journal of Physical Chemistry B, 2006. 110(25): p. 12438 12445.
- 893 124. Israelachvili, J.N., Intermolecular and surface forces. 2015, University of California, USA: Academic press. 710.
- van Oss, C.J., *The Extended DLVO Theory*, in *The Properties of Water and their Role in Colloidal and Biological Systems*, C.J. van Oss, Editor. 2008, Elsevier. p. 31-48.
- 896 126. Guo, J.X., et al., Fouling behavior of negatively charged PVDF membrane in membrane distillation for removal of
 897 antibiotics from wastewater. J. Membr. Sci., 2018. 551: p. 12-19.
- Zuo, G. and R. Wang, Novel membrane surface modification to enhance anti-oil fouling property for membrane
 distillation application. J. Membr. Sci., 2013. 447: p. 26-35.
- 900 128. Chang Liu, L.C., Liang Zhu, Fouling behavior of lysozyme on different membrane surfaces during the MD operation:
 901 An especial interest in the interaction energy evaluation. Water Research, 2017. 119: p. 33-46.
- Wu, H.H., et al., *Membrane fouling in vacuum membrane distillation for ionic liquid recycling: Interaction energy analysis with the XDLVO approach.* J. Membr. Sci., 2018. 550: p. 436-447.
- 130. Tanudjaja, H.J. and J.W. Chew, *Assessment of oil fouling by oil-membrane interaction energy analysis*. J. Membr.
 905 Sci., 2018. 560: p. 21-29.
- 906131.Wen, X., et al., Effect of surfactants on the treatment of radioactive laundry wastewater by direct contact907membrane distillation. Journal of Chemical Technology and Biotechnology, 2018. **93**(8): p. 2252-2261.
- 908132.Chen, Y., et al., Anti-wetting behavior of negatively charged superhydrophobic PVDF membranes in direct contact909membrane distillation of emulsified wastewaters. J. Membr. Sci., 2017. 535: p. 230-238.
- 910 133. An, A.K., et al., *High flux and antifouling properties of negatively charged membrane for dyeing wastewater*911 *treatment by membrane distillation.* Water Research, 2016. **103**: p. 362-371.
- 912 134. Jamal, K., M.A. Khan, and M. Kamil, *Mathematical modeling of reverse osmosis systems*. Desalination, 2004.
 913 160(1): p. 29-42.
- 914 135. Kim, S. and E.M.V. Hoek, *Modeling concentration polarization in reverse osmosis processes*. Desalination, 2005.
 915 186(1-3): p. 111-128.
- 916 136. Bouchard, C.R., et al., *Modeling of Ultrafiltration Predictions of Concentration Polarization Effects*. J. Membr.
 917 Sci., 1994. 97: p. 215-229.
- 918 137. Hou, D.Y., et al., Biomimetic superhydrophobic membrane for membrane distillation with robust wetting and

- 919 *fouling resistance.* J. Membr. Sci., 2020. **599**: p. 117708.
- 138. Liu, Y.J., et al., Anisotropic performance of a superhydrophobic polyvinyl difluoride membrane with corrugated
 pattern in direct contact membrane distillation. Desalination, 2020. 481: p. 114363.
- Wang, J., et al., Zwitterionic surface modification of forward osmosis membranes using N-aminoethyl piperazine
 propane sulfonate for grey water treatment. Process Safety and Environmental Protection, 2018. 116: p. 632639.
- Yiao, T.T., et al., *Concentrating greywater using hollow fiber thin film composite forward osmosis membranes: Fouling and process optimization*. Chem. Eng. Sci., 2018. **190**: p. 140-148.
- 927 141. Grewal, H.S., et al., *Effect of topography on the wetting of nanoscale patterns: experimental and modeling studies.*928 Nanoscale, 2014. 6(24): p. 15321-32.
- Wu, H.P., et al., *Influence of structured sidewalls on the wetting states and superhydrophobic stability of surfaces*with dual-scale roughness. Applied Surface Science, 2016. **382**: p. 111-120.
- 931 143. BingBing, W., et al., *Thermodynamic analysis of stable wetting states and wetting transition of micro/nanoscale* 932 *structured surface.* Acta Physica Sinica, 2015. 64(17).
- 933 144. Das, R., et al., *Bio-inspired gas-entrapping membranes (GEMs) derived from common water-wet materials for*934 *green desalination.* J. Membr. Sci., 2019. **588**: p. 117185.
- 935 145. Stokes, G.G., On the effect of the internal friction of fluids on the motion of pendulums. Transactions of the
 936 Cambridge Philosophical Society, 1851. 9: p. 1-86.
- 937 146. Navier, C., *Mémoire sur les lois du mouvement des fluides*. Mémoires de l'Académie Royale des Sciences de
 938 l'Institut de France, 1823. 6(1823): p. 389-440.
- Maxwell, J.C., *III. On stresses in rarefied gases arising from inequalities of temperature.* Proceedings of the Royal
 Society of London, 1878. **27**(185-189): p. 304-308.
- 941148.Bocquet, L., P. Tabeling, and S. Manneville, Comment on "Large slip of aqueous liquid flow over a nanoengineered942superhydrophobic surface". Physical Review Letters, 2006. 97(10): p. 109601.
- 943 149. Kitamura, Y., et al., *Pain-related somatosensory evoked magnetic fields following lower limb stimulation.* Journal
 944 of the Neurological Sciences, 1997. 145(2): p. 187-94.
- 945 150. Baudry, J., et al., *Experimental evidence for a large slip effect at a nonwetting fluid-solid interface.* Langmuir, 2001.
 946 **17**(17): p. 5232-5236.
- 947 151. Tretheway, D.C. and C.D. Meinhart, *Apparent fluid slip at hydrophobic microchannel walls.* Physics of Fluids, 2002.
