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Understanding the evolution of organic fouling in membrane distillation through driving force and resistance analysis / Ricceri, F.; Blankert, B.; Ranieri, L.; Piciooreanu, C.; Ghaffour, N.; Vrouwenvelder, J. S.; Tiraferri, A.; Fortunato, L.. - In: JOURNAL OF MEMBRANE SCIENCE. - ISSN 0376-7388. - 686:(2023), p. 121993. [10.1016/j.memsci.2023.121993]

*Availability:*

This version is available at: 11583/2982027 since: 2023-09-12T07:18:06Z

*Publisher:*

Elsevier

*Published*

DOI:10.1016/j.memsci.2023.121993

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<http://doi.org/10.1016/j.memsci.2023.121993>

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**Understanding the evolution of organic fouling in membrane distillation  
through driving force and resistance analysis**

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22 **Highlights**

- 23 • Flux decline and fouling thickness are linearly correlated.
- 24 • The feed to permeate heat transfer decreases during fouling.
- 25 • OCT allows direct analysis of the fouling layer development.
- 26 • Fouling thickness is governed by the permeate drag force and shear stress  
27 increment.
- 28 • The balance between driving force and resistance yields a stationary flux.

29

30 **Abstract**

31 Fouling is one of the main issues hampering the implementation of thermally-driven membrane  
32 distillation (MD). While the mutual influence of driving force and fouling deposition has been  
33 critically assessed in pressure- and osmotically-driven processes, fouling mechanisms have not  
34 been fully understood in MD. Using non-invasive optical coherence tomography, this study  
35 describes for the first time the evolution of resistance and driving force evolution during the  
36 development of the organic fouling layer in direct contact MD. Foulant layer thickness was  
37 found to be strongly and linearly correlated to water flux under different conditions of feed  
38 temperature and cross-flow velocity. Experimental and modeling results indicate that this  
39 phenomenon is associated to the increase of the overall resistance to water vapor transport.  
40 With a clean membrane, heat loss is mainly governed by the permeate flux and by temperature  
41 polarization. As fouling evolves over time, temperature polarization increases and affects,  
42 together with the additional fouling resistance, the water flux and the heat transfer from feed  
43 to permeate. Indeed, foulant accumulation was observed to lead to a gradual reduction of heat  
44 transfer from the feed to the permeate side, causing a steady increase of the average nominal  
45 driving force, i.e., difference between vapor tension in the feed bulk and in the permeate bulk.  
46 The driving force and the resistance evolved together during this dynamic process of fouling  
47 development, resulting in the achievement of a near-stable flux value over time.

48

49 **Keywords:** membrane distillation; optical coherence tomography (OCT); organic fouling;  
50 fouling evolution; driving force.

## 51 **1 Introduction**

52 Membrane distillation (MD) is a thermally-driven process for water desalination and for  
53 the concentration of challenging wastewater and hypersaline feed [1]. The simplest of the  
54 MD configurations is the so-called direct contact membrane distillation (DCMD). In  
55 DCMD, the warmer feed solution is separated from the colder distillate product by a semi-  
56 permeable hydrophobic membrane that only allows, under ideal conditions, the passage of  
57 water vapor [2]. The driving force is linked to the temperature difference between the  
58 warmer feed solution and the colder distillate stream. MD has been mainly investigated for  
59 desalination purposes, but recent interest has grown also for the treatment of produced  
60 waters, surface waters, and groundwaters with the goals of reuse and/or stream  
61 concentration [3-7]. These feed solutions are all characterized by the presence of organic  
62 substances, often consisting of natural organic matter and humic acids (HA). Srisurichan *et*  
63 *al.* showed that when HA is combined with  $\text{CaCl}_2$ , a heavy and dense HA foulant layer  
64 forms during MD operation and results in a significant flux decline and increase of the heat  
65 transfer resistance [8].

66 It is generally accepted that organic fouling in pressure-driven membrane processes is more  
67 severe than in MD [9, 10]. On the other hand, fouling in MD is also still believed to be one  
68 of the main factors limiting the commercial use of this technology [11]. In direct contact  
69 membrane distillation, fouling involves both mass and heat transfer, which are highly  
70 interconnected with each other. Here, fouling formation on the membrane surface affects  
71 the mass transfer across the membrane, causing a decline in permeate flux. Since the  
72 permeate flux is also responsible for transferring latent heat of vaporization from the feed  
73 to the permeate side, as fouling evolves, also the heat flow decreases. In particular, the  
74 overall heat transfer decreases during fouling in MD both due to the permeate flux decline  
75 and for the formation of an additional thermally insulating layer [12]. Moreover, the fouling

76 layer results in temperature polarization, causing large temperature deviations with respect  
77 to the nominal gradient [13]. In this complex phenomenon, the degree of resistance can be  
78 theoretically calculated based on the characteristics of the fouling layer, such as its  
79 thickness and porosity [8, 14]. However, the available data are usually not sufficiently  
80 accurate as the fouling layer has been mainly characterized by destructive techniques,  
81 limiting the possibility of providing insight into its development over time [15]. Indeed, so  
82 far, most studies on fouling in MD have limited their scope to the water vapor productivity  
83 along the filtration time or the recovery rate value [16, 17]. In recent years, optical coherence  
84 tomography (OCT) has been used to conduct non-invasive dynamic analysis of the fouling  
85 development in membrane systems [18, 19]. OCT allows spatial and time monitoring of  
86 fouling development on the membrane module with micron resolution, as well as  
87 morphological investigation of the deposited layer [20].

88 For the first time in this study, the OCT technology is used in combination with continuous  
89 flux and temperature measurements to provide a complete assessment of fouling behavior  
90 in direct contact membrane distillation and to identify the main factors dominating mass  
91 and thermal transfer during this process. For this purpose, a feed with high load of humic  
92 acids is used as of particular interest for MD applications and also due to the homogeneous  
93 deposition that this matrix is able to form on the membrane surface, allowing more reliable  
94 data analysis through the OCT. Moreover, the contributions of the various resistances to  
95 mass transport are simultaneously analyzed and correlated to the loss of water vapor  
96 productivity. As in the osmotic and pressure driven membrane processes, fouling thickness  
97 evolution and the overall fouling behavior are linked to the variation of the driving force  
98 and the fouling resistance. The permeate drag force and the shear stress also increase during  
99 distillation showing a counteracting effect on the foulant deposition. Finally, important  
100 insight into the fouling mechanism in MD under a wide range of realistic operating

101 conditions is provided and a new mechanism relating fouling to the magnitude of driving  
102 force and resistance in DCMD is discussed.

## 103 **2 Materials and Methods**

### 104 **2.1 Membrane characteristics and feed solution composition.**

105 A synthetic feed solution with an initial humic acid (HA, Sigma-Aldrich) concentration of 500  
106 mg/L was employed in this study. To accelerate the fouling deposition and to enhance high  
107 load of HA solubilization, 20 mM of calcium chloride (CaCl<sub>2</sub>, Sigma-Aldrich) was also added  
108 to the feed solution [8, 25]. These concentrations of organics and salts can be typical of  
109 produced water streams [17], for which MD is particularly appealing, but it is important to note  
110 that a high load were mainly selected to accelerate fouling and to simulate an overall mass flow  
111 of foulants that can be observed under long term operation in up-scaled systems. Initial volumes  
112 of 1 L were used for both the feed and the distillate solutions. For the feed, 500 mL of pure  
113 water were initially used for each test to evaluate a stable initial water flux. After stabilization,  
114 a stock solution was added to reach the desired feed volume and concentrations. The  
115 concentrate stock addition indicates the beginning of the fouling test. For all the experiments,  
116 a commercially available membrane consisting of a hydrophobic polytetrafluoroethylene  
117 active layer with a polypropylene support (PP-PTFE) (Membrane Solutions corp., US) was  
118 used. The membrane characteristics are listed in Table 1, with several data provided by the  
119 manufacturer. The membrane permeability coefficient was experimentally determined by  
120 measuring the water flux and dividing it by the calculated vapor pressure difference across the  
121 membrane at the operating temperatures.

