

A scalable dual-layer PAN/SAN nanofibrous membrane for treatment of saline oily water using membrane distillation

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Desalination

A scalable dual-layer PAN/SAN nanofibrous membrane for treatment of saline oily water using membrane distillation

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Abstract:	Single-layer hydrophobic membranes are prone to fouling while subjected to a feed containing hydrophobic contaminants. In this study, using the green solvent Dimethyl sulfoxide (DMSO), dual-layer nanofibrous poly-acrylonitrile (PAN)/styrene-acrylonitrile (SAN) membranes were fabricated using the highly productive electroblowing process. Then through a simple hot-pressing process, the desirable hydrophilicity was achieved for PAN/SAN membrane. The water contact angle (WCA) for the top layer fell from $112.2 \pm 1^\circ$ to $37.5 \pm 1^\circ$ after hot-pressing, while the WCA for the bottom layer decreased slightly from $147.1 \pm 1^\circ$ to $142.3 \pm 1^\circ$. Moreover, an underwater oil contact angle (UOCA) of $158.1 \pm 1^\circ$ was achieved for the PAN/SAN membrane. Direct contact membrane distillation (DCMD) tests were performed for synthetic saline water and synthetic saline oily water. While the permeate flux dropped for the single-layer SAN membrane, the dual-layer PAN/SAN membrane, due to underwater superoleophobicity, achieved a stable permeate flux for 24 h with a nearly complete salt rejection (>99.9%). This study addresses the pore wetting and declines in the permeate flux of the membrane distillation (MD) application in the treatment of saline oily water by implementing scalable, cost-efficient, and eco-friendly approaches.
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1 **A scalable dual-layer PAN/SAN nanofibrous membrane for treatment of saline oily water**
2 **using membrane distillation**

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21

22 **Abstract**

23 Single-layer hydrophobic membranes are prone to fouling while subjected to a feed
 24 containing hydrophobic contaminants. In this study, using the green solvent Dimethyl sulfoxide
 25 (DMSO), dual-layer nanofibrous poly-acrylonitrile (PAN)/styrene-acrylonitrile (SAN)
 26 membranes were fabricated using the highly productive electroblowing process. Then through a
 27 simple hot-pressing process, the desirable hydrophilicity was achieved for PAN/SAN membrane.
 28 The water contact angle (WCA) for the top layer fell from $112.2 \pm 1^\circ$ to $37.5 \pm 1^\circ$ after hot-
 29 pressing, while the WCA for the bottom layer decreased slightly from $147.1 \pm 1^\circ$ to $142.3 \pm 1^\circ$.
 30 Moreover, an underwater oil contact angle (UOCA) of $158.1 \pm 1^\circ$ was achieved for the PAN/SAN
 31 membrane. Direct contact membrane distillation (DCMD) tests were performed for synthetic
 32 saline water and synthetic saline oily water. While the permeate flux dropped for the single-layer
 33 SAN membrane, the dual-layer PAN/SAN membrane, due to underwater superoleophobicity,
 34 achieved a stable permeate flux for 24 h with a nearly complete salt rejection (>99.9%). This study
 35 addresses the pore wetting and declines in the permeate flux of the membrane distillation (MD)
 36 application in the treatment of saline oily water by implementing scalable, cost-efficient, and eco-
 37 friendly approaches.

38
 39 **Keywords:** Hydrophilicity; Underwater superoleophobicity; Hot-pressing; Dual-layer; DCMD.

40

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59 **1. Introduction**

60 Saline wastewater production has increased in recent decades due to considerable
61 development in varied industries [1,2]. Wastewater treatment can be done using methods like
62 physicochemical processes, aerobic treatment, anaerobic digestion, and membrane separation
63 technologies [3-6]. Considering membrane-based separation, the membrane distillation (MD)
64 process has been regarded as a next-generation, sustainable approach to treating hypersaline
65 waters. The MD is a non-isothermal process that uses a porous hydrophobic membrane to direct
66 hot water vapor to produce pure water [7,8]. Interestingly, MD can make full use of inexpensive
67 heat resources to supply clean water and due to its operational condition, it will not be influenced
68 by the quality of wastewater, making it a sought-after technology for desalination and wastewater
69 treatment [9-13].

70 Surface fouling and pore wetting are however the downsides of the MD process due to the
71 complex composition of hypersaline wastewaters [14]. In general, membrane performance can be
72 detrimentally affected by fouling [15-17]. Severe reduction in membrane permeation because of
73 foulant accumulation on/in the membrane can be followed by pore wetting and worsening of
74 treated water quality [18,19]. Although the MD process experiences lower fouling compared to
75 the pressure-driven membrane processes, the MD membranes are vulnerable to oil due to strong
76 hydrophobic-hydrophobic interaction [20]. Low-surface-energy materials like surfactants can also
77 increase the pore wetting of the MD membrane. These contaminants can easily invade the

78 membrane pores and render the membrane more hydrophilic which will lead to the failure in
79 rejecting salts [21-23].

80 To tackle the problem of traditional MD membranes, the concept of dual-layer structure
81 including hydrophilic/hydrophobic design has been proposed to reduce fouling and wetting
82 [24,25]. As dual-layer structures have two layers with hydrophilic and hydrophobic characteristics,
83 researchers called them the Janus membranes after the imaginary Greek god with two faces [26].
84 The hydrophilic layer of a dual-layer structure can be fabricated by coating with hydrophilic
85 materials [27], electrospinning [28], electrospraying [29], and film casting using non-solvent-
86 induced phase separation (NIPS) [30] to form a hydrophilic or even superhydrophilic top layer
87 with superior underwater oil repellency. The hydrophobic/superhydrophobic or even omniphobic
88 support layer can also be applied to reject salts to avoid pore wetting, while the hydrophilic top
89 layer reduces fouling.

90 The robustness of the top layer is of vital importance in using dual-layer membranes.
91 Delamination or removal of the top layer during the MD process allows oil droplets to attach to
92 the membrane surface and reduce the permeate flux [31]. It also causes a severe reduction in
93 rejection because of pore wetting. Another issue is the environmental concern for using
94 hydrophilic materials, fluoroalkyl silanes, and also the complexity of the membrane fabrication
95 process. From an industrial point of view, a fabrication process should be time-efficient and as
96 simple as possible with a considerably lower production cost for both applied materials and the
97 fabrication process.

98 In this study, a practical dual-layer structure was fabricated using inexpensive
99 polyacrylonitrile (PAN) and styrene-acrylonitrile (SAN) polymers. To make the fabrication
100 process more productive and less time-consuming, a modified version of the conventional

101 electrospinning, electroblowing process was used. The electroblowing or air-assisted
102 electrospinning process makes use of dry airflow to boost the fiber production rate [32,33]. The
103 PAN polymer and its nanofibers are intrinsically hydrophilic but not hydrophilic enough to be used
104 as a decent top layer for reducing oil fouling. The surface hydrophilicity was impressively
105 improved using a fast-hot-pressing process. The fabricated structure turned from a spongy and soft
106 structure to a dense and firm structure that: 1) reduced the chance of top-layer detachment during
107 the direct contact MD (DCMD) process, 2) decreased the hydrophobicity of the surface to
108 sufficiently reduce underwater interaction between membrane surface and oil droplets, 3)
109 minimized the carbon footprint resulted from the application of different materials that are
110 currently applied to make more hydrophilic surfaces. The membrane fabrication process was also
111 eco-friendly because of the use of dimethyl sulfoxide (DMSO) as the solvent during the
112 electroblowing process. To our knowledge, this is the first report of constructing an underwater
113 superoleophobic and in-air highly hydrophilic dual-layer structure for the MD process using a
114 straightforward hot-pressing process without any excessive post or pre-modification processes.

115

116 **2. Experimental**

117 *2.1. Materials and chemicals*

118 Commercial PAN polymer was purchased from the Isfahan Textile Co, Iran. Commercially
119 available SAN polymer (SAN-4) was purchased from Ghaed Basir Co., Iran. DMSO, acetone,
120 NaCl, and isopropyl alcohol (IPA) (extra-pure grade) were provided by Amertat Shimi, Co, Iran.
121 Cetyltrimethylammoniumbromide (CTAB) and **sodium dodecyl sulfate (SDS) were** purchased
122 from Merck, Germany. A commercial non-woven fabric made of polypropylene (PP) polymer was

123 used as support for nanofiber collection during the electroblowing process. Gasoline was provided
124 by a local supplier.

125

126 2.2. Membrane fabrication process

127 The neat dual-layer PAN/SAN nanofibrous membrane was fabricated using PAN/DMSO
128 + acetone (80 wt% DMSO and 20 wt% acetone; 8 wt% PAN) and SAN/DMSO + acetone (70 wt%
129 DMSO and 30 wt% acetone; 17.5 wt% SAN) spinning solutions. Also, a small amount of CTAB
130 salt was added to the spinning solution to reduce bead-on-string nanofibers. The electroblowing
131 condition is summarized in [Table 1](#). A co-axial electroblowing needle and syringe were attached
132 via a polyethylene (PE) tube. With the help of a dry air flow, a continuous nanofiber jet was formed
133 on the PP non-woven mat. First, a nanofibrous SAN layer was fabricated and then a nanofibrous
134 PAN layer was fabricated on the support SAN layer. After completing the electroblowing process,
135 the neat PAN/SAN nanofibrous membrane (designated as PAN/SAN) was immediately hot-
136 pressed (H-PAN/SAN) under 2000 psi pressure at a temperature of 85 °C for 30 s to improve the
137 physical integrity of the produced dual-layer nanofibrous membrane. A single-layer SAN
138 nanofibrous membrane (designated as SAN) was also fabricated and hot-pressed (designated as
139 H-SAN) to form a more uniform structure.

140

141 [Table 1](#). Process parameters of the electroblowing process.

Nanofibrous layer	Voltage (kV)	Working distance (cm)	Polymer injection rate ($\mu\text{L}/\text{min}$)	Air flowrate (NL/min)	Spinning time (min)
PAN	22	30	90	2.5	45
SAN	18	30	90	2	45

142

143 2.3. Characterization

144 Surface morphology of the prepared nanofibrous layers and cross-sectional images of
145 PAN/SAN nanofibrous membrane were observed by scanning electron microscopy (SEM, AIS
146 2100C, Korean Republic). The dual-layer H-PAN/SAN membrane was fractured in liquid nitrogen
147 before the SEM test. Fiber diameter was measured by Digimizer software, and the average value
148 of 100 fiber diameters was reported.

149 The thickness of the samples was measured using an accurate micrometer and cross-
150 sectional images. The mean value of the three tests was reported as the mean thickness value.

151 The porosity was evaluated using the gravimetric method. First, membrane tickets were
152 heated at 80 °C using a digital oven for 4 h to remove moisture and then weighed to determine the
153 samples' dry weight. For the next step, pre-dried samples were submerged in IPA and reweighed.
154 A full description of the process can be found in Zhou et al. [34].

155 The surface hydrophobicity of the prepared samples was determined by measurement of
156 the water contact angle (WCA) using a drop shape analyzer device (KRUSS analyzer-G10 Drop
157 Shape Analyzer, Germany). The underwater oleophobicity of the fabricated samples was measured
158 by underwater oil contact angle (UOCA) using the same device.

159 The pore size of the single-layer SAN and dual-layer PAN/SAN membranes were
160 measured using a lab-made bubble-point set-up. See Niknejad et al. [35] for more information.

161 The liquid entry pressure (LEP) of water was evaluated by a homemade set-up. Briefly, a
162 circular-shaped sample of the dual-layer PAN/SAN and single-layer SAN membranes were placed
163 between semi-cell modules. Pressure (kPa) was gradually increased to the point where the first
164 deionized (DI) water droplet was observable on the membrane surface, and this pressure was
165 regarded as the LEP value. The mean value of the three tests using independent membranes was
166 reported.