 948 14(3): p. L9-L12.
- 949 152. Vinogradova, O.I. and G.E. Yakubov, *Dynamic effects on force measurements. 2. Lubrication and the atomic force* 950 *microscope.* Langmuir, 2003. **19**(4): p. 1227-1234.
- 153. Liu, Y., et al., Synergy of slippery surface and pulse flow: An anti-scaling solution for direct contact membrane
 distillation. J. Membr. Sci., 2020. 603: p. 118035.
- 953 154. Chen, G., et al., *Performance enhancement and scaling control with gas bubbling in direct contact membrane*954 *distillation.* Desalination, 2013. **308**: p. 47-55.
- 955 155. Naidu, G., S. Jeong, and S. Vigneswaran, *Influence of feed/permeate velocity on scaling development in a direct*956 *contact membrane distillation.* Sep. Purif. Technol., 2014. **125**: p. 291-300.
- 957 156. Ding, Z., et al., *The use of intermittent gas bubbling to control membrane fouling in concentrating TCM extract*958 *by membrane distillation.* J. Membr. Sci., 2011. **372**(1-2): p. 172-181.
- 157. Choi, J., et al., *Effect of aeration on CaSO4 scaling in membrane distillation process*. Desalination and Water
 Treatment, 2017. **90**: p. 7-15.
- 961 158. Warsinger, D.M., et al., *Combining air recharging and membrane superhydrophobicity for fouling prevention in membrane distillation.* J. Membr. Sci., 2016. **505**: p. 241-252.

- 963159.Rezaei, M., D.M. Warsinger, and W.M. Samhaber, Wetting prevention in membrane distillation through964superhydrophobicity and recharging an air layer on the membrane surface. J. Membr. Sci., 2017. 530: p. 42-52.
- 965 160. Ding, Z.W., et al., Concentrating the extract of traditional Chinese medicine by direct contact membrane
 966 distillation. J. Membr. Sci., 2008. **310**(1-2): p. 539-549.
- 967 161. Lee, C. and C.J. Kim, *Influence of surface hierarchy of superhydrophobic surfaces on liquid slip*. Langmuir, 2011.
 968 27(7): p. 4243-8.
- 162. Lee, C. and C. Kim, Wetting and Active Dewetting Processes of Hierarchically Constructed Superhydrophobic
 Surfaces Fully Immersed in Water. Journal of Microelectromechanical Systems, 2012. 21(3): p. 712-720.
- 163. Lee, C. and C.-J. Kim, Underwater Restoration and Retention of Gases on Superhydrophobic Surfaces for Drag
 972 *Reduction.* Physical Review Letters, 2011. **106**(1): p. 014502.
- 973 164. Thomas, N., et al., *3D printed spacers based on TPMS architectures for scaling control in membrane distillation.*974 J. Membr. Sci., 2019. **581**: p. 38-49.
- 975 165. Castillo, E.H.C., et al., *3D printed spacers for organic fouling mitigation in membrane distillation*. J. Membr. Sci.,
 976 2019. 581: p. 331-343.
- 977 166. Thomas, N., et al., 3D printed triply periodic minimal surfaces as spacers for enhanced heat and mass transfer in
 978 membrane distillation. Desalination, 2018. 443: p. 256-271.
- 979 167. Tijing, L.D., et al., *3D printing for membrane separation, desalination and water treatment.* Applied Materials
 980 Today, 2020. 18: p. 100486.
- 981168.Ye, Y., et al., Microbubble aeration enhances performance of vacuum membrane distillation desalination by982alleviating membrane scaling. Water Research, 2019. 149: p. 588-595.
- 983 169. Zhu, C. and G.L. Liu, *Modeling of ultrasonic enhancement on membrane distillation*. J. Membr. Sci., 2000. 176(1):
 984 p. 31-41.
- Hou, D.Y., et al., *An ultrasonic assisted direct contact membrane distillation hybrid process for desalination*. J.
 Membr. Sci., 2015. **476**: p. 59-67.
- 987 171. Hou, D.Y., et al., Ultrasonic assisted direct contact membrane distillation hybrid process for membrane scaling
 988 mitigation. Desalination, 2015. 375: p. 33-39.
- Hou, D.Y., et al., Ultrasonic irradiation control of silica fouling during membrane distillation process. Desalination,
 2016. 386: p. 48-57.
- 991 173. Hou, D.Y., et al., *Humic acid fouling mitigation by ultrasonic irradiation in membrane distillation process.* Sep.
 992 Purif. Technol., 2015. **154**: p. 328-337.
- 993 174. Choudhury, M.R., et al., *Fouling and wetting in the membrane distillation driven wastewater reclamation process* 994 A review. Advances in Colloid and Interface Science, 2019. 269: p. 370-399.
- 995 175. Gryta, M., Desalination of thermally softened water by membrane distillation process. Desalination, 2010. 257(1996 3): p. 30-35.
- 997 176. Meindersma, G.W., C.M. Guijt, and A.B. de Haan, *Desalination and water recycling by air gap membrane*998 *distillation*. Desalination, 2006. **187**(1-3): p. 291-301.
- 999177.Karakulski, K., M. Gryta, and A. Morawski, *Membrane processes used for potable water quality improvement.*1000Desalination, 2002. **145**(1-3): p. 315-319.
- 1001178.Song, L., et al., Pilot plant studies of novel membranes and devices for direct contact membrane distillation-based1002desalination. J. Membr. Sci., 2008. **323**(2): p. 257-270.
- 1003 179. He, F., et al., *Potential for scaling by sparingly soluble salts in crossflow DCMD.* J. Membr. Sci., 2008. **311**(1): p.
 1004 68-80.
- 1005