122 **Table 1.** Porous PP-PTFE membrane characteristics

Parameter	Value	Units	Source
Thickness	174 - 245	µm	manufacturer
Mean pore size	0.22	µm	manufacturer
Bubble point	16-20.3	psi	manufacturer

Permeability coefficient	144	$\text{kg m}^{-2} \text{h}^{-1} \text{bar}^{-1}$	experiments
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123

## 124 **2.2 Direct contact membrane distillation lab system**

125 All the MD tests were performed in direct contact membrane distillation (DCMD)  
126 configuration with a lab-scale flow-cell where the warm feed and the cold permeate were  
127 flowed in countercurrent mode. The warm liquid stream is in direct contact with the membrane,  
128 which allows vapors to pass and then condense at the distillate side in the cold water stream  
129 that is also in contact with the membrane. The DCMD flow-cell was made of polymethyl  
130 methacrylate and customized to allow in-situ characterization with OCT (see section 2.4). The  
131 flow-cell had an active membrane area of  $33 \text{ cm}^2$  with dimensions of  $10 \times 3.3 \text{ cm}$  (length  $\times$   
132 width). Flow-cell images are reported in Fig S1 of the Supporting Information file (SI) together  
133 with the overall setup describe here below. The temperatures in the warm feed and cold  
134 permeate inlet streams were maintained constant throughout each experiment using two  
135 separate heating circulators keeping the desired water temperature inside an insulated stainless-  
136 steel bath(Corio-CD, Julabo, Germany), in which the coil circulating the streams was  
137 immersed. The temperature sensors were integrated in the conductivity meters (TetraCon 325,  
138 Xylem Analytics, Germany) located just before the inlet of the flow-cell. Before foulant  
139 addition, those sensors allowed measurements of the stream temperatures entering the flow-  
140 cell and the right settings of the heating circulators to get the desired inlet temperature of the  
141 two streams. Two more sensors were used to measure the outlet temperature values of the feed  
142 and the permeate streams during operation. Cross-flow velocities of both water streams were  
143 measured by digital flow meters (MINI CORI-FLOW<sup>TM</sup>, Bronkhorst, Netherlands). The flux  
144 across the membrane was calculated from the change in weight of the permeate tank over time,  
145 measured through a computer-interfaced balance. All the instruments were digitally connected  
146 and controlled by Lab View software (National Instruments, United States).

### 147 **2.3 Operating conditions and protocol of the fouling experiments**

148 In this study, we investigated feed temperatures in the range of 35 - 65 °C and feed cross-flow  
149 velocities in the range of 0.2 - 0.4 m/s. Constant temperature of 20 °C and cross-flow velocity  
150 of 0.1 m/s were maintained on the permeate side. The central composite design method was  
151 used in Design Expert software to identify an efficient set of experiments within the ranges of  
152 the selected feed temperatures and flow velocities (see Table S1, SI). For all the experiments,  
153 the flux was first stabilized using de-ionized water as feed solution, without organic foulants,  
154 thus obtaining a steady-state flux value referred to as  $J_{w0}$ . The fouling phase started when an  
155 appropriate volume of organic foulant stock solution was added into the feed tank and it was  
156 run until a volume concentration factor of 2.5 was achieved. A schematic presentation of the  
157 described protocol is showed in Fig. S2. The decrement of flux ( $J_w$ ) observed during the fouling  
158 phase can be largely attributed to foulant deposition as salinity in the feed solution was low.  
159 The maximum reduction of the feed vapor tension during tests was 0.02% from the initial value  
160 due to  $\text{CaCl}_2$  concentration (reduction due to HA concentration was even more negligible,  
161 since HA accounted for less than 20% of the total contaminants weight). Therefore, the flux  
162 decline ratio ( $J_w/J_{w0}$ ) decreased during operation due to fouling. This parameter was adopted  
163 to allow an easier correlation between flux and the fouling layer thickness analyzed through  
164 the OCT, which is described in the next section.

### 165 **2.4 Direct monitoring of the fouling thickness with OCT**

166 A spectral-domain optical coherence tomography (SD-OCT) system (Ganymede II, Thorlabs  
167 GmbH, Germany) was used to assess the fouling deposition on the membrane surface. The  
168 instrument was equipped with a scan lens (LSM 03BB). The OCT probe was positioned on top  
169 of the middle point along the length of the DCMD flow-cell, to monitor the fouling layer  
170 development over time. Two-dimensional cross-section OCT scans were taken over a  
171 transversal area of  $8.0 \times 2.6 \text{ mm}^2$  (length  $\times$  depth). FiJi software was used to process the OCT

172 images by reducing the noise and adjusting contrast and brightness. The fouling layer thickness  
 173 was calculated from the OCT images using a custom-made MATLAB code.

## 174 2.5 Heat transfer analysis

### 175 *Heat balances*

176 The heat balances over permeate volume (eq. (1)) and over the whole flow-cell (eq. (2)) can be  
 177 written in terms of heat flows (or power),  $Q$  (J/s), here with incoming heat streams on the left-  
 178 hand side and outgoing on the right-hand side of the balance equations:

$$179 \quad F_{P,in} \rho C_P T_{P,in} + Q_M = (F_{P,in} + F_w) \rho C_P T_{P,out} + Q_{P,loss} \quad (1)$$

$$180 \quad F_{F,in} \rho C_P T_{F,in} + F_{P,in} \rho C_P T_{P,in} = (F_{F,in} - F_w) \rho C_P T_{F,out} + (F_{P,in} + F_w) \rho C_P T_{P,out} + Q_{F,loss} + Q_{P,loss} \quad (2)$$

181  $F_F$  and  $F_P$  are the volumetric flow rates (m<sup>3</sup>/s) on the feed and permeate side of the membrane;  
 182  $T_F$  and  $T_P$  are the bulk temperatures (K) of feed and permeate, all at inlet and outlet (denoted  
 183 by indices *in* and *out*). It is assumed that the heat capacity of water is approximately constant  
 184 between 20 and 60 °C, with  $C_P = 4180 \text{ J kg}^{-1} \text{ K}^{-1}$ , and the water density can also be taken as  
 185 constant,  $\rho = 998 \text{ kg/m}^{-3}$ . The heat balances can be further simplified by assuming that the total  
 186 flowrate of water passing the membrane,  $F_w$ , is negligibly small compared with the flows of  
 187 feed and permeate ( $F_w \ll F_{P,in}, F_{F,in}$ ). Also, the heat loss from the permeate side to exterior,  
 188  $Q_{P,loss}$ , can be neglected because the permeate temperature is very close to the ambient  
 189 temperature, thus heat losses predominately occur at the hot side of the system as  $Q_{F,loss}$ . By  
 190 introducing the notations for heat flows between inlet and outlet,  $Q_P$  for permeate side and  $Q_F$   
 191 for feed side:

$$192 \quad Q_P = F_P \rho C_P (T_{P,out} - T_{P,in}) \quad (3)$$

$$193 \quad Q_F = F_F \rho C_P (T_{F,in} - T_{F,out}) \quad (4)$$

194 the heat balances over permeate (eq. (5)) and over the flow-cell (eq. (6)) become:

$$195 \quad Q_M = Q_P \quad (5)$$

$$196 \quad Q_{F,loss} = Q_F - Q_P \quad (6)$$

197 Eq. (5) means that the permeate heat gain,  $Q_P$ , is a result of the total heat transfer through the  
198 membrane  $Q_M = Q_w + Q_m$  caused by the condensation of water,  $Q_w$ , and by conduction,  $Q_m$ .

199 Eq. (6) allows the estimation of heat loss through the feed channel walls to the exterior, as the  
200 difference between the power change between inlet and outlet for feed and permeate.

### 201 *Temperature drop from feed to permeate*

202 In DCMD, heat is transferred from the feed to the permeate side by several mechanisms. First,  
203 there is conduction from the warmer feed solution (bulk temperature  $T_F$ ) across a thermal  
204 boundary layer to the surface of the fouling layer (temperature  $T_{F,L}$ ), which links to the  
205 temperature polarization on the feed side. Second, if there is a fouling layer, this will induce an  
206 additional heat transfer resistance by conduction, usually named cake-enhanced temperature  
207 polarization, with a temperature drop from  $T_{F,L}$  to  $T_{F,M}$  at the membrane surface. Third, several  
208 heat transfer mechanisms take place in the membrane: conduction through the membrane  
209 polymeric material, conduction through the vapors in the pores (which may be negligible), and  
210 an important heat flux due to evaporation/condensation at the feed/permeate interfaces. Finally,  
211 there is also temperature polarization on the permeate side, with conduction in the quasi-  
212 stagnant water layer adjacent to the membrane driven by the difference between  $T_{P,M}$  at the  
213 membrane surface at  $T_P$  in the bulk permeate.