167

168 *2.4. DCMD process*

169 A lab-scale DCMD set-up was used to evaluate the prepared membranes for saline and
170 saline oily feeds. The representation of the DCMD device can be found in Bonyadi et al. [36]. The
171 synthetic saline oily water was prepared by adding 1 g gasoline and 35 g NaCl to the DI water
172 using a high-speed blender (rotating speed, 5000 rpm; mixing time, 1 h). Feed and permeate
173 temperatures were 60 ± 1 °C and 25 ± 1 °C, respectively. Feed and permeate streams were both set
174 at 0.48 L/min. The feed water was mixed every 2 hours using the blender for about 5 minutes to
175 ensure that the oil dispersion was uniform when it comes in contact with the active side of the
176 membrane (hydrophilic layer). Also, the components of the DCMD set-up were mostly made from
177 polyurethane (pipes) and polyethylene (feed tanks and membrane module). Therefore, the saline
178 oily feed was circulated at least three times before starting the DCMD tests using a pump to ensure
179 that the oil adhesion on the equipment was kept at a minimum during the DCMD tests to ensure a
180 more accurate result. The mass and quality of the purified water were regularly monitored using a
181 digital balance and an electrical conductivity (EC) meter, respectively. By knowing the active
182 membrane surface area (m^2), the period of the recorded weight (h), and the amount of added water
183 into the permeate tank (kg), the permeate flux (kg/m^2 h) could be determined.

184

185 **3. Results and discussion**

186 *3.1. Morphology*

187 The surface morphology of the top and bottom layers of the PAN/SAN membrane and the
188 cross-sectional SEM image of the H-PAN/SAN membrane are shown in Fig 1. It is noteworthy
189 that the morphology of the single-layer SAN was the same as the bottom layer of the PAN/SAN

190 membrane, as they were fabricated and hot-pressed under the same operating conditions.
191 Therefore, only one SEM image is presented.

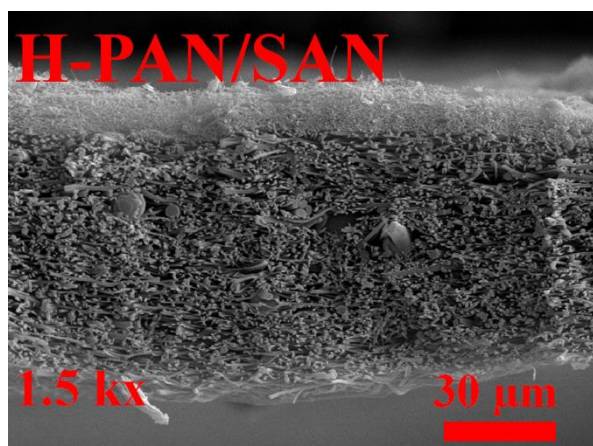
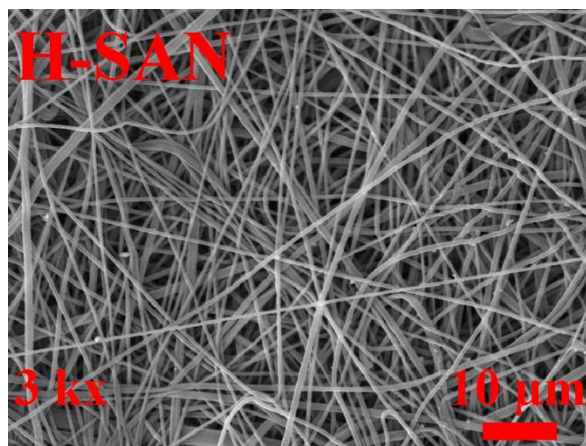
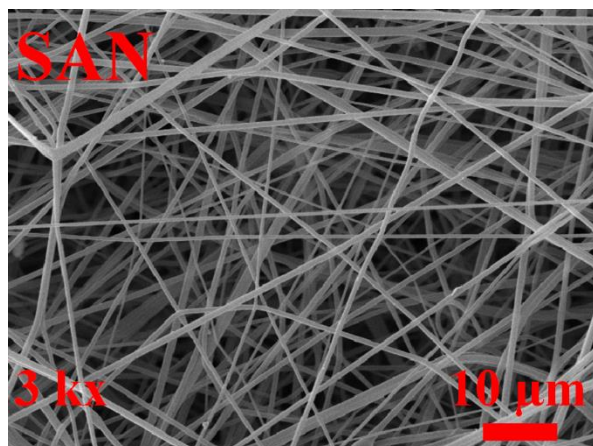
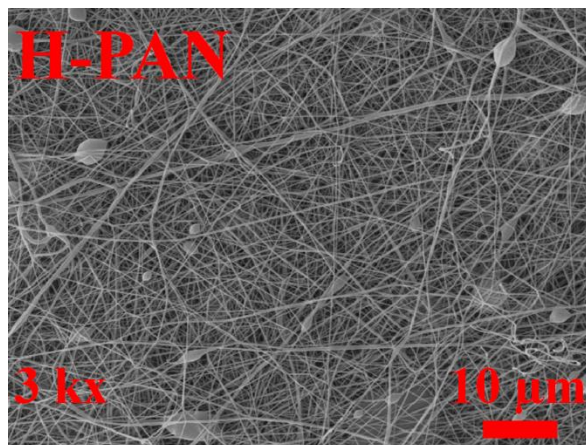
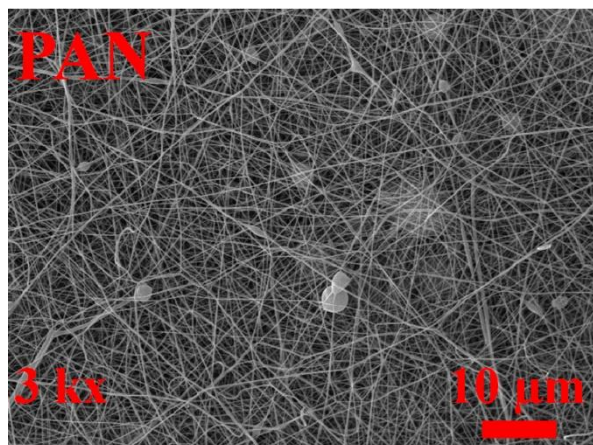
192 The polymer concentration in the dope solution is one of the deciding factors of the
193 electrospinning process. For example, under the same electrospinning parameters, using dope
194 solutions with low polymer concentrations will lead to the formation of cup-like defects and
195 beaded fibers. However, raising the polymer concentration might result in a fiber diameter increase
196 [37,38]. Therefore, the desirable morphology for the nanofibers can be obtained by controlling the
197 polymer concentration. As observed, a defect-free nanofibrous SAN substrate with 3D
198 microporous interconnected networks was fabricated with a suitable polymer concentration and
199 CTAB addition to the dope solution [39]. For the PAN top layer, to maintain a balance between
200 defects and fiber diameter enhancement, a microporous dense interconnected with minimal defects
201 was fabricated by choosing the suitable polymer concentration.

202 For the dual-layer membrane, the mean fiber diameter of the neat SAN, hot-pressed SAN,
203 neat PAN, and hot-pressed PAN was measured as 431 ± 58 , 453 ± 32 , 157 ± 48 , and 174 ± 34 nm,
204 respectively. Throughout the hot-pressing process, the mean fiber diameter was essentially
205 constant because the temperature, pressure, and duration were not high enough to lead to an
206 increase in fiber diameter while they were sufficient to increase fiber density by effectively
207 compacting more nanofibers in a specific area [40]. Fig S1 Shows the cross-sectional SEM image
208 for the H-PAN/SAN membrane after sonication to prove the robustness of the formed layer.

209 Visible changes in the pore size of the membranes can be observed after the hot-pressing
210 process (Table 2). The hot-pressed samples had a smaller mean pore size compared to the neat
211 membranes, which is evident by the naked eye. The cross-section image shows that the PAN and
212 SAN layers are closely bonded with no signs of delamination at the PAN/SAN interface (Fig 1).

213 This can be attributed to the effective hot-pressing and the residual DMSO in the nanofibers, which
214 further facilitate the adhesion at the PAN/SAN interface and reduces the probability of layer
215 delamination.

216



217 Fig 1. The surface morphology of the top layer, the bottom layer, and also the cross-section
218 morphology of the fabricated PAN/SAN and H-PAN/SAN membranes. The SEM images'
219 magnification with their scale bar is also presented.

220

221 3.2. Porosity and thickness

222 Electrospun nanofibrous membranes typically have higher porosities when compared to
223 membranes fabricated via other membrane fabrication methods [35]. A membrane fabricated via
224 the electroblowing process has a higher porosity than a membrane fabricated via the conventional
225 electrospinning process (>95%). Moreover, using a longer spinning duration and a PP nonwoven
226 mat while the charge density is kept constant can assist in making the fabricated membrane more
227 porous by increasing the resistance against the electrical charge [41].

228 Higher porosity is favorable as permeability correlates positively with the porosity of the
229 applied membrane in the MD process due to trapped air in the membrane pores that act as an
230 insulator, thus reducing the heat loss by conduction and the water vapors having more space to
231 pass through as a result of an increase in mean free path [35]. However, the downside is that these
232 membranes have a larger pore size, loose and random fiber structure, wider pore size distribution,
233 and insufficient mechanical strength that makes them inapplicable in the MD process [32]. After
234 the hot-pressing process, the porosity of the membranes showed a declining trend. The porosity
235 for neat SAN and PAN/SAN membranes dropped from $97.8 \pm 2\%$ and $95.7 \pm 2\%$ to $78.5 \pm 1\%$
236 and $75.4 \pm 1\%$, respectively. This result is also in conformity with the declining trend reported by
237 Yao et al. [42].

238

239 **Table 2.** Thickness, δ ; porosity, ϵ ; mean pore size, r_{mean} ; maximum pore size, r_{max} ; water contact
 240 angle, WCA; liquid entry pressure, LEP of the fabricated membranes.

Membrane	δ (μm)	ϵ (%)	r_{mean} (μm)	r_{max} (μm)	WCA ($^{\circ}$)	UOCA ($^{\circ}$)	LEP (kPa)
SAN	540 ± 50	97.8 ± 2	1.64 ± 0.03	4.12 ± 0.04	147.1 ± 1	76.2 ± 1	41.1 ± 2
H-SAN	64 ± 3	78.5 ± 1	0.43 ± 0.02	0.91 ± 0.02	142.3 ± 1	70.4 ± 1	120.3 ± 2
PAN/SAN	845 ± 50	95.7 ± 2	0.58 ± 0.02	1.32 ± 0.01	$112.2 \pm 1^{\text{a}}$ $147.1 \pm 1^{\text{b}}$	122.5 ± 1	65.3 ± 2
H-PAN/SAN	77 ± 3	75.4 ± 1	0.27 ± 0.01	0.52 ± 0.02	$37.5 \pm 1^{\text{a}}$ $141.7 \pm 1^{\text{b}}$	158.1 ± 1	156.2 ± 2

241 ^a top layer WCA

242 ^b bottom side WCA of SAN layer

243

244 Membrane thickness is another important parameter that affects the permeate flux,
 245 mechanical properties, and salinity the membrane can efficiently handle. The increase in salinity
 246 causes a drop in feed vapor pressure, consequently, if the transmembrane temperature is not high
 247 enough the loss in energy efficiency becomes considerable [43]. Although thicker membranes have
 248 higher energy efficiency, the driving force is insufficient to fully boost permeation. These
 249 membranes are preferable in the treatment of highly saline waters due to possible mass transfer
 250 resistance and a lower permeate flux [44,45]. Therefore, to achieve higher rejection and permeate
 251 flux, it is essential to determine a suitable balance between porosity and thickness. The thickness
 252 value for the neat SAN and PAN/SAN membranes reduced from 540 ± 50 and 845 ± 50 μm to 64
 253 ± 3 and 77 ± 3 μm for the H-SAN and H-PAN/SAN, respectively. The porosity and thickness of
 254 the fabricated membranes show that the hot-pressed membranes have lower porosity and thickness
 255 values compared to the neat samples [42]. Thus, the permeability and rejection can be enhanced
 256 through a straightforward hot-pressing process [32].

257

258 3.3. Wettability

259 One of the major obstacles to the universality of MD is membrane wetting. The wetting
260 phenomenon starts with the larger pores, and then gradually spreads throughout the whole
261 membrane. Therefore, a larger maximum pore size is not favorable. While the pore size range
262 applicable for MD membranes is between 0.1 and 1 μm , the preferred pore size for membranes
263 applied for the MD process is reported to be in the range of 0.2 - 0.5 μm [12,46]. There are several
264 factors to assess the wetting tendency of a membrane during the MD process such as WCA,
265 maximum pore size, and LEP, which will be discussed later in this section. Moreover, the
266 relationship of WCA, maximum pore size, and LEP is governed by the Laplace-Young equation
267 ($\text{LEP} = -(\beta\gamma_1 \cos \theta)/r_{\text{max}}$) [47]. In simpler terms, to fabricate an optimal membrane, a balance
268 between the abovementioned factors must be met. A membrane suitable for MD application should
269 have a higher WCA, smaller maximum pore size, and a higher LEP value [48]. However, a
270 hydrophobic membrane in the presence of oil in the saline feed is prone to pore blockage and pore
271 wetting due to the hydrophobic-hydrophobic interaction between the oily content and the
272 membrane surface. Therefore, the top layer that is in contact with the saline oily feed should be
273 oleophobic enough to prevent pore blockage and wetting by forming a hydration layer at the
274 membrane feed interface [20,49].

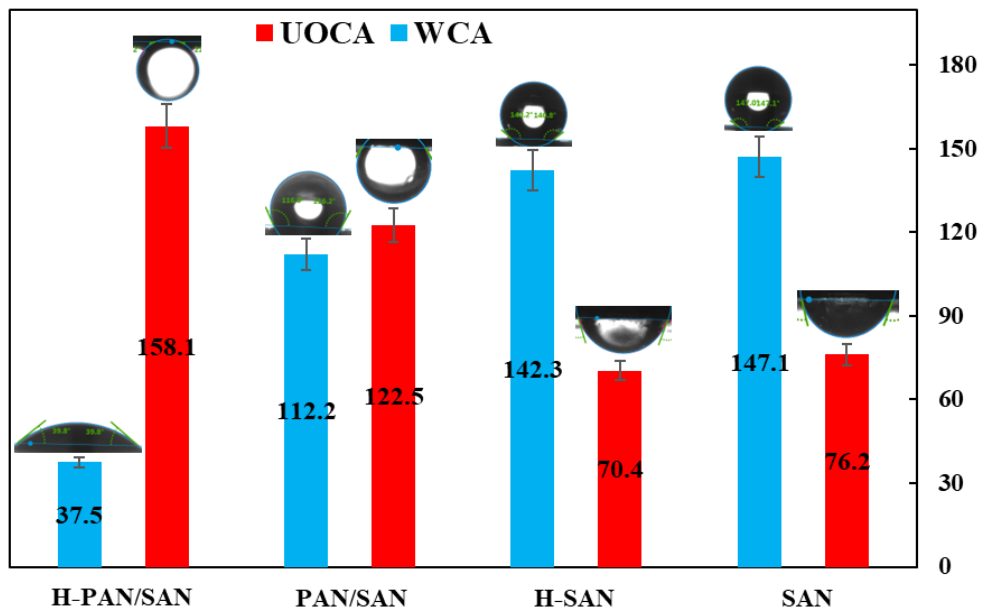
275 The WCA and UOCA values of the fabricated membranes are tabulated in Table 2 and
276 related images are shown in Fig 2. Surface hydrophobicity can be manipulated by altering surface
277 roughness using various methods [50,51]. It is worth stating that membranes fabricated via the
278 electrospinning process (using hydrophobic polymers) have intrinsically higher WCA compared
279 to membranes fabricated via other methods (i.e., NIPS). This can be ascribed to the non-woven
280 nature of the fabricated membranes, which elevates surface roughness to form a re-entrant
281 structure [52]. The WCA for the neat and H-SAN was measured as $147.1 \pm 1^\circ$ and $142.3 \pm 1^\circ$,

282 respectively. Since the surface energy is constant, the reduction can be attributed to a decrease in
283 surface roughness caused by the hot-pressing process [32,42]. Additionally, the WCA for the
284 bottom layer of the PAN/SAN membrane was measured as $147.1 \pm 1^\circ$ and $141.7 \pm 1^\circ$ for neat and
285 hot-pressed ones, respectively. It is essentially the same as the H-SAN membrane since they were
286 fabricated and hot-pressed under the same parameters. The WCA for the top layer of the neat and
287 hot-pressed PAN/SAN membranes was measured as $112.2 \pm 1^\circ$ and $37.5 \pm 1^\circ$, respectively. This
288 sharp decline can be ascribed to the highly rough surface of the neat PAN membrane that increases
289 the amount of trapped air underneath the membrane. Moreover, the reported WCAs in Table 2
290 were measured immediately after placing a water droplet on the surface. Once the hot-pressing
291 process was applied, surface roughness was reduced to considerably boost hydrophilicity. In
292 addition, UOCA was improved from 122.5° for the PAN/SAN membrane to 158.1° for the H-
293 PAN/SAN membrane. So, the oil repellency of the top layer underwent substantial enhancement
294 by simply employing the hot-pressing process. A film showing the behavior of a gasoline droplet
295 when contacting the top surface of the H-PAN/SAN is provided as supporting data (Video S1).

296 As mentioned previously, the existence of large pores may lead to partial pore wetting
297 which will eventually lead to total wetting. Therefore, a hot-pressing process can significantly
298 enhance the wetting resistance of the fabricated membrane. As seen in Table 2, the maximum pore
299 size for the neat SAN and the neat PAN/SAN membrane decreased from 4.12 ± 0.04 and $1.32 \pm$
300 $0.01 \mu\text{m}$ to 0.91 ± 0.02 and $0.52 \pm 0.02 \mu\text{m}$, respectively. The reported values are in the favorable
301 range reported by Pan et al. [46]. The largest maximum pore size and mean pore size were
302 measured for the neat SAN membrane, which results in a larger fiber diameter with a fluffy
303 structure of the fabricated membrane. The smallest pore size was for the hot-pressed PAN/SAN
304 membrane due to its compact structure.

305 The LEP value is the minimum transmembrane pressure exerted that will lead to the liquid
 306 feed overcoming the repellency of the hydrophobic surface and wetting the pores. [49] LEP value
 307 is one of the most important determining factors indicating the wetting resistance of the fabricated
 308 membranes because higher LEP values can guarantee a superior anti-wetting performance
 309 throughout the MD process. Table 2 demonstrates that higher LEP values have a better anti-wetting
 310 performance for the fabricated membranes. For the hot-pressed membranes compared to the
 311 corresponding neat membranes, the LEP value increased considerably. The LEP value for the neat
 312 SAN and neat PAN/SAN membranes increased from 41.1 ± 2 and 65.3 ± 2 kPa to 120.3 ± 2 and
 313 156.2 ± 2 kPa for the H-SAN and H-PAN/SAN membrane, respectively. This can be attributed to
 314 a decline in the maximum pore size because they are inversely correlated according to the Laplace-
 315 Young equation [53,54].

316



317

318 Fig. 2. A diagram showing the in-air WCA and UOCA measurements for the used
 319 membranes in this study. The top layer of the membranes was used to measure these values. As an

320 example, in-air WCA for H-PAN/SAN was measured by placing DI water on the top of the
321 membrane (PAN nanofibrous layer). To measure UOCA using the same membrane, it was
322 immersed in water to contact the gasoline droplet to the top layer. [Video S1](#) clearly shows how
323 UOCA tests were performed.

324

325 3.4. DCMD

326 DCMD performance of the H-SAN and H-PAN/SAN membranes using saline water and
327 oily saline water as a feed was thoroughly investigated. The neat membrane was not further
328 assessed due to low mechanical strength (see ref. [\[52\]](#)), large maximum pore size ($>1\ \mu\text{m}$, see
329 [Table 2](#)), low LEP value, as well as high thickness [\[32\]](#). It is a well-known fact that the existence
330 of contaminants in the feed water can lead to partial wetting or pore blockage of the membrane,
331 which will adversely affect MD performance [\[55,56\]](#). Due to the composition of the saline oily
332 feed, the wetting phenomena can be identified by observing the water conductivity in the permeate.
333 The DCMD operating condition such as temperature difference ($\Delta T = 35\ ^\circ\text{C}$), feed concentration,
334 and permeate flow rates (0.48 L/min) were kept constant during the 24 h test.

335 [Fig 3](#) shows flux-time and conductivity-time profiles for the hot-pressed SAN and H-
336 PAN/SAN membranes using saline water ([Fig 3-A](#)) and oily saline water ([Fig 3-B](#)) as a feed. Using
337 the saline feed, a mean permeate flux of 42.26 and 34.89 $\text{kg}/\text{m}^2\ \text{h}$ was measured for the H-SAN
338 and H-PAN/SAN, respectively. The H-SAN membrane achieved a higher flux compared to the
339 dual-layer H-PAN/SAN membrane in saline water. The lower permeate flux for the H-PAN/SAN
340 membrane can be attributed to the additional mass transfer resistance of the PAN top layer. The
341 final EC value for the tested membranes did not exceed 5 $\mu\text{S}/\text{cm}$. The EC value showed no sign of
342 membrane wetting in both cases since it does not demonstrate a rising trend. Also, both membranes

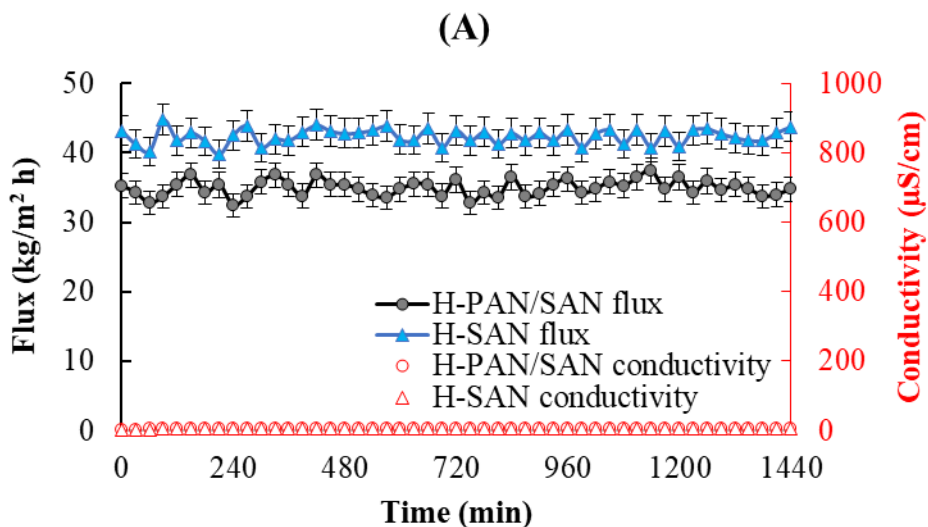
343 demonstrated high rejection (>99.9%) without a decline in permeate flux during the DCMD
344 process due to high hydrophobicity and a proper LEP value.

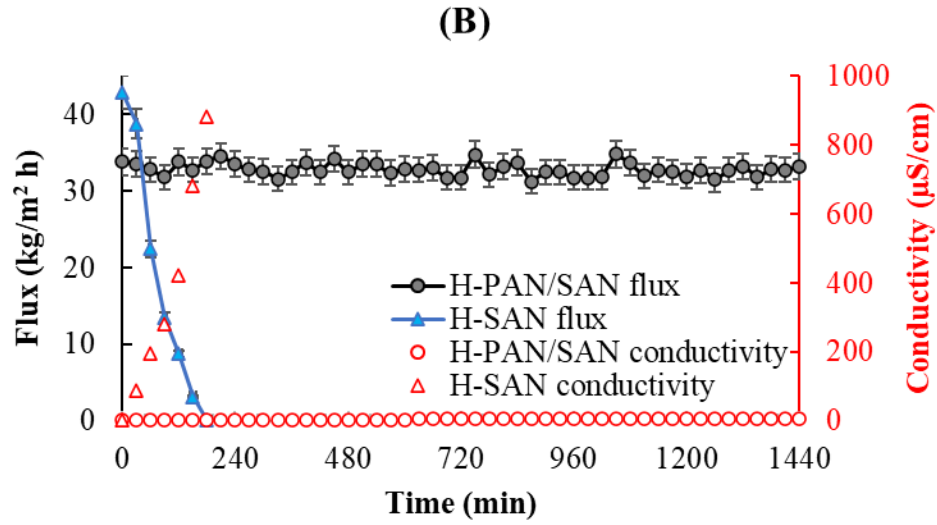
345 **Fig 3-B** shows the DCMD performance of the membranes for treatment of the saline oily
346 feed. In the presence of oil, the H-PAN/SAN membrane showed a high rejection (>99.9%), without
347 a decline in permeate flux during the DCMD process, while in the case of the single-layer H-SAN
348 membrane, the permeate flux sharply dropped due to pore blockage caused by the hydrophobic-
349 hydrophobic interaction. Moreover, the adsorption of oil can increase the probability of pore
350 wetting [57]. The membrane wetting is confirmed by the increase in EC value depicted in **Fig 3-**
351 **B**. The mean permeate flux for the H-PAN/SAN membrane was 32.80 kg/m² h, which shows a 6%
352 reduction in the permeate flux when compared to the saline water. This flux reduction can be
353 caused by the formation of an oily layer that restricts the evaporation area [58]. The salt rejection
354 of the H-PAN/SAN membrane also demonstrated the effect of a strong hydration layer between
355 the membrane and oil droplets.