214 The average temperature value in the feed and permeate side,  $T_F$  and  $T_P$ , was the arithmetic  
215 mean of measured inlet and outlet water temperatures. The difference between the feed and

216 permeate bulk temperature give the total temperature drop between the feed and permeate  
 217 across the thermal boundary layers ( $\Delta T_F, \Delta T_P$ ), foulant layer ( $\Delta T_L$ ) and membrane ( $\Delta T_M$ ):

$$218 \quad T_F - T_P = \Delta T_F + \Delta T_L + \Delta T_M + \Delta T_P \quad (7)$$

219 However, the individual temperature differences can also be estimated. Assuming the existence  
 220 of a fouling layer, the continuity of total heat flux through the membrane,  $q_M$  ( $\text{J m}^{-2}\text{s}^{-1}$ ), implies:

$$221 \quad q_M = h_F (T_F - T_{F,L}) = h_L (T_{F,L} - T_{F,M}) = h_M (T_{F,M} - T_{P,M}) = h_P (T_{P,M} - T_P) \quad (8)$$

222 with the four heat transfer coefficients ( $\text{J m}^{-2}\text{s}^{-1}\text{K}^{-1}$ ) as  $h_F$  and  $h_P$  for thermal boundary layers  
 223 on the feed and permeate side,  $h_L$  through the fouling layer, and  $h_M$  through the membrane (a  
 224 lumped value involving both evaporation/condensation and conduction). With the heat flux as  
 225 heat flow  $Q_M = Q_P$  divided by membrane area,  $A_M$  ( $0.0033 \text{ m}^2$ ), one can express the  
 226 temperature differences across the different layers:

$$227 \quad \Delta T_F = T_F - T_{F,L} = \frac{Q_P}{h_F A_M}, \quad \Delta T_L = T_{F,L} - T_{F,M} = \frac{Q_P}{h_L A_M}$$

$$228 \quad \Delta T_M = T_{F,M} - T_{P,M} = \frac{Q_P}{h_M A_M}, \quad \Delta T_P = T_{P,M} - T_P = \frac{Q_P}{h_P A_M}$$

229 Average heat transfer coefficients through the thermal boundary layers,  $h_F$  and  $h_P$ , may be  
 230 estimated from correlations for the Nusselt number,  $\text{Nu} = hH/k$ , function of Reynolds  
 231 number,  $\text{Re} = uH\rho/\mu$ , and Prandtl number,  $\text{Pr} = C_p\mu/k$ . These involve the physical  
 232 properties of water (density  $\rho$ , dynamic viscosity  $\mu$ , specific heat  $C_p$  and thermal conductivity  
 233  $k$ ), as well as the water velocity  $u$  and the height  $H$  of the specific channel (feed or permeate)  
 234 that decreases at the feed side in time due to the growth of the fouling layer. While  $\rho$ ,  $C_p$  and  $k$   
 235 ( $0.6 \text{ J s}^{-1}\text{m}^{-1}\text{K}^{-1}$ ) can be assumed constant in the interval of temperatures, viscosity has a  
 236 significant change taken as  $\mu = 0.497(42.5 + T)^{-1.5}$  with  $T$  in  $^\circ\text{C}$ . Generally, convective heat

237 transfer correlations are developed based on the assumption of small rate of mass transfer. We  
 238 adopted the Nusselt relation for heat transfer between two plates, for both feed and permeate  
 239 channels,  $Nu = 0.664 Re^{1/2} Pr^{1/3}$ . This allows estimation of  $\Delta T_F = \frac{Q_P}{A_M} \frac{H_F}{k_F Nu_F}$  and  
 240  $\Delta T_P = \frac{Q_P}{A_M} \frac{H_P}{k_P Nu_P}$ . The fitting of experiments before foulant addition also allowed a  
 241 determination of the temperature difference across the membrane as a function of the measured  
 242 flux (see Fig. S3),  $\Delta T_M = f(J_w)$ , where the water flux is  $J_w = F_w/A_M$ . Finally, the  
 243 temperature drop over the fouling layer can be computed during each test by:

$$244 \quad \Delta T_L = T_F - T_P - \Delta T_F - \Delta T_M - \Delta T_P = \frac{Q_P}{A_M} \frac{\delta_L}{k_L}$$

245 This assumes heat transfer through the fouling layer occurs predominately by conduction.  
 246 Equations were implemented in custom MATLAB code processing OCT and MD data  
 247 acquired during each test. The value of  $k_L$  was thus retrieved for each test prior assuming this  
 248 value as  $0.6 \text{ W m}^{-1}\text{K}^{-1}$ , i.e., water thermal conductivity. Thus, this value was assumed constant  
 249 to retrieve the Nusselt number during fouling evolution for each test.

## 250 **2.6 Driving force and fouling resistance analysis**

251 In MD, the driving force for the mass transfer is provided by the water vapor pressure  
 252 difference between the feed,  $p_F$ , and the permeate side,  $p_P$ . The vapor pressure  $p$  (Pa) for  
 253 water can be calculated from the Antoine equation  $p = \exp(23.238 - 3841/(T - 45))$  with  $T$   
 254 in K. The nominal driving force calculated in this study is based on the average value from the  
 255 inlet and outlet bulk temperatures of the feed stream,  $T_F$ , and the permeate stream,  $T_P$ . The  
 256 overall resistance to mass transfer between feed and permeate,  $R$ , was calculated as ratio  
 257 between the driving force  $DF$  and the measured water vapor flux  $J_w$  [24]:

258 
$$R = \frac{DF}{J_w} = \frac{p_F - p_P}{J_w} \quad (9)$$

259 Changes in the driving force and in the resistance were evaluated during the tests to determine  
260 the mechanism of fouling development.

261

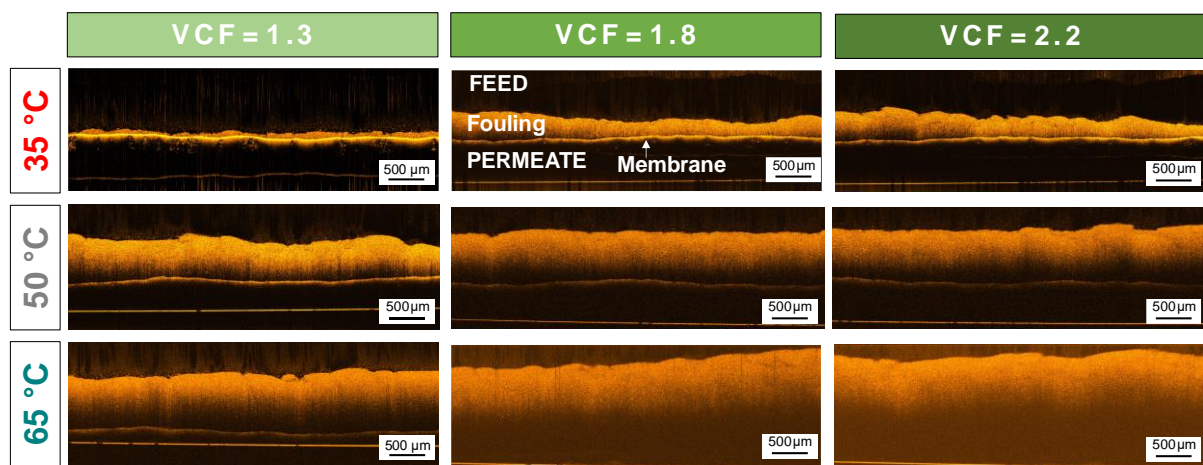
## 262 **3 Results and discussion**

### 263 **3.1 Impact of temperature and cross-flow velocity on process performance and fouling** 264 **development**

265 Fouling evolution in membrane distillation was evaluated in this study under different realistic  
266 conditions of feed inlet temperature ( $T_{F,in}$ ) and cross-flow velocity ( $u_F$ ). As expected, the initial  
267 flux was strongly correlated to the applied feed inlet temperature. Results reported in Fig. S4  
268 suggest that the initial flux can be increased from ~3 to 22.5 kg m<sup>-2</sup>h<sup>-1</sup> by increasing  $T_{F,in}$  from  
269 35 to 65 °C. This is a result of the nature of the MD driving force, i.e., the vapor tension  
270 difference between the feed and the permeate [26]. On the other hand, an almost negligible  
271 effect on  $J_w$  was observed when increasing the cross-flow velocity. Indeed, despite  $u_F$  plays a  
272 role on the heat transfer coefficient and consequent temperature polarization, this effect was  
273 negligible compared to the applied feed temperature. It is also important to note that in this  
274 study the membrane housing length was sufficiently small to minimize the temperature profiles  
275 along the cross-flow direction.

276 The fouling layer development over time was monitored with OCT microscopy. Fig. 1 presents  
277 representative OCT scans obtained for tests performed with applied feed inlet temperatures of  
278 35, 50, and 65 °C, and acquired at the three volume concentration factors (VCF) of 1.3, 1.8,  
279 and 2.5. Images refer to the tests performed at a cross-flow velocity of 0.3 m/s. The fouling  
280 layer always increased during distillation: in details, the measured thickness when operating at

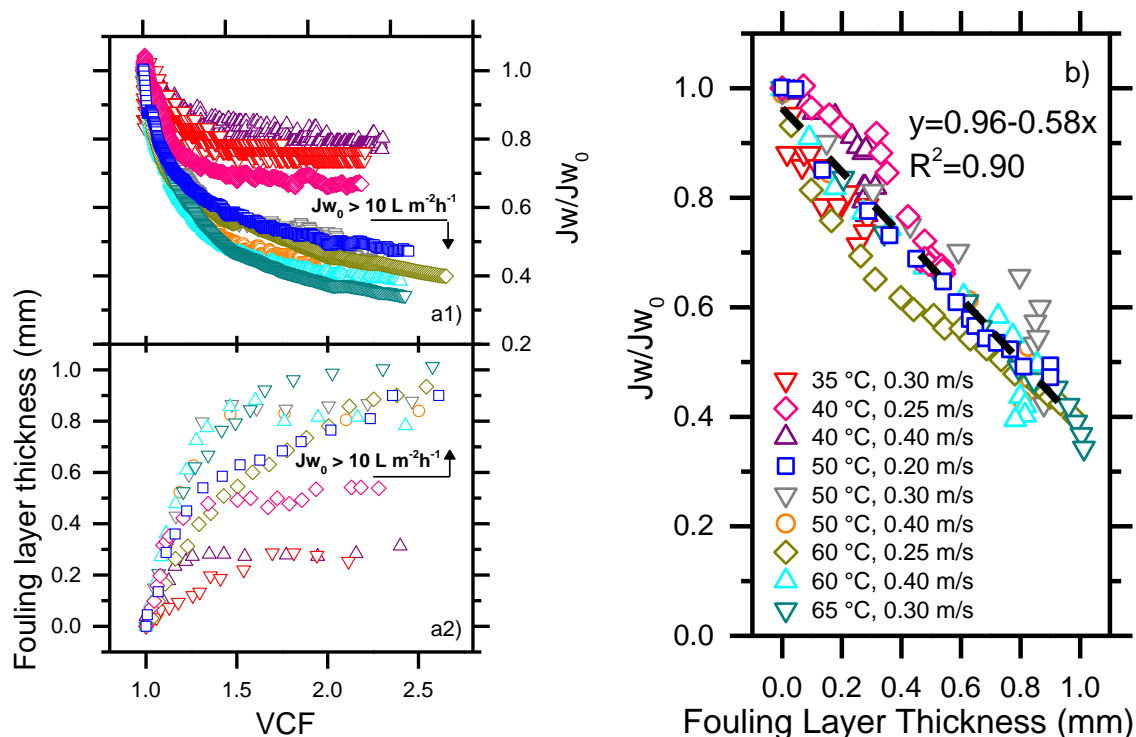
281 65 °C and 50 °C changed from 622 μm to 1013 μm and from 355 μm to 878 μm, respectively,  
 282 when the VCF was increased from 1.3 to 2.2. Indeed, for all VCF values reported in Fig 1, a  
 283 decrease of fouling layer thickness was observed when the feed inlet temperature was lowered.  
 284 Interestingly, considerable lower deposition was observed for the experiment performed at 35  
 285 °C, whereby thickness only changed from 196 μm to 273 μm in the same VCF range.  
 286 Therefore, the fouling deposition rate in DCMD may be directly linked to the feed temperature:  
 287 severe organic fouling is observed at higher temperatures.



288 **Fig. 1.** Cross-sectional OCT scans of the fouling layer deposited on the membrane surface, at  
 289 three VCF values, for experiments performed at fixed cross-flow velocity of 0.3 m/s and with  
 290 different inlet feed temperatures (35, 50, 65 °C). The OCT scans were acquired at the middle  
 291 position of the membrane cell during continuous operation.  
 292

293  
 294 The dependency of flux decline ratio and fouling thickness on the VCF is shown in Fig. 2. In  
 295 general, the flux decline (Fig. 2a1) showed a similar behavior of fouling layer thickness (Fig.  
 296 2a2). This evidence highlights how these parameters are similarly influenced by the different  
 297 applied conditions of  $T_{F,in}$  and  $u_F$ . The cross-flow velocity mainly influenced the flux and  
 298 fouling deposition at lower inlet feed temperatures: the  $J_w/J_{w0}$  varied from 0.8 to 0.6 (higher  
 299 flux decline) when decreasing  $u_F$  from 0.40 to 0.25 m/s at 40 °C, while negligible influence on  
 300 the final value of  $J_w/J_{w0}$  was observed by changing the  $u_F$  for the experiments performed at 50  
 301 and 60 °C. Symmetrically, lower final layer thickness was observed when increasing the cross-

302 flow velocity at 40 °C, from 538 μm to 313 μm, while negligible difference was obtained when  
 303 the  $u_F$  was increased at a  $T_{F,in}$  of 50 °C and 60 °C. This effect could be attributed to the reduced  
 304 ability of the cross-flow velocity in counteracting fouling when operating at higher flux. On  
 305 the other hand, a strong effect was played by  $T_{F,in}$ , whose increase generally reduced the value  
 306 of  $J_w/J_{w0}$  and evidently increased the fouling deposition along the VCF. This result is in good  
 307 agreement with previous studies and may be correlated to the role of temperature in increasing  
 308 both initial flux (see Fig. S4) and temperature polarization [27-29].



309 **Fig. 2.** (a1) Normalized flux  $J_w/J_{w0}$  and (a2) fouling thickness development plotted against  
 310 VCF. The experiments were performed with the synthetic feed water in the presence of humic  
 311 acid and calcium at different initial permeate flux  $J_{w0}$  obtained by varying the feed inlet  
 312 temperature  $T_{F,in}$  and the cross-flow velocity  $u_F$  in DCMD configuration. Fouling layer  
 313 thickness was determined from the OCT scans acquired in the middle position of the cell during  
 314 continuous operation. (b) The correlation between fouling layer thickness and normalized  
 315 permeate flux. The coefficient of determination  $R^2$  is for the line fitting all the experimental  
 316 data.

317

318 Interestingly, from the data presented in both Fig. 2a1 and 2a2, it is possible to notice the  
 319 presence of a low- and a high- fouling region, respectively, below and above the initial flux of

320 roughly  $10 \text{ L m}^{-2}\text{h}^{-1}$ . Note that  $J_{w0}$  below this value are obtained when experiments are  
321 performed at a feed temperature below  $50 \text{ }^\circ\text{C}$  (see Fig. S4), confirming previous findings [7,  
322 19, 25]. In parallel, below this  $T_{F,in}$  value, also considerable lower foulant accumulation was  
323 measured (see Fig. 2a1). Previous studies linked the presence of different fouling regions to  
324 the existence of a possible threshold flux [30]. The concept of critical or threshold flux has  
325 been widely reported in osmotically-and pressure-driven membrane processes [22, 31].

326 Fig. 2b shows the flux decline  $J_w/J_{w0}$  as a function of the fouling layer thickness, both measured  
327 at different times during the various experiments. Overall, the data reflect the inverse linear  
328 dependency between the two parameters, regardless of the experimental conditions ( $R^2=0.9$  for  
329 the aggregate regression). This result is in agreement with previous studies on wastewater  
330 treatment with MD and confirms how, as in the other membrane separation process, the flux  
331 decline during long-term operation is directly correlated to the amount of fouling deposited on  
332 the membrane surface [32, 33]. A possible explanation of this strong correlation is associated  
333 with the magnitude of the driving force for water separation (vapor tension difference between  
334 feed and permeate side of the membrane). Any loss of flux may be caused by a corresponding  
335 percentage of the driving force lost along the fouling layer thickness, a phenomenon named  
336 cake-enhanced temperature polarization [28, 29, 34]. Such simple linear correlation implies the  
337 possibility to obtaining a reasonable estimation of the foulant accumulation based on flux data  
338 during DCMD operation for a wide range of feed inlet temperatures and cross-flow velocities.  
339 From this prospective, there is still a lack of knowledge related to modelling of foulant  
340 deposition in DCMD.