356 **Fig 4 shows the DCMD performance of the H-PAN/SAN membrane for treating SDS-**
357 **including saline oily feed (SDS concentration, 0.2 mM; salt concentration, 35 g/L; gasoline**
358 **concentration, 1 g/L). Permeate flux and salt rejection were measured as 31.97 ± 2 kg/m² h**
359 **and >99.9%, respectively, during 9 h continuous test. Applied DCMD conditions were the**
360 **same as the previous tests (Temperature differences. 35 °C; feed and permeate flow rates,**
361 **0.48 L/min). A negligible reduction in permeate flux was observed due to temporary fouling**
362 **by smaller oil droplets. However, superior under water oil repellency of the H-PAN/SAN**
363 **membrane by creating a strong hydration layer made a proper barrier for reversable fouling**
364 **of oil droplets as these small oil particles can join together to form a bigger oil droplet to**

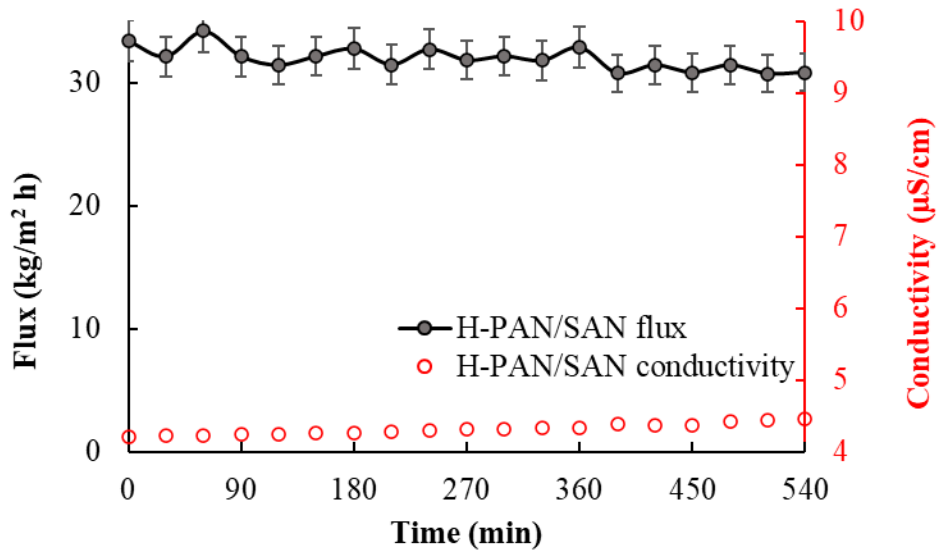
365 **detach easily for the surface. Also, small pore size of the nanofibrous PAN layer can help to**
366 **repel oil droplets to keep DCMD process going.**

367 A literature survey of recent work regarding dual-layer membranes is provided in Table 3.
368 The tabulated works were used for saline oily water treatment using the DCMD process. The salt
369 (35 g/L) and oil concentrations (1 g/L crude oil expect for this work) were the same when
370 compared to the reported results. The H-PAN/SAN membrane was comparable with the literature
371 considering UOCA. Due to the superior hydrophilicity of the PAN top layer in the dual-layer
372 structure, a superoleophobic surface was observed. It can sufficiently repel oil droplets to keep the
373 DCMD performance at a good level (i.e., high salt rejection without any change in flux).
374 Considering environmental issues and cost-effectiveness, the proposed dual-layer membrane
375 outperforms the other membranes by using a straightforward and eco-friendly hot-pressing, low-
376 toxic DMSO solvent, productive electroblowing process, and low-priced membrane materials.
377





378 **Fig 3.** DCMD performance of the H-SAN and H-PAN/SAN using (A) saline water (35 g/L NaCl)
 379 and (B) oily saline water as feed. The temperature of feed and permeate were 60 ± 1 and 25 ± 1
 380 $^{\circ}\text{C}$, respectively. Moreover, the flow rate of 0.48 L/min was applied to the feed and permeate sides.
 381



382
 383 **Fig 4. DCMD performance of H-PAN/SAN membrane for treating SDS-including saline oily**
 384 **water feed solution. Temperature difference and feed/permeate flow rate were set at 35°C**
 385 **and 0.48 mL/min, respectively.**

386 **Table 3.** Physical characteristics and DCMD performance of recently published flat-sheet membranes for saline oily treatment (35 g
 387 NaCl + 1 g oil/L).

Membrane	UOCA (°)	ϵ (%)	r_{mean} (μm)	δ (μm)	LEP (kPa)	Flux ($\text{kg}/\text{m}^2 \text{ h}$)	ΔT (°C)	t_{DCMD} (h)	R (%)	Reference
Janus NFMs	164	-	1.45	66	136.0	25.4	40	30	100	[29]
Modified PVDF	149.5	72.5	0.38	180.1	326	26.1	40	36	100	[18]
PTFE/PAN-OH	161.7	69.8	0.21	267.8	375	15.2	33	25	~100	[59]
CTS/PFO-PVDF	>130	-	-	177.5	300	27.0	40	36	99.9	[60]
PTFE/PVA-Si-GA	156.5	41.6	0.41	348.0	-	17.5	33	50	100	[20]
PTFE/CA-SiNPs	154.2	50.6	0.47	303.0	-	~19.9 ^a	33	30	-	[28]
PTFE-9CA	158	62.5	0.21	248	371	16.85	33	18	100	[61]
H-PAN/SAN	158.1	75.4	0.27	77	156.2	32.80	35	24	>99.9	Current work

388 ^a Initial flux

389

390 **4. Conclusion**

391 For the treatment of saline oily water by DCMD, an eco-friendly and inexpensive
392 PAN/SAN membrane was fabricated. In order to boost the production rate, the electroblowing
393 process was implemented using a low-toxic DMSO solvent to fabricate a dual-layer PAN/SAN
394 membrane. Then, through a simple hot-pressing process, the membrane characteristics including
395 a decrease in surface hydrophobicity and an increase in the LEP value were manipulated in a way
396 to meet the demands of the MD process. Interaction between oil and the hydrophobic surface was
397 mitigated by a layer of PAN nanofibers. As the PAN layer of the hot-pressed PAN/SAN membrane
398 became underwater superoleophobic, nearly complete salt rejection without any considerable
399 increase in EC value was measured while for the hot-pressed single-layer SAN membrane, the
400 wetting started from the beginning of the DCMD process. It is hopeful that the anti-wetting and
401 anti-fouling properties of the fabricated membrane can address the challenging issue of saline oily
402 water treatment in a more scalable, eco-friendly, and cost-efficient manner.

403

404 **Declaration of competing interest**

405 The authors declare that they have no known competing financial interests or personal
406 relationships that could have appeared to influence the work reported in this paper.

407

408 **Acknowledgment**

409 This work is dedicated to my father (Bahram Sallakh Niknejad) who backed me a lot during
410 the past years. He is the sole provider of my published papers (11 papers) and I enjoy having him
411 on my side.

412

413 **Appendix A. Supplementary data**

414 Cross-sectional morphology of sonicated H-PAN/SAN membrane is also provided in [Fig](#)
415 [S1](#). A video showing the nonstick character of the H-PAN/SAN membrane against gasoline was
416 also provided in [video S1](#).

417

418 **References**

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**A scalable dual-layer PAN/SAN nanofibrous membrane for treatment of saline oily water
using membrane distillation**

Dear Prof. Tong,

Guest Editor of VSI: MD & MCr,

We would like to thank you and the respected reviewers. Revised sections were shown using the bold red color font for the readers to notice. A DCMD test with surfactant-including feed water was added to the manuscript.

Kind regards,

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Reviewer#3

1. The authors have not addressed the use of the surfactant containing feed. Unfortunately, the first author having moved to another institute does not seem to be a sufficient reason not to address this point.

Response: Revised sections are in bold red color font. Please refer to the following to see the revised sections below:

“Fig 4 shows the DCMD performance of the H-PAN/SAN membrane for treating SDS-including saline oily feed (SDS concentration, 0.2 mM; salt concentration, 35 g/L; gasoline concentration, 1 g/L). Permeate flux and salt rejection were measured as 31.97 ± 2 kg/m² h and >99.9%, respectively, during 9 h continuous test. Applied DCMD conditions were the same as the previous tests (Temperature differences, 35 °C; feed and permeate flow rates, 0.48 L/min). A negligible reduction in permeate flux was observed due to temporary fouling by smaller oil droplets. However, superior under water oil repellency of the H-PAN/SAN membrane by creating a strong hydration layer made a proper barrier for reversable fouling of oil droplets as these small oil particles can join together to form a bigger oil droplet to detach easily for the surface. Also, small pore size of the nanofibrous PAN layer can help to repel oil droplets to keep DCMD process going.

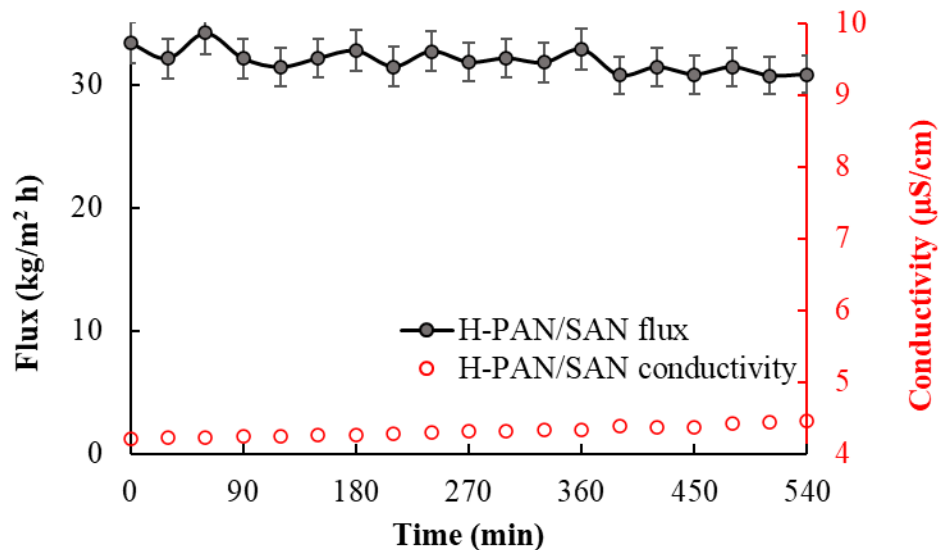


Fig 4. DCMD performance of H-PAN/SAN membrane for treating SDS-including saline oily water feed solution. Temperature difference and feed/permeate flow rate were set at 35 °C and 0.48 mL/min, respectively. “

2. If the authors' main novelty is hot pressing, they need to show what the hot press does physically and chemically, with sufficient characterization and impact of pressing conditions. Simply showing that hot press improves hydrophilicity does not seem to be sufficient to support the claimed novelty.

Response: The pressing process concept to improve the physical characteristics of the nanofibrous structures is well established in the literature. As the hot-pressing temperature is well below the melting and glass transition temperatures of the used polymers, chemical investigation is not necessary as we used these membranes without *any chemical modification*. Hot-pressing process gives more uniform physical characteristics like reduced pore size and thickness, improved mechanical strength as well as reduced hydrophobicity because of roughness reduction. It needs to be stated that polyacrylonitrile (PAN) is a hydrophilic polymer and water contact angle (WCA) of the neat fibrous structure depends on different factors during the membrane fabrication process. Air/gas-assisted electrospinning or electroblowing can make nanofibrous membrane surface even more rough, since we used non-conductive PP non-woven layer as support to collect nanofibers instead of aluminum foil. The spinning speed of the electroblowing is so much higher than regular electrospinning process making nanofibrous layer less organized to increase surface roughness as air flow adds another turbulency to the fibers' journey toward the collector. Nanofibrous membrane is getting thicker and thicker by passing of time due to increasing fiber repulsion as evident in Table 2. Also, polarity of the polymer is another factor to have either a uniform or less organized fibrous layer. Based on our experience, an electroblown PVDF nanofiber membrane is more compact, and porosity of the neat fibrous structure is lower than 94% showing the effect of polymer polarity on the characteristics of final product. As a result, above mentioned factors led to a higher porosity (> 97%) for electroblown nanofibrous membranes compared to that of electrospun nanofibers. Based on the literature review we did, a wide range of WCA was reported for *neat* electrospun PAN nanofibers from 118.2 [1] down to 66.1° [2]. So, surface roughness is the main

reason for these variations in WCA, and after hot-pressing process the surface becomes uniform to reduce WCA. In our previous work conducted by Sadeghzadeh et al. [3], nanofibrous polystyrene (PS) membranes were fabricated using the same electroblowing device we used in this study and the mean surface roughness was reduced from 428 to 290 nm after hot-pressing. Also, Shirazi et al. [4] used the same device to form electrospun PS nanofibers and they reported mean roughness of 301 nm showing that electroblowing forms a surface with more roughness. We mentioned these factors inside the manuscript to explain why WCA reduced sharply.

As we mentioned in the first revision stage, it is the first report to use pressing process to design a **Janus nanofibrous membrane for saline oily water treatment with no chemical modification**.

[1] Zhang, L., He, Y., Ma, L., Chen, J., Fan, Y., Zhang, S., Shi, H., Li, Z. and Luo, P., 2019. Hierarchically stabilized PAN/ β -FeOOH nanofibrous membrane for efficient water purification with excellent antifouling performance and robust solvent resistance. *ACS applied materials & interfaces*, 11(37), pp.34487-34496.

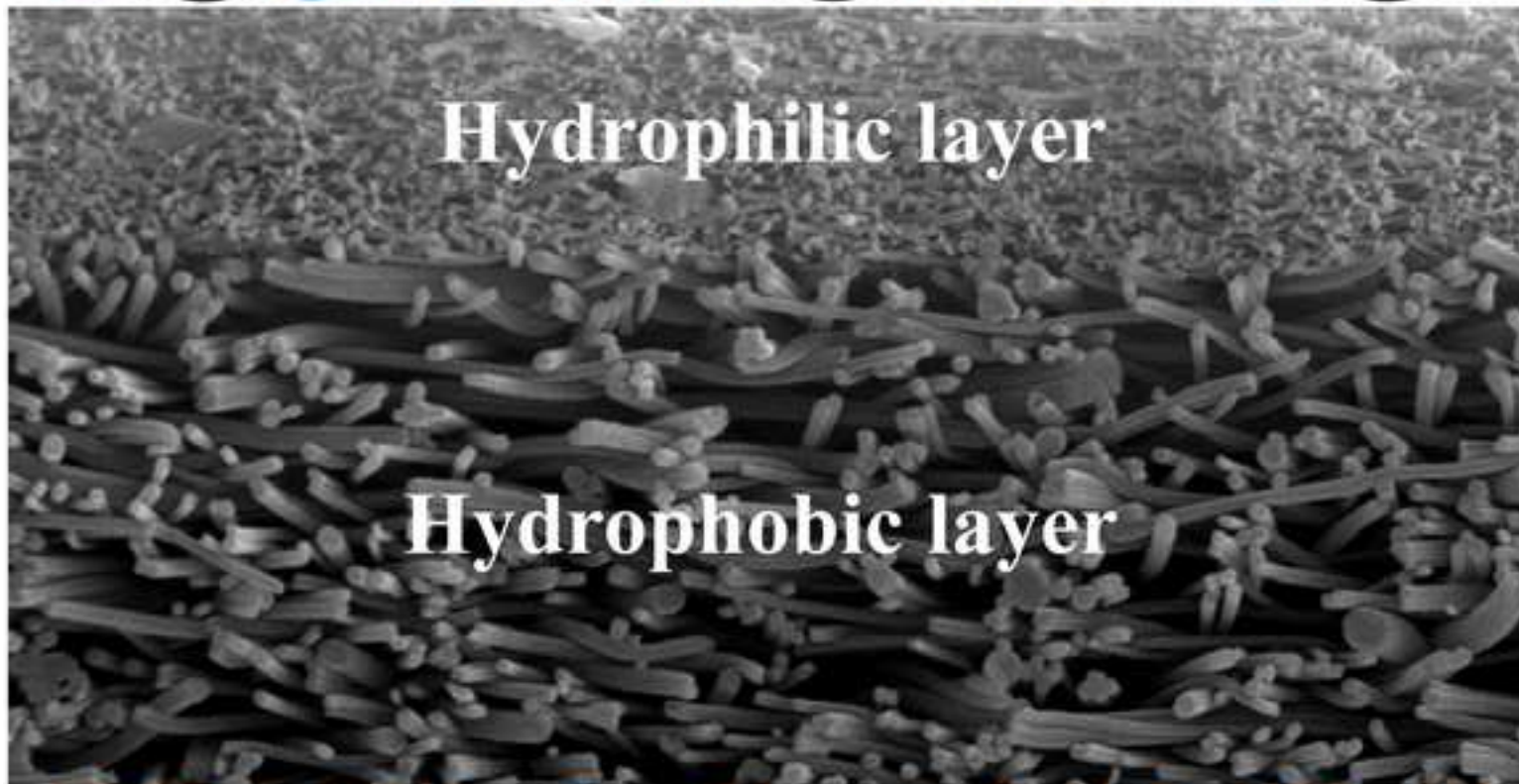
[2] Yalcinkaya, F., Yalcinkaya, B., Pazourek, A., Mullerova, J., Stuchlik, M. and Maryska, J., 2016. Surface modification of electrospun PVDF/PAN nanofibrous layers by low vacuum plasma treatment. *International Journal of Polymer Science*, 2016.

[3] Sadeghzadeh, A., Bazgir, S., & Shirazi, M. M. A. (2020). Fabrication and characterization of a novel hydrophobic polystyrene membrane using electroblowing technique for desalination by direct contact membrane distillation. *Separation and Purification Technology*, 239, 116498.

[4] Shirazi, M. M. A., Kargari, A., Bazgir, S., Tabatabaei, M., Shirazi, M. J. A., Abdullah, M. S., ... & Ismail, A. F. (2013). Characterization of electrospun polystyrene membrane for treatment of biodiesel's water-washing effluent using atomic force microscopy. *Desalination*, 329, 1-8.

Highlights

- ✓ Nanofibrous PAN/SAN membrane fabrication using electroblowing process.
- ✓ Fast hot-pressing process to form underwater superoleophobic membrane.
- ✓ UOCA of $\sim 158^\circ$ and in-air WCA of $\sim 37^\circ$ because of hot-pressing.
- ✓ Robust DCMD performance using saline oily water as feed.



● Salt ● Oil ● Vapor ● Distillate

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

CRedit authorship contribution statement

Ali Sallakh Niknejad: Investigation, Writing - Original Draft, Writing - Review and Editing
Conceptualization, Visualization, Supervision. **Ali Kargari:** Writing - Review and Editing,
Validation, Supervision. **Mahsa Namdari:** Writing - Review and Editing. **Mohammad
Pishnamazi:** Writing - Review and Editing. **Reza Sallakhniknezhad:** Writing - Original Draft.
Masoud Barani: Resources. **Esmail Ranjbari:** Resources. **Saeed Bazgir:** Resources. **Mohsen
Rasouli:** Resources. **Drew McAvoy:** Writing - Review and Editing.

1 **A scalable dual-layer PAN/SAN nanofibrous membrane for treatment of saline oily water**
2 **using membrane distillation**

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21

22 **Abstract**

23 Single-layer hydrophobic membranes are prone to fouling while subjected to a feed
 24 containing hydrophobic contaminants. In this study, using the green solvent Dimethyl sulfoxide
 25 (DMSO), dual-layer nanofibrous poly-acrylonitrile (PAN)/styrene-acrylonitrile (SAN)
 26 membranes were fabricated using the highly productive electroblowing process. Then through a
 27 simple hot-pressing process, the desirable hydrophilicity was achieved for PAN/SAN membrane.
 28 The water contact angle (WCA) for the top layer fell from $112.2 \pm 1^\circ$ to $37.5 \pm 1^\circ$ after hot-
 29 pressing, while the WCA for the bottom layer decreased slightly from $147.1 \pm 1^\circ$ to $142.3 \pm 1^\circ$.
 30 Moreover, an underwater oil contact angle (UOCA) of $158.1 \pm 1^\circ$ was achieved for the PAN/SAN
 31 membrane. Direct contact membrane distillation (DCMD) tests were performed for synthetic
 32 saline water and synthetic saline oily water. While the permeate flux dropped for the single-layer
 33 SAN membrane, the dual-layer PAN/SAN membrane, due to underwater superoleophobicity,
 34 achieved a stable permeate flux for 24 h with a nearly complete salt rejection (>99.9%). This study
 35 addresses the pore wetting and declines in the permeate flux of the membrane distillation (MD)
 36 application in the treatment of saline oily water by implementing scalable, cost-efficient, and eco-
 37 friendly approaches.

38
 39 **Keywords:** Hydrophilicity; Underwater superoleophobicity; Hot-pressing; Dual-layer; DCMD.

40

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59 **1. Introduction**

60 Saline wastewater production has increased in recent decades due to considerable
61 development in varied industries [1,2]. Wastewater treatment can be done using methods like
62 physicochemical processes, aerobic treatment, anaerobic digestion, and membrane separation
63 technologies [3-6]. Considering membrane-based separation, the membrane distillation (MD)
64 process has been regarded as a next-generation, sustainable approach to treating hypersaline
65 waters. The MD is a non-isothermal process that uses a porous hydrophobic membrane to direct
66 hot water vapor to produce pure water [7,8]. Interestingly, MD can make full use of inexpensive
67 heat resources to supply clean water and due to its operational condition, it will not be influenced
68 by the quality of wastewater, making it a sought-after technology for desalination and wastewater
69 treatment [9-13].

70 Surface fouling and pore wetting are however the downsides of the MD process due to the
71 complex composition of hypersaline wastewaters [14]. In general, membrane performance can be
72 detrimentally affected by fouling [15-17]. Severe reduction in membrane permeation because of
73 foulant accumulation on/in the membrane can be followed by pore wetting and worsening of
74 treated water quality [18,19]. Although the MD process experiences lower fouling compared to
75 the pressure-driven membrane processes, the MD membranes are vulnerable to oil due to strong
76 hydrophobic-hydrophobic interaction [20]. Low-surface-energy materials like surfactants can also
77 increase the pore wetting of the MD membrane. These contaminants can easily invade the

78 membrane pores and render the membrane more hydrophilic which will lead to the failure in
79 rejecting salts [21-23].

80 To tackle the problem of traditional MD membranes, the concept of dual-layer structure including
81 hydrophilic/hydrophobic design has been proposed to reduce fouling and wetting [24,25]. As dual-
82 layer structures have two layers with hydrophilic and hydrophobic characteristics, researchers
83 called them the Janus membranes after the imaginary Greek god with two faces [26]. The
84 hydrophilic layer of a dual-layer structure can be fabricated by coating with hydrophilic materials
85 [27], electrospinning [28], electrospraying [29], and film casting using non-solvent-induced phase
86 separation (NIPS) [30] to form a hydrophilic or even superhydrophilic top layer with superior
87 underwater oil repellency. The hydrophobic/superhydrophobic or even omniphobic support layer
88 can also be applied to reject salts to avoid pore wetting, while the hydrophilic top layer reduces
89 fouling.

90 The robustness of the top layer is of vital importance in using dual-layer membranes.
91 Delamination or removal of the top layer during the MD process allows oil droplets to attach to
92 the membrane surface and reduce the permeate flux [31]. It also causes a severe reduction in
93 rejection because of pore wetting. Another issue is the environmental concern for using
94 hydrophilic materials, fluoroalkyl silanes, and also the complexity of the membrane fabrication
95 process. From an industrial point of view, a fabrication process should be time-efficient and as
96 simple as possible with a considerably lower production cost for both applied materials and the
97 fabrication process.