341 In summary, this investigation highlights how flux decline rate and fouling layer thickness  
342 similarly increased with the feed temperature and closely correlated with initial flux. On the  
343 other hand, the value of the cross-flow velocity did not show a clear influence on flux, while it  
344 mainly decreased the fouling layer thickness. Interestingly, a low fouling region was identified

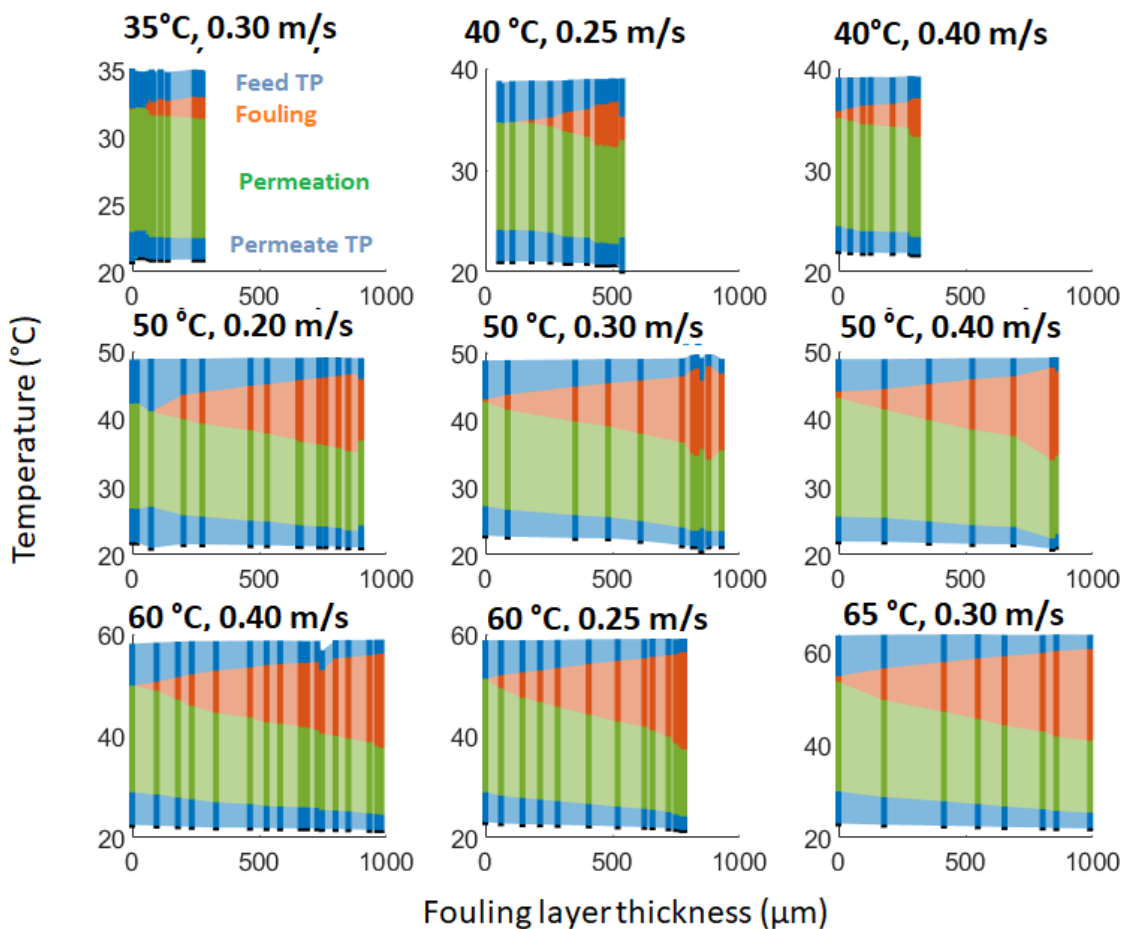
345 when operating below 50°C of inlet feed temperature. Finally, strong linear correlation  
346 between the fouling layer development and the vapor permeate flux was observed.

### 347 **3.2 Analysis of the factors contributing to the temperature evolution during fouling**

348 The membrane, the fouling layer, and temperature polarization layers can be seen as a series  
349 of resistances to water flux, as each layer accounts for a certain amount of heat loss from  
350 the hot to the cold side. Thus, the nominal driving force (vapor tension difference between  
351 bulk feed and permeate) is lowered to a net driving force across the membrane (vapor  
352 tension difference between the two membrane interfaces, at the feed and at the permeate  
353 side). The temperature profile on both the feed and the permeate side before foulant  
354 addition (clean membrane) was retrieved for all the experiments from Eq.7, which also  
355 accounts for temperature polarization. The temperature drop across the membrane was then  
356 retrieved as a difference between the temperature values as a result of polarization in the  
357 two channels. Linear interpolation of these results, shown in Figure S3, allowed estimation  
358 of the temperature drop across the membrane for any flux values observed during the  
359 experiments. The growth of a fouling layer exacerbated the driving force losses, which  
360 added to the effects already present for clean membranes.

361 The separate contribution of each heat transfer resistance from feed to permeate during the  
362 fouling process is presented in Fig.3. The temperature profile was plotted against the  
363 fouling layer thickness and calculated by Eqs. 1-7. In all tests, the temperature loss due to  
364 polarization decreased during fouling (see blue color bands in Fig 3), due to the decrement  
365 of the heat flow from feed to permeate (Eq. 3). This is due to the increment of the total heat  
366 subtracted by the increasing fouling thickness fouling and by the decrement of permeation  
367 (see orange and green color bar in Fig 3, respectively). According to the model, the feed  
368 temperature polarization ( $\Delta T_F$ ) reduction was more pronounced than that in the permeate

369 stream ( $\Delta T_p$ ), because the fouling layer growth also decreased the effective height of the  
 370 feed channel. This effect can be observed under all the tested conditions in Fig 3, by  
 371 comparing the two blue bands with each other. The foulant layer thickness influences the  
 372 feed temperature polarization term, due to the heat flow reduction from feed to permeate  
 373 and also because the reduction of flow channel height increases the cross-flow velocity,  
 374 which thereby decreases the temperature boundary layer thickness. On the other hand, an  
 375 enhanced cross-flow velocity leads to more shear stress over the fouling layer, which can  
 376 be accountable for the decreasing effective deposition of foulants in time. This mechanism  
 377 can explain the gradual approach of a foulant thickness plateau during the last phase of the  
 378 experiments (see Fig. 2a2).



379

380 **Fig. 3.** Separate contributions of each heat transfer resistance in the overall temperature loss,  
 381 estimated during fouling development for experiments performed in different conditions. The

382 uppermost and lowermost values indicate the bulk temperatures in the feed and permeate  
383 during fouling, as average between the measured inlet and outlet temperature. Blue areas:  
384 temperature polarization in feed ( $\Delta T_F$ , top) and permeate ( $\Delta T_P$ , bottom); Red area:  
385 temperature drop through fouling layer ( $\Delta T_L$ ); Green area: temperature drop over the  
386 membrane (water vapor flux contribution,  $\Delta T_M$ ).

387

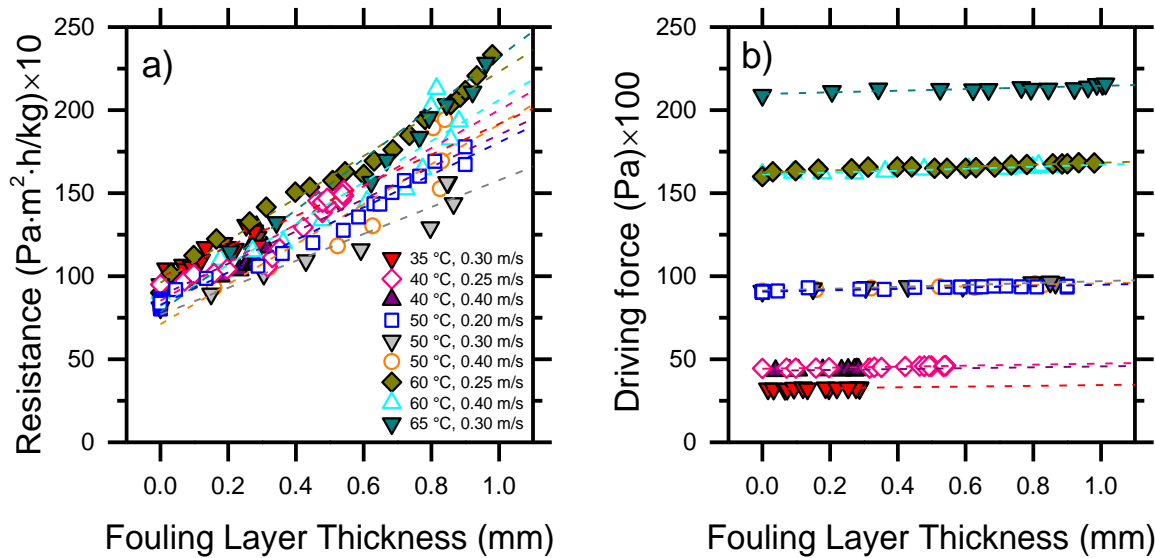
388 In all tests, the water vapor heat flow generally decreased as fouling accumulation occurred  
389 (see green band in Fig. 3). Indeed, higher feed temperatures generate more rapid flux  
390 decline, which is here reflected by the higher discrepancy in the amount of heat loss due to  
391 permeation from the beginning to the end of the tests when increasing the feed inlet  
392 temperature. As an example, the test at 35 °C shows a heat loss due to permeation of roughly  
393 10 °C during the entire duration of the test, while at 65°C feed bulk temperature, the related  
394 heat loss decreased from 30°C to 20 °C throughout the test. In parallel, the analysis allows  
395 estimation of the amount of heat subtracted by the growing fouling layer. This portion  
396 gradually increased in all the experiments as fouling layer thickness evolved as a result of  
397 foulant deposition, while both temperature polarizations and convective heat decreased.  
398 Once again, as the fouling thickness is mainly governed by the feed temperature, heat  
399 subtracted by the fouling layer increased more for tests performed at higher temperatures.  
400 As an example, the highest difference can be observed by comparing again the 35 °C and  
401 65 °C test, where the final temperature decline within the fouling thickness was about 3 °C  
402 and 20 °C, respectively. In other words, while the loss of driving force is related mainly to  
403 temperature polarizations and water vapor flux with a clean membrane, fouling becomes  
404 relatively more and more significant in terms of driving force losses compared to the other  
405 two phenomena during operation. Interestingly, this behavior evolved similarly regardless of  
406 the operational conditions.

407 Another consideration resulting from the analysis is that a small variation of the two average  
408 bulk temperature profiles from initial values occurred during operation. Specifically, the

409 average bulk feed temperature was estimated to increase while the average permeate  
410 temperature to decrease slightly as organic foulants deposited onto the membranes. This  
411 mechanism translated into an overall small increment of the nominal (bulk) driving force, the  
412 net effect of a gradually lower amount of heat transferred from the feed to the permeate side  
413 due to fouling accumulation and the concomitant flux decline. In other words, the average  
414 nominal driving force in the membrane housing increased in time, while the net driving force  
415 decreased due to foulant accumulation. Despite the effect on the bulk driving force was not  
416 particularly pronounced in this study due to the small size of the membrane, it has important  
417 implications on the fouling evolution, discussed in depth below, and it would be much more  
418 significant in large-scale systems.

### 419 **3.3 Overall driving force and resistance analysis during fouling in DCMD**

420 To approach a mechanistic explanation of how fouling evolves in DCMD, the driving force  
421 ( $DF$ ) and the fouling resistance ( $R$ ) are investigated in this section in the light of the measured  
422 fouling layer thickness. Fig. 4 shows the values of the two parameters calculated for  
423 experiments performed under different conditions of feed inlet temperature and cross-flow  
424 velocity. A linear fit was calculated for each experiment, with intercept and standard error  
425 values reported in Table S2 (SI). The overall resistance to the permeate flux was calculated by  
426 Eq. 8. All tests started with similar resistance in the range between 700 and 1000 Pa m<sup>2</sup> h kg<sup>-1</sup>,  
427 as highlighted by the intercept values in Figure 4a. Results imply that fouling deposition  
428 inevitably leads to the development of an additional resistance: the good quality of the linear  
429 fit implies the role of the fouling thickness on the proportional increment of total resistance,  
430 consistent with the discussion of the sections above. Furthermore, the rate of resistance  
431 increment was dependent on the operating conditions, possibly due to the different flux decline  
432 rates (Fig. 2).



433 **Fig. 4.** (a) Total resistance,  $R$ , and (b) nominal driving force,  $DF$ , calculated from the data  
 434 reported in Fig. 1, as a function of the foulant thickness. The fits are shown by dash line with  
 435 the respective colors. The multiplicative factors indicates that the showed y-axes values must  
 436 be multiplied for ten and one hundred to get the real  $R$  and  $DF$  values, respectively.

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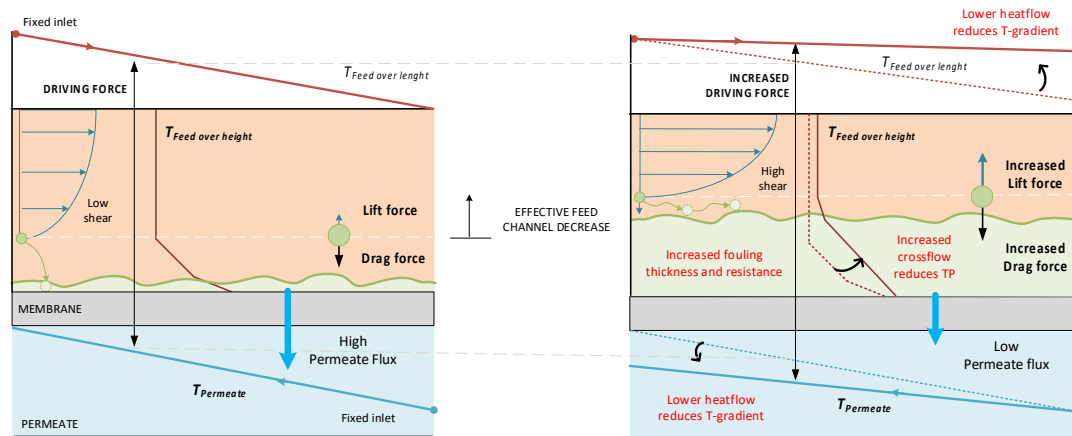
438 The initial values of the total driving force depend solely on the initial operating feed  
 439 temperatures. As discussed in the previous section, organic fouling caused an increase in the  
 440 average nominal driving force, rationalized with the decrement of the heat transfer from the  
 441 feed to the permeate [35]. The slopes reported in Table S2 suggest that also this effect was  
 442 somewhat proportional to the initial temperature. In summary, both the total resistance and the  
 443 bulk driving force increased during operation. A clearer picture of this mutual increment can  
 444 be observed in Fig. S5, reporting results for all the experiments performed at 50 °C. It is  
 445 important to note that, while the reduction in polarization phenomena with fouling is present  
 446 in all membrane-based filtration processes, the increment of the nominal driving force during  
 447 fouling is not a mechanism shared by all filtration processes. For example, in pressure-driven  
 448 membrane processes, the nominal driving force is largely independent of foulant deposition, as  
 449 the fouling layer has not been found to significantly influence the pressure profiles within the  
 450 channels of the membrane housing or module [22, 24]. To summarize, during fouling  
 451 deposition both the total resistance and the average nominal driving force increased, translating

452 into a nearly constant net driving force, hence stabilized flux, attained after a certain time. This  
453 phenomenon is mainly attributed to a decrement of the convective heat flow from the feed to  
454 the permeate as an additional resistance is generated by fouling layer accumulation.

### 455 **3.4 Proposed fouling evolution mechanism in DCMD**

456 Although fouling is a continuous process, it can be also described as the result of discreet  
457 steps to mechanistically depict the evolution of deposition as governed by the mutual  
458 increment of the driving force and mass transfer resistance (Fig. 5). This type of  
459 mechanistic model has already been used in osmotically- and pressure-driven processes,  
460 since it is not dependent on the nature of the driving force [21]. According to the results  
461 obtained in this study, the increase of the fouling layer thickness on the membrane surface  
462 linearly increased the total resistance to the water vapor flux. This phenomenon was found  
463 to be analogous under a wide range of investigated conditions. The increase in resistance  
464 translated into a heat transfer reduction from the feed to the permeate side and a consequent  
465 increment of the average nominal driving force, i.e., the difference between the average  
466 bulk temperature of the feed and of the permeate stream. This increase in driving force and  
467 the reduction of polarization outside the fouling layer inevitably caused the permeate drag  
468 force to increase, likely causing more foulant deposition. The feedback between driving  
469 force and resistance continued to evolve as fouling thickness increased in a framework whereby  
470 also hydrodynamic conditions were influenced by the growing layer. In the schematic of Fig.  
471 5, it can be observed how in the initial stage of fouling, the permeate drag should dominate  
472 fouling deposition as only partially counterbalanced by the shear stress. A strong decrement of  
473 the permeate flux is observed as result of fouling accumulation (Fig. 5a). However, with layer  
474 growth, the feed channel would tend to narrow with a consequent increment of the effective  
475 cross-flow velocity (Fig. 5b, feed side). The shear stress thus thwarts the further deposition of  
476 foulants and promotes foulant back-transport, therefore preventing further growth of the

477 fouling layer [36-38]. During the late stage of filtration, the fouling layer thickness approached  
 478 a near-stable value as the lift and drag forces reached equilibrium in the feed channel (see Fig  
 479 2a2). In parallel, also the flux approached a near-stable value (see Fig 2a1). Therefore, as  
 480 overall effect, the mutual increase of both the average nominal driving force and of the overall  
 481 resistance should lead to a self-compensation phenomenon during which the fouling thickness,  
 482 the effective cross-flow velocity and the cake-enhanced temperature polarization reach near  
 483 equilibrium and productivity reaches a near steady-state condition.