98 In this study, a practical dual-layer structure was fabricated using inexpensive polyacrylonitrile
99 (PAN) and styrene-acrylonitrile (SAN) polymers. To make the fabrication process more
100 productive and less time-consuming, a modified version of the conventional electrospinning,

101 electroblowing process was used. The electroblowing or air-assisted electrospinning process
102 makes use of dry airflow to boost the fiber production rate [32,33]. The PAN polymer and its
103 nanofibers are intrinsically hydrophilic but not hydrophilic enough to be used as a decent top layer
104 for reducing oil fouling. The surface hydrophilicity was impressively improved using a fast-hot-
105 pressing process. The fabricated structure turned from a spongy and soft structure to a dense and
106 firm structure that: 1) reduced the chance of top-layer detachment during the direct contact MD
107 (DCMD) process, 2) decreased the hydrophobicity of the surface to sufficiently reduce underwater
108 interaction between membrane surface and oil droplets, 3) minimized the carbon footprint resulted
109 from the application of different materials that are currently applied to make more hydrophilic
110 surfaces. The membrane fabrication process was also eco-friendly because of the use of dimethyl
111 sulfoxide (DMSO) as the solvent during the electroblowing process. To our knowledge, this is the
112 first report of constructing an underwater superoleophobic and in-air highly hydrophilic dual-layer
113 structure for the MD process using a straightforward hot-pressing process without any excessive
114 post or pre-modification processes.

115

116 **2. Experimental**

117 *2.1. Materials and chemicals*

118 Commercial PAN polymer was purchased from the Isfahan Textile Co, Iran. Commercially
119 available SAN polymer (SAN-4) was purchased from Ghaed Basir Co., Iran. DMSO, acetone,
120 NaCl, and isopropyl alcohol (IPA) (extra-pure grade) were provided by Amertat Shimi, Co, Iran.
121 Cetyltrimethylammoniumbromide (CTAB) and sodium dodecyl sulfate (SDS) were purchased from
122 Merck, Germany. A commercial non-woven fabric made of polypropylene (PP) polymer was used

123 as support for nanofiber collection during the electroblowing process. Gasoline was provided by a
124 local supplier.

125

126 2.2. Membrane fabrication process

127 The neat dual-layer PAN/SAN nanofibrous membrane was fabricated using PAN/DMSO
128 + acetone (80 wt% DMSO and 20 wt% acetone; 8 wt% PAN) and SAN/DMSO + acetone (70 wt%
129 DMSO and 30 wt% acetone; 17.5 wt% SAN) spinning solutions. Also, a small amount of CTAB
130 salt was added to the spinning solution to reduce bead-on-string nanofibers. The electroblowing
131 condition is summarized in [Table 1](#). A co-axial electroblowing needle and syringe were attached
132 via a polyethylene (PE) tube. With the help of a dry air flow, a continuous nanofiber jet was formed
133 on the PP non-woven mat. First, a nanofibrous SAN layer was fabricated and then a nanofibrous
134 PAN layer was fabricated on the support SAN layer. After completing the electroblowing process,
135 the neat PAN/SAN nanofibrous membrane (designated as PAN/SAN) was immediately hot-
136 pressed (H-PAN/SAN) under 2000 psi pressure at a temperature of 85 °C for 30 s to improve the
137 physical integrity of the produced dual-layer nanofibrous membrane. A single-layer SAN
138 nanofibrous membrane (designated as SAN) was also fabricated and hot-pressed (designated as
139 H-SAN) to form a more uniform structure.

140

141 [Table 1](#). Process parameters of the electroblowing process.

Nanofibrous layer	Voltage (kV)	Working distance (cm)	Polymer injection rate ($\mu\text{L}/\text{min}$)	Air flowrate (NL/min)	Spinning time (min)
PAN	22	30	90	2.5	45
SAN	18	30	90	2	45

142

143 2.3. Characterization

144 Surface morphology of the prepared nanofibrous layers and cross-sectional images of
145 PAN/SAN nanofibrous membrane were observed by scanning electron microscopy (SEM, AIS
146 2100C, Korean Republic). The dual-layer H-PAN/SAN membrane was fractured in liquid nitrogen
147 before the SEM test. Fiber diameter was measured by Digimizer software, and the average value
148 of 100 fiber diameters was reported.

149 The thickness of the samples was measured using an accurate micrometer and cross-
150 sectional images. The mean value of the three tests was reported as the mean thickness value.

151 The porosity was evaluated using the gravimetric method. First, membrane tickets were heated at
152 80 °C using a digital oven for 4 h to remove moisture and then weighed to determine the samples'
153 dry weight. For the next step, pre-dried samples were submerged in IPA and reweighed. A full
154 description of the process can be found in Zhou et al. [34].

155 The surface hydrophobicity of the prepared samples was determined by measurement of the water
156 contact angle (WCA) using a drop shape analyzer device (KRUSS analyzer-G10 Drop Shape
157 Analyzer, Germany). The underwater oleophobicity of the fabricated samples was measured by
158 underwater oil contact angle (UOCA) using the same device.

159 The pore size of the single-layer SAN and dual-layer PAN/SAN membranes were measured using
160 a lab-made bubble-point set-up. See Niknejad et al. [35] for more information.

161 The liquid entry pressure (LEP) of water was evaluated by a homemade set-up. Briefly, a circular-
162 shaped sample of the dual-layer PAN/SAN and single-layer SAN membranes were placed between
163 semi-cell modules. Pressure (kPa) was gradually increased to the point where the first deionized
164 (DI) water droplet was observable on the membrane surface, and this pressure was regarded as the
165 LEP value. The mean value of the three tests using independent membranes was reported.

166

167 2.4. DCMD process

168 A lab-scale DCMD set-up was used to evaluate the prepared membranes for saline and
169 saline oily feeds. The representation of the DCMD device can be found in Bonyadi et al. [36]. The
170 synthetic saline oily water was prepared by adding 1 g gasoline and 35 g NaCl to the DI water
171 using a high-speed blender (rotating speed, 5000 rpm; mixing time, 1 h). Feed and permeate
172 temperatures were 60 ± 1 °C and 25 ± 1 °C, respectively. Feed and permeate streams were both set
173 at 0.48 L/min. The feed water was mixed every 2 hours using the blender for about 5 minutes to
174 ensure that the oil dispersion was uniform when it comes in contact with the active side of the
175 membrane (hydrophilic layer). Also, the components of the DCMD set-up were mostly made from
176 polyurethane (pipes) and polyethylene (feed tanks and membrane module). Therefore, the saline
177 oily feed was circulated at least three times before starting the DCMD tests using a pump to ensure
178 that the oil adhesion on the equipment was kept at a minimum during the DCMD tests to ensure a
179 more accurate result. The mass and quality of the purified water were regularly monitored using a
180 digital balance and an electrical conductivity (EC) meter, respectively. By knowing the active
181 membrane surface area (m^2), the period of the recorded weight (h), and the amount of added water
182 into the permeate tank (kg), the permeate flux (kg/m^2 h) could be determined.

183

184 3. Results and discussion

185 3.1. Morphology

186 The surface morphology of the top and bottom layers of the PAN/SAN membrane and the
187 cross-sectional SEM image of the H-PAN/SAN membrane are shown in Fig 1. It is noteworthy
188 that the morphology of the single-layer SAN was the same as the bottom layer of the PAN/SAN

189 membrane, as they were fabricated and hot-pressed under the same operating conditions.
190 Therefore, only one SEM image is presented.

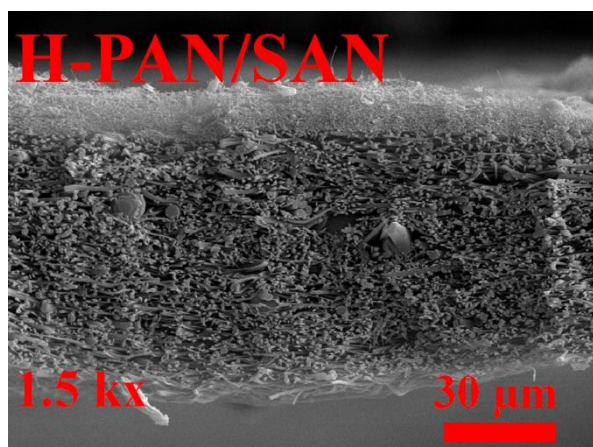
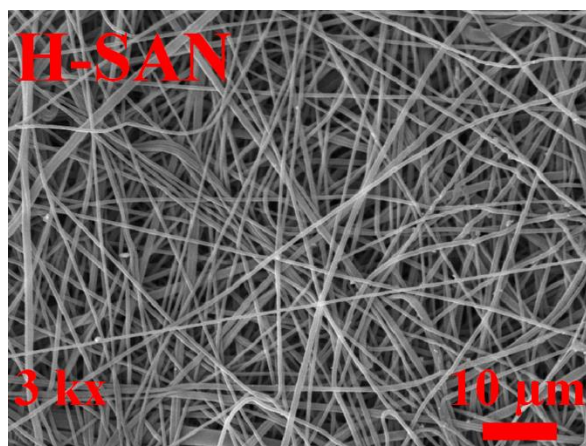
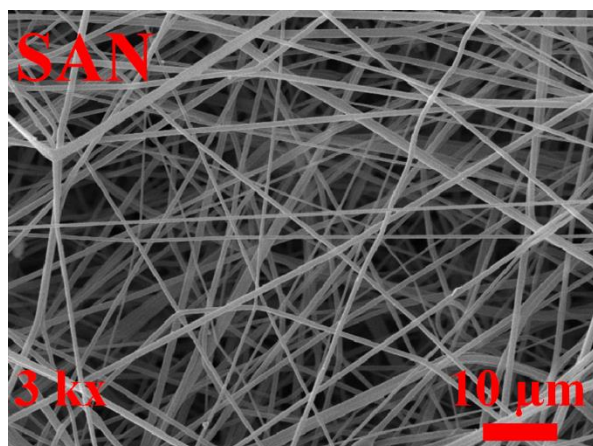
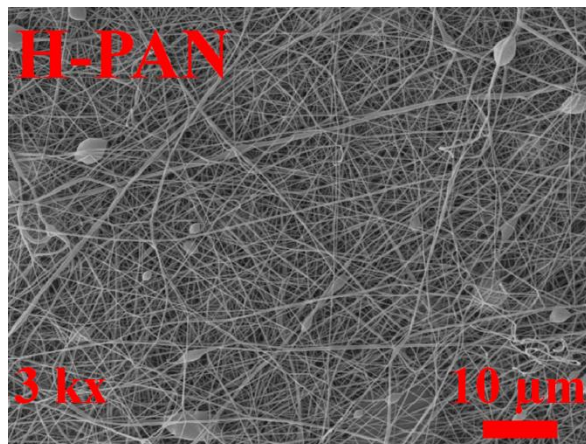
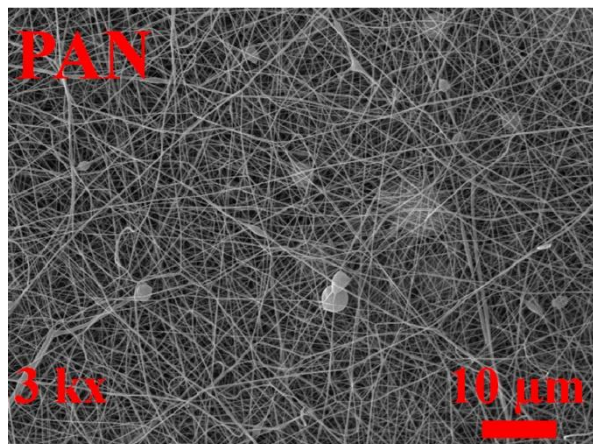
191 The polymer concentration in the dope solution is one of the deciding factors of the electrospinning
192 process. For example, under the same electrospinning parameters, using dope solutions with low
193 polymer concentrations will lead to the formation of cup-like defects and beaded fibers. However,
194 raising the polymer concentration might result in a fiber diameter increase [37,38]. Therefore, the
195 desirable morphology for the nanofibers can be obtained by controlling the polymer concentration.
196 As observed, a defect-free nanofibrous SAN substrate with 3D microporous interconnected
197 networks was fabricated with a suitable polymer concentration and CTAB addition to the dope
198 solution [39]. For the PAN top layer, to maintain a balance between defects and fiber diameter
199 enhancement, a microporous dense interconnected with minimal defects was fabricated by
200 choosing the suitable polymer concentration.

201 For the dual-layer membrane, the mean fiber diameter of the neat SAN, hot-pressed SAN, neat
202 PAN, and hot-pressed PAN was measured as 431 ± 58 , 453 ± 32 , 157 ± 48 , and 174 ± 34 nm,
203 respectively. Throughout the hot-pressing process, the mean fiber diameter was essentially
204 constant because the temperature, pressure, and duration were not high enough to lead to an
205 increase in fiber diameter while they were sufficient to increase fiber density by effectively
206 compacting more nanofibers in a specific area [40]. Fig S1 Shows the cross-sectional SEM image
207 for the H-PAN/SAN membrane after sonication to prove the robustness of the formed layer.

208 Visible changes in the pore size of the membranes can be observed after the hot-pressing process
209 (Table 2). The hot-pressed samples had a smaller mean pore size compared to the neat membranes,
210 which is evident by the naked eye. The cross-section image shows that the PAN and SAN layers
211 are closely bonded with no signs of delamination at the PAN/SAN interface (Fig 1). This can be

212 attributed to the effective hot-pressing and the residual DMSO in the nanofibers, which further
213 facilitate the adhesion at the PAN/SAN interface and reduces the probability of layer delamination.

214



215 Fig 1. The surface morphology of the top layer, the bottom layer, and also the cross-section
216 morphology of the fabricated PAN/SAN and H-PAN/SAN membranes. The SEM images'
217 magnification with their scale bar is also presented.

218

219 *3.2. Porosity and thickness*

220 Electrospun nanofibrous membranes typically have higher porosities when compared to
221 membranes fabricated via other membrane fabrication methods [35]. A membrane fabricated via
222 the electroblowing process has a higher porosity than a membrane fabricated via the conventional
223 electrospinning process (>95%). Moreover, using a longer spinning duration and a PP nonwoven
224 mat while the charge density is kept constant can assist in making the fabricated membrane more
225 porous by increasing the resistance against the electrical charge [41].

226 Higher porosity is favorable as permeability correlates positively with the porosity of the applied
227 membrane in the MD process due to trapped air in the membrane pores that act as an insulator,
228 thus reducing the heat loss by conduction and the water vapors having more space to pass through
229 as a result of an increase in mean free path [35]. However, the downside is that these membranes
230 have a larger pore size, loose and random fiber structure, wider pore size distribution, and
231 insufficient mechanical strength that makes them inapplicable in the MD process [32]. After the
232 hot-pressing process, the porosity of the membranes showed a declining trend. The porosity for
233 neat SAN and PAN/SAN membranes dropped from $97.8 \pm 2\%$ and $95.7 \pm 2\%$ to $78.5 \pm 1\%$ and
234 $75.4 \pm 1\%$, respectively. This result is also in conformity with the declining trend reported by Yao
235 et al. [42].

236

237 **Table 2.** Thickness, δ ; porosity, ϵ ; mean pore size, r_{mean} ; maximum pore size, r_{max} ; water contact
 238 angle, WCA; liquid entry pressure, LEP of the fabricated membranes.

Membrane	δ (μm)	ϵ (%)	r_{mean} (μm)	r_{max} (μm)	WCA ($^{\circ}$)	UOCA ($^{\circ}$)	LEP (kPa)
SAN	540 ± 50	97.8 ± 2	1.64 ± 0.03	4.12 ± 0.04	147.1 ± 1	76.2 ± 1	41.1 ± 2
H-SAN	64 ± 3	78.5 ± 1	0.43 ± 0.02	0.91 ± 0.02	142.3 ± 1	70.4 ± 1	120.3 ± 2
PAN/SAN	845 ± 50	95.7 ± 2	0.58 ± 0.02	1.32 ± 0.01	$112.2 \pm 1^{\text{a}}$ $147.1 \pm 1^{\text{b}}$	122.5 ± 1	65.3 ± 2
H-PAN/SAN	77 ± 3	75.4 ± 1	0.27 ± 0.01	0.52 ± 0.02	$37.5 \pm 1^{\text{a}}$ $141.7 \pm 1^{\text{b}}$	158.1 ± 1	156.2 ± 2

239 ^a top layer WCA

240 ^b bottom side WCA of SAN layer

241

242 Membrane thickness is another important parameter that affects the permeate flux, mechanical
 243 properties, and salinity the membrane can efficiently handle. The increase in salinity causes a drop
 244 in feed vapor pressure, consequently, if the transmembrane temperature is not high enough the loss
 245 in energy efficiency becomes considerable [43]. Although thicker membranes have higher energy
 246 efficiency, the driving force is insufficient to fully boost permeation. These membranes are
 247 preferable in the treatment of highly saline waters due to possible mass transfer resistance and a
 248 lower permeate flux [44,45]. Therefore, to achieve higher rejection and permeate flux, it is
 249 essential to determine a suitable balance between porosity and thickness. The thickness value for
 250 the neat SAN and PAN/SAN membranes reduced from 540 ± 50 and $845 \pm 50 \mu\text{m}$ to 64 ± 3 and
 251 $77 \pm 3 \mu\text{m}$ for the H-SAN and H-PAN/SAN, respectively. The porosity and thickness of the
 252 fabricated membranes show that the hot-pressed membranes have lower porosity and thickness
 253 values compared to the neat samples [42]. Thus, the permeability and rejection can be enhanced
 254 through a straightforward hot-pressing process [32].

255

256 3.3. Wettability

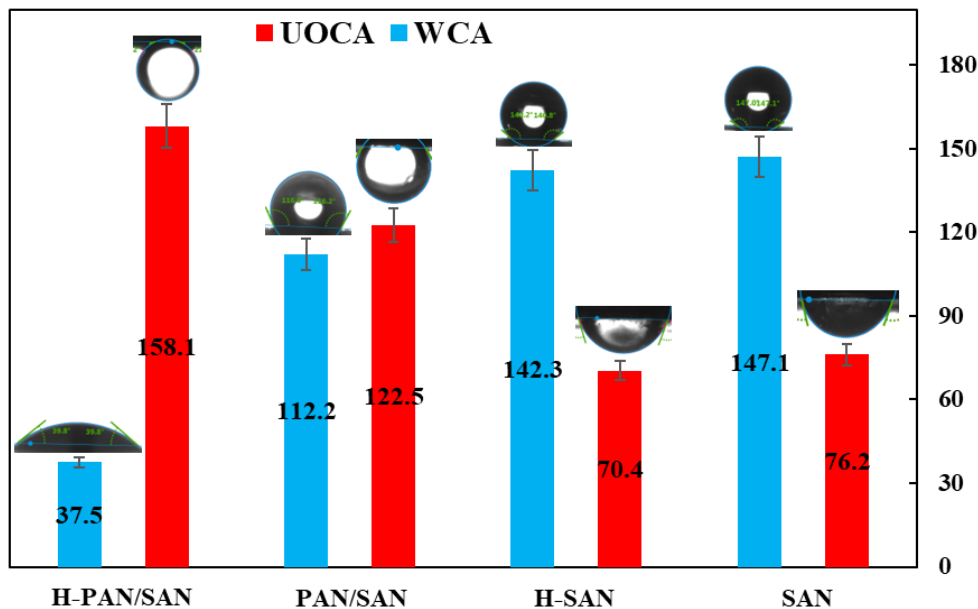
257 One of the major obstacles to the universality of MD is membrane wetting. The wetting
258 phenomenon starts with the larger pores, and then gradually spreads throughout the whole
259 membrane. Therefore, a larger maximum pore size is not favorable. While the pore size range
260 applicable for MD membranes is between 0.1 and 1 μm , the preferred pore size for membranes
261 applied for the MD process is reported to be in the range of 0.2 - 0.5 μm [12,46]. There are several
262 factors to assess the wetting tendency of a membrane during the MD process such as WCA,
263 maximum pore size, and LEP, which will be discussed later in this section. Moreover, the
264 relationship of WCA, maximum pore size, and LEP is governed by the Laplace-Young equation
265 ($\text{LEP} = -(\beta\gamma_1 \cos \theta)/r_{\text{max}}$) [47]. In simpler terms, to fabricate an optimal membrane, a balance
266 between the abovementioned factors must be met. A membrane suitable for MD application should
267 have a higher WCA, smaller maximum pore size, and a higher LEP value [48]. However, a
268 hydrophobic membrane in the presence of oil in the saline feed is prone to pore blockage and pore
269 wetting due to the hydrophobic-hydrophobic interaction between the oily content and the
270 membrane surface. Therefore, the top layer that is in contact with the saline oily feed should be
271 oleophobic enough to prevent pore blockage and wetting by forming a hydration layer at the
272 membrane feed interface [20,49].

273 The WCA and UOCA values of the fabricated membranes are tabulated in Table 2 and
274 related images are shown in Fig 2. Surface hydrophobicity can be manipulated by altering surface
275 roughness using various methods [50,51]. It is worth stating that membranes fabricated via the
276 electrospinning process (using hydrophobic polymers) have intrinsically higher WCA compared
277 to membranes fabricated via other methods (i.e., NIPS). This can be ascribed to the non-woven
278 nature of the fabricated membranes, which elevates surface roughness to form a re-entrant
279 structure [52]. The WCA for the neat and H-SAN was measured as $147.1 \pm 1^\circ$ and $142.3 \pm 1^\circ$,

280 respectively. Since the surface energy is constant, the reduction can be attributed to a decrease in
281 surface roughness caused by the hot-pressing process [32,42]. Additionally, the WCA for the
282 bottom layer of the PAN/SAN membrane was measured as $147.1 \pm 1^\circ$ and $141.7 \pm 1^\circ$ for neat and
283 hot-pressed ones, respectively. It is essentially the same as the H-SAN membrane since they were
284 fabricated and hot-pressed under the same parameters. The WCA for the top layer of the neat and
285 hot-pressed PAN/SAN membranes was measured as $112.2 \pm 1^\circ$ and $37.5 \pm 1^\circ$, respectively. This
286 sharp decline can be ascribed to the highly rough surface of the neat PAN membrane that increases
287 the amount of trapped air underneath the membrane. Moreover, the reported WCAs in [Table 2](#)
288 were measured immediately after placing a water droplet on the surface. Once the hot-pressing
289 process was applied, surface roughness was reduced to considerably boost hydrophilicity. In
290 addition, UOCA was improved from 122.5° for the PAN/SAN membrane to 158.1° for the H-
291 PAN/SAN membrane. So, the oil repellency of the top layer underwent substantial enhancement
292 by simply employing the hot-pressing process. A film showing the behavior of a gasoline droplet
293 when contacting the top surface of the H-PAN/SAN is provided as supporting data ([Video S1](#)).
294 As mentioned previously, the existence of large pores may lead to partial pore wetting which will
295 eventually lead to total wetting. Therefore, a hot-pressing process can significantly enhance the
296 wetting resistance of the fabricated membrane. As seen in [Table 2](#), the maximum pore size for the
297 neat SAN and the neat PAN/SAN membrane decreased from 4.12 ± 0.04 and 1.32 ± 0.01 μm to
298 0.91 ± 0.02 and 0.52 ± 0.02 μm , respectively. The reported values are in the favorable range
299 reported by Pan et al. [46]. The largest maximum pore size and mean pore size were measured for
300 the neat SAN membrane, which results in a larger fiber diameter with a fluffy structure of the
301 fabricated membrane. The smallest pore size was for the hot-pressed PAN/SAN membrane due to
302 its compact structure.

303 The LEP value is the minimum transmembrane pressure exerted that will lead to the liquid feed
 304 overcoming the repellency of the hydrophobic surface and wetting the pores. [49] LEP value is
 305 one of the most important determining factors indicating the wetting resistance of the fabricated
 306 membranes because higher LEP values can guarantee a superior anti-wetting performance
 307 throughout the MD process. Table 2 demonstrates that higher LEP values have a better anti-wetting
 308 performance for the fabricated membranes. For the hot-pressed membranes compared to the
 309 corresponding neat membranes, the LEP value increased considerably. The LEP value for the neat
 310 SAN and neat PAN/SAN membranes increased from 41.1 ± 2 and 65.3 ± 2 kPa to 120.3 ± 2 and
 311 156.2 ± 2 kPa for the H-SAN and H-PAN/SAN membrane, respectively. This can be attributed to
 312 a decline in the maximum pore size because they are inversely correlated according to the Laplace-
 313 Young equation [53,54].