484  
 485 **Fig. 5.** Micro to macroscale analysis of the mechanisms occurring upon organic foulant  
 486 deposition and fouling layer formation in direct contact membrane distillation, including  
 487 influence on the hydrodynamic parameters, effects on temperature profiles and on the driving  
 488 force. Left panel refers to conditions of clean membrane, right panel to conditions after cake  
 489 layer formation. The experiment were performed with a feed solution consisting of 500 mg/L  
 490 of humic acid and 20 mM of CaCl<sub>2</sub>.

491

#### 492 4 Conclusion

493 This study presented an analysis of organic fouling in membrane distillation under a wide range  
 494 of temperature and cross-flow velocity conditions. During operation, the analysis of the fouling  
 495 layer with OCT highlighted the linear correlation between layer thickness increase and flux  
 496 reduction. An investigation of the main resistances to water vapor flux confirmed that the  
 497 heat transfer was reduced due to fouling accumulation. In particular, the amount of heat

498 loss within the fouling layer grew at the expenses of lower heat loss due to convective heat  
499 (i.e., heat transported by water vapor flux) and to the two temperature polarizations at the  
500 feed and permeate side. Also, the average nominal driving force increased while the overall  
501 resistance also increased, overall reducing the water vapor flux. Results suggest that fouling  
502 resistance and the driving force evolved together and governed the fouling evolution dynamics  
503 over time. Fouling was found to be a dynamic phenomenon, whereby governing factors  
504 evolved together resulting in a final near steady-state productivity value as net result. This  
505 continuous process may be discretized in steps as follows:

- 506 (i) Fouling deposition increases the overall resistance to the water vapor flux.
- 507 (ii) The fouling layer and the related water flux decrement reduce the heat transferred  
508 from the feed to the permeate stream with the overall effect of an increase in  
509 average nominal driving force, i.e., bulk temperature difference between the  
510 feed and the permeate side.
- 511 (iii) As in the other membrane process, the driving force increase inevitably leads to  
512 an increment of the permeate drag force, which thereby promotes foulant transport  
513 and accumulation onto the membrane surface.
- 514 (iv) The mutual increments of the driving force and fouling resistance generate a self-  
515 compensation phenomenon which is responsible for the near-stable flux gradually  
516 approached during fouling development.
- 517 (v) The plateau is reached for both flux and fouling thickness as the gradual fouling  
518 accumulation also leads to an increase of the shear force in the feed channel that  
519 thwarts foulant deposition and counterbalances the increasing permeate drag force  
520 of foulant toward the membrane.

521

522 **Acknowledgements**

523 The research reported in this paper was supported by funding from King Abdullah University  
524 of Science and Technology (KAUST), Saudi Arabia and by Politecnico di Torino, Italy.  
525 Francesco Ricceri acknowledges funding from the CleanWaterCenter@PoliTo for his Ph.D.  
526 scholarship (01\_TRIN\_CI\_CWC).

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## *Supplementary Material*

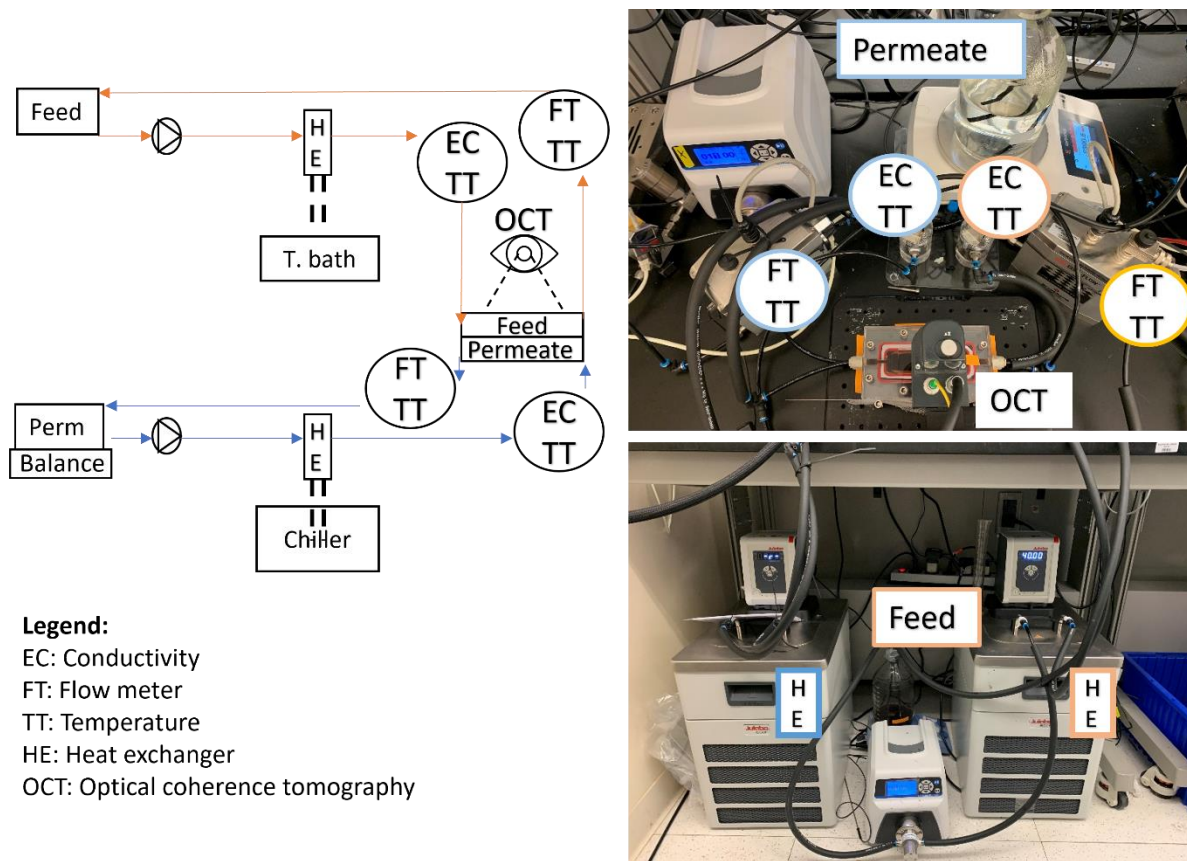
### **Understanding organic fouling evolution in membrane distillation through driving force and resistance analysis**

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1: Department of Environment, Land and Infrastructure Engineering, Politecnico di Torino, Corso Duca degli Abruzzi, 24 – 10129 Torino (Italy)

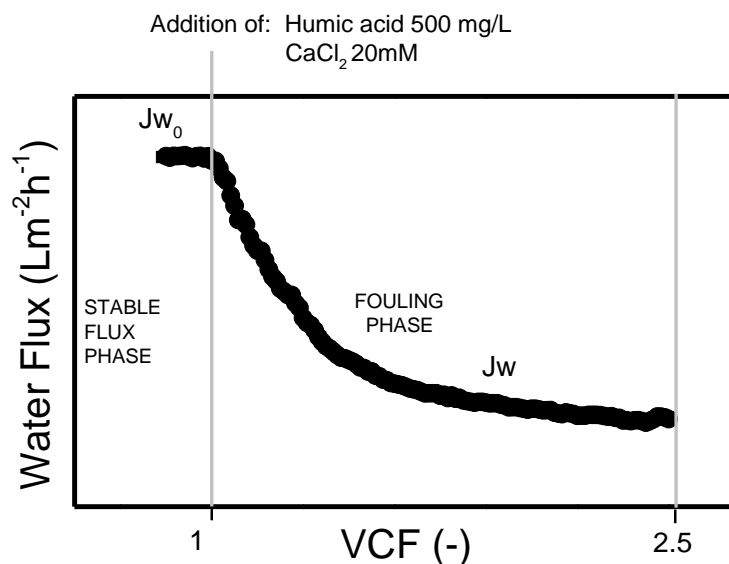
2: CleanWaterCenter@PoliTo, Corso Duca degli Abruzzi, 24 – 10129 Torino (Italy), web:

<http://cleanwater.polito.it/>



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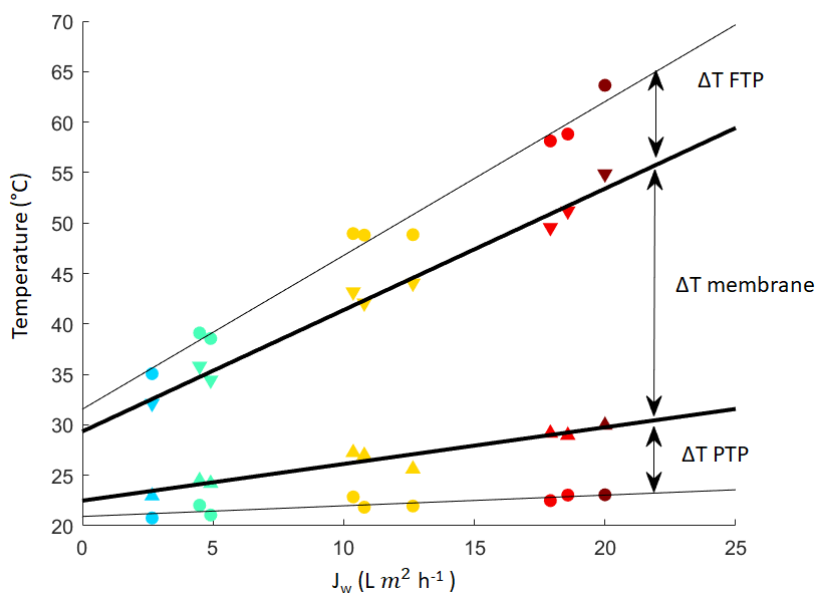
553 **Fig. S1.** Schematic representation and images of the setup used for this study. The orange  
 554 and blue lines are used for the warm feed and cold permeate respectively, the legend indicates  
 555 the acronyms used for each component. Regarding the OCT, only the camera positioned on  
 556 the transparent cell is shown in this picture.



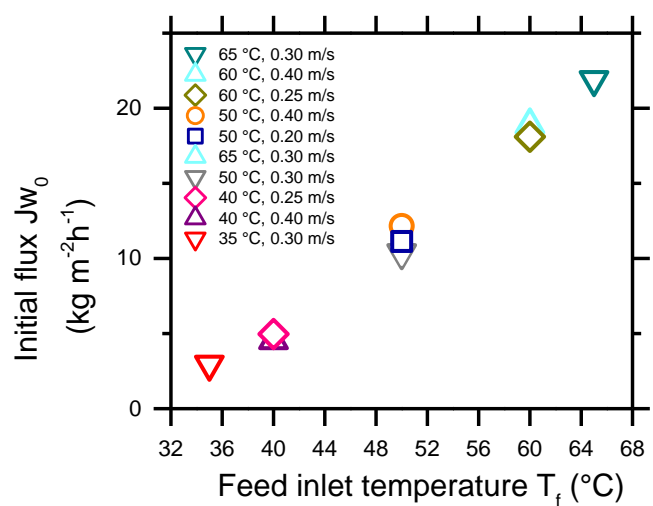
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558 **Fig. S2.** Representative experimental determination of water flux through the MD membrane.  
 559 The protocol consisted of two stages: (i) the initial stabilization of flux,  $J_{w0}$ , using deionized  
 560 water, for roughly 30 min; (ii) the fouling phase started at the volume concentration (VCF)

561 equal to 1 and was carried out for a volume concentration factor of 2.5. Here, the flux is  
 562 indicated by  $J_w$ .  
 563



564  
 565 **Fig. S3.** Temperature profile between the feed and permeate bulk solutions before fouling  
 566 (clean membrane). The profile was retrieved by implementing Eq. 3, related to the temperature  
 567 profile in the presence of temperature polarization, for all the performed experiments (Table  
 568 S1). The temperature drop across the membrane was retrieved as difference between the  
 569 temperature values at the membrane interface. The fitting was performed to assess the  
 570 temperature polarization and temperature difference across the membrane for any measured  
 571 flux even during fouling.

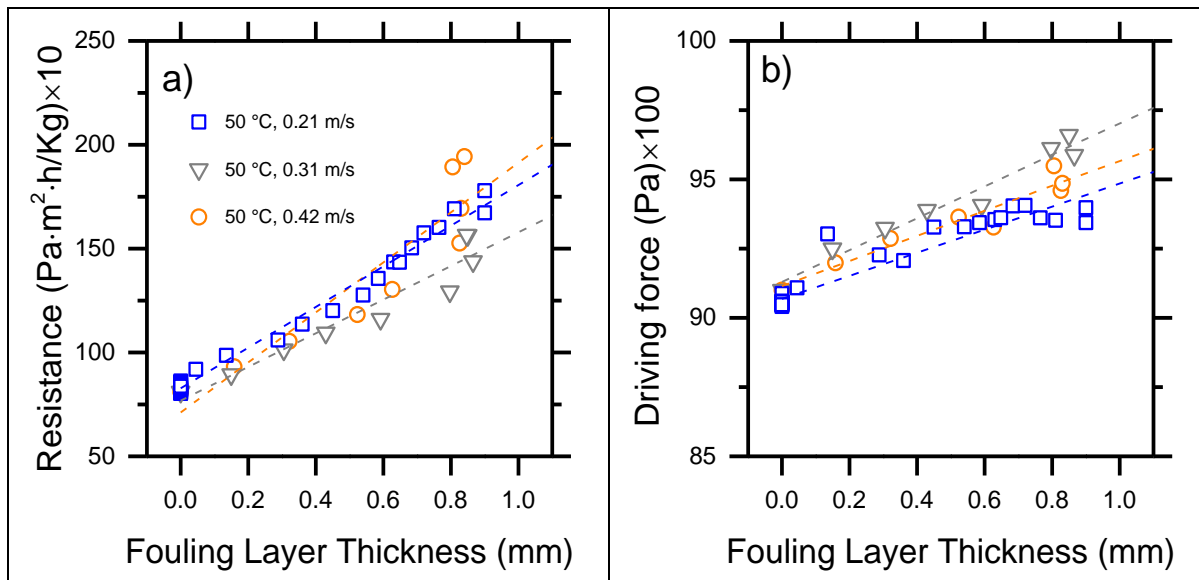


572  
 573 **Fig. S4.** Initial flux ( $J_w0$ ) as a function of the feed inlet temperature prior to foulant addition  
 574 for the nine different tests reported in legend, each run with a different combination of  
 575 temperature and cross-flow velocity. The list of experiment was designed by central composite

576 design method through Design Expert software, from a selected temperature range of 35-65 °C  
 577 and a range of cross-flow velocity of 0.20-0.40 m/s.

578

579



580 **Fig. S5.** Evolution of the (a) overall resistance and (b) average nominal driving force during  
 581 fouling for the experiments performed at 50 °C. Results are included in Fig. 4 and are here  
 582 reported by narrowing the y-axes range to better assess the increasing trends.

583

584 **Table S1.** List of experiments determined by a central composite design method in Design  
 585 Expert software, a tool used to get efficient experimental protocols.

Experiment	
Feed temperature (°C)	Feed cross-flow velocity (m/s)
35	0.30
40	0.25
40	0.40
50	0.20
50	0.30
50	0.40
60	0.40
60	0.25
65	0.30

586

587

588 **Table S2.** Intercept, slopes and related standard error values of best lines fitting the average  
 589 nominal driving force and foulant resistance when each is plotted against fouling thickness  
 590 (dash lines showed in Fig. 4 of the main manuscript)

Experiment			Resistance (Pam2h/Kg)		Driving force (Pa)	
Feed Temperature (°C)	Cross-flow velocity (m/s)		Value	St.Error	Value	St.Error
35	0.30	Intercept	993.30	24.26	3211.02	14.3
		Slope	0.92	0.13	0.23	0.07
40	0.25	Intercept	852.61	35.50	4430.06	10.73
		Slope	1.14785	0.08	0.30	0.02
40	0.40	Intercept	881.13	46.97	4300.45	13.58
		Slope	0.97	0.19	0.27	0.05
50	0.20	Intercept	827.48	6.11	9068.42	9.53
		Slope	0.97	0.01	0.41	0.02
50	0.30	Intercept	768.28	55.62	9129.78	27.86
		Slope	0.81	0.08	0.57	0.04
50	0.40	Intercept	711.14	113.89	9114.81	31.03
		Slope	1.20	0.18	0.45	0.05
60	0.25	Intercept	961.08	26.19	16250.98	40.6
		Slope	1.27	0.04	0.58	0.06
60	0.40	Intercept	819.94	96.47	16121.9	27.25
		Slope	1.24	0.15	0.58	0.04
65	0.30	Intercept	784.43	97.04	20972.12	60.9
		Slope	1.53	0.13	0.48	0.08

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