314



315

316 Fig 2. A diagram showing the in-air WCA and UOCA measurements for the used membranes in
 317 this study. The top layer of the membranes was used to measure these values. As an example, in-

318 air WCA for H-PAN/SAN was measured by placing DI water on the top of the membrane (PAN
319 nanofibrous layer). To measure UOCA using the same membrane, it was immersed in water to
320 contact the gasoline droplet to the top layer. [Video S1](#) clearly shows how UOCA tests were
321 performed.

322

323 3.4. DCMD

324 DCMD performance of the H-SAN and H-PAN/SAN membranes using saline water and
325 oily saline water as a feed was thoroughly investigated. The neat membrane was not further
326 assessed due to low mechanical strength (see ref. [\[52\]](#)), large maximum pore size ($>1 \mu\text{m}$, see
327 [Table 2](#)), low LEP value, as well as high thickness [\[32\]](#). It is a well-known fact that the existence
328 of contaminants in the feed water can lead to partial wetting or pore blockage of the membrane,
329 which will adversely affect MD performance [\[55,56\]](#). Due to the composition of the saline oily
330 feed, the wetting phenomena can be identified by observing the water conductivity in the permeate.
331 The DCMD operating condition such as temperature difference ($\Delta T = 35 \text{ }^\circ\text{C}$), feed concentration,
332 and permeate flow rates (0.48 L/min) were kept constant during the 24 h test.

333 [Fig 3](#) shows flux-time and conductivity-time profiles for the hot-pressed SAN and H-PAN/SAN
334 membranes using saline water ([Fig 3-A](#)) and oily saline water ([Fig 3-B](#)) as a feed. Using the saline
335 feed, a mean permeate flux of 42.26 and 34.89 $\text{kg/m}^2 \text{ h}$ was measured for the H-SAN and H-
336 PAN/SAN, respectively. The H-SAN membrane achieved a higher flux compared to the dual-layer
337 H-PAN/SAN membrane in saline water. The lower permeate flux for the H-PAN/SAN membrane
338 can be attributed to the additional mass transfer resistance of the PAN top layer. The final EC value
339 for the tested membranes did not exceed 5 $\mu\text{S/cm}$. The EC value showed no sign of membrane
340 wetting in both cases since it does not demonstrate a rising trend. Also, both membranes

341 demonstrated high rejection (>99.9%) without a decline in permeate flux during the DCMD
342 process due to high hydrophobicity and a proper LEP value.

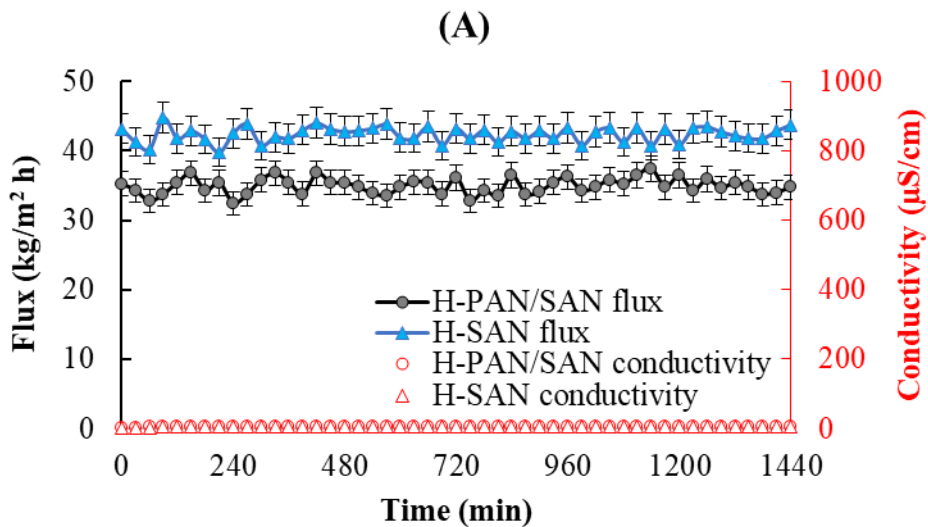
343 Fig 3-B shows the DCMD performance of the membranes for treatment of the saline oily feed. In
344 the presence of oil, the H-PAN/SAN membrane showed a high rejection (>99.9%), without a
345 decline in permeate flux during the DCMD process, while in the case of the single-layer H-SAN
346 membrane, the permeate flux sharply dropped due to pore blockage caused by the hydrophobic-
347 hydrophobic interaction. Moreover, the adsorption of oil can increase the probability of pore
348 wetting [57]. The membrane wetting is confirmed by the increase in EC value depicted in Fig 3-
349 B. The mean permeate flux for the H-PAN/SAN membrane was 32.80 kg/m² h, which shows a 6%
350 reduction in the permeate flux when compared to the saline water. This flux reduction can be
351 caused by the formation of an oily layer that restricts the evaporation area [58]. The salt rejection
352 of the H-PAN/SAN membrane also demonstrated the effect of a strong hydration layer between
353 the membrane and oil droplets.

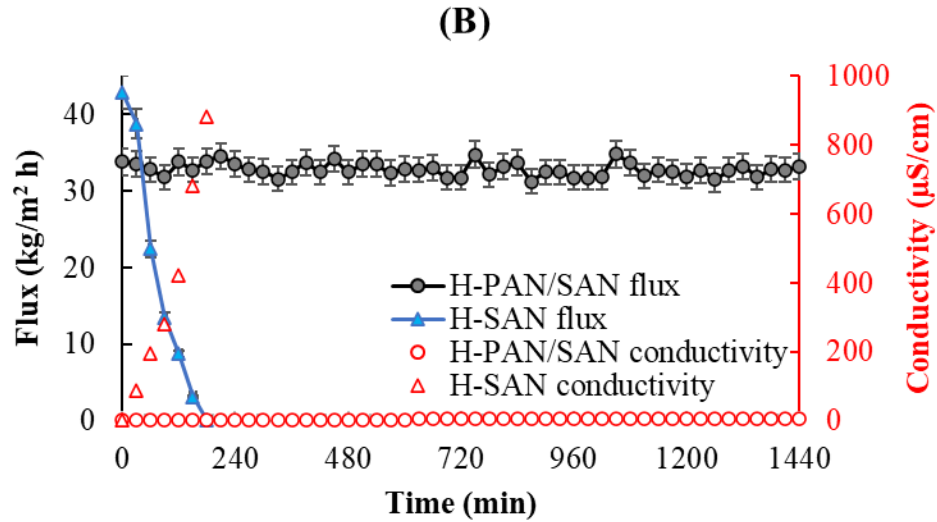
354 Fig 4 shows the DCMD performance of the H-PAN/SAN membrane for treating SDS-
355 including saline oily feed (SDS concentration, 0.2 mM; salt concentration, 35 g/L; gasoline
356 concentration, 1 g/L). Permeate flux and salt rejection were measured as 31.97 ± 2 kg/m² h and
357 >99.9%, respectively, during 9 h continuous test. Applied DCMD conditions were the same as the
358 previous tests (Temperature differences. 35 °C; feed and permeate flow rates, 0.48 L/min). A
359 negligible reduction in permeate flux was observed due to temporary fouling by smaller oil
360 droplets. However, superior under water oil repellency of the H-PAN/SAN membrane by creating
361 a strong hydration layer made a proper barrier for reversable fouling of oil droplets as these small
362 oil particles can join together to form a bigger oil droplet to detach easily for the surface. Also,

363 tight pore size of the nanofibrous PAN layer can help to repel oil droplets to keep DCMD process
 364 going.

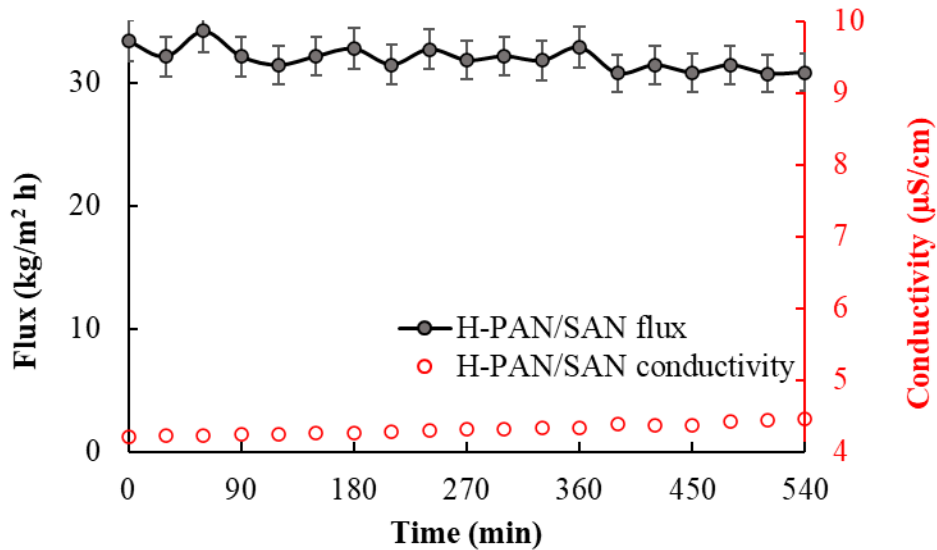
365 A literature survey of recent work regarding dual-layer membranes is provided in [Table 3](#). The
 366 tabulated works were used for saline oily water treatment using the DCMD process. The salt (35
 367 g/L) and oil concentrations (1 g/L crude oil expect for this work) were the same when compared
 368 to the reported results. The H-PAN/SAN membrane was comparable with the literature
 369 considering UOCA. Due to the superior hydrophilicity of the PAN top layer in the dual-layer
 370 structure, a superoleophobic surface was observed. It can sufficiently repel oil droplets to keep the
 371 DCMD performance at a good level (i.e., high salt rejection without any change in flux).
 372 Considering environmental issues and cost-effectiveness, the proposed dual-layer membrane
 373 outperforms the other membranes by using a straightforward and eco-friendly hot-pressing, low-
 374 toxic DMSO solvent, productive electroblowing process, and low-priced membrane materials.

375





376 **Fig 3.** DCMD performance of the H-SAN and H-PAN/SAN using (A) saline water (35 g/L NaCl)
 377 and (B) oily saline water as feed. The temperature of feed and permeate were 60 ± 1 and 25 ± 1
 378 $^{\circ}\text{C}$, respectively. Moreover, the flow rate of 0.48 L/min was applied to the feed and permeate sides.
 379



380
 381 **Fig 4.** DCMD performance of H-PAN/SAN membrane for treating SDS-including saline oily
 382 water feed solution. Temperature difference and feed/permeate flow rate were set at $35\text{ }^{\circ}\text{C}$ and 0.48
 383 mL/min, respectively.

384 **Table 3.** Physical characteristics and DCMD performance of recently published flat-sheet membranes for saline oily treatment (35 g
 385 NaCl + 1 g oil/L).

Membrane	UOCA (°)	ϵ (%)	r_{mean} (μm)	δ (μm)	LEP (kPa)	Flux ($\text{kg}/\text{m}^2 \text{ h}$)	ΔT (°C)	t_{DCMD} (h)	R (%)	Reference
Janus NFMs	164	-	1.45	66	136.0	25.4	40	30	100	[29]
Modified PVDF	149.5	72.5	0.38	180.1	326	26.1	40	36	100	[18]
PTFE/PAN-OH	161.7	69.8	0.21	267.8	375	15.2	33	25	~100	[59]
CTS/PFO-PVDF	>130	-	-	177.5	300	27.0	40	36	99.9	[60]
PTFE/PVA-Si-GA	156.5	41.6	0.41	348.0	-	17.5	33	50	100	[20]
PTFE/CA-SiNPs	154.2	50.6	0.47	303.0	-	~19.9 ^a	33	30	-	[28]
PTFE-9CA	158	62.5	0.21	248	371	16.85	33	18	100	[61]
H-PAN/SAN	158.1	75.4	0.27	77	156.2	32.80	35	24	>99.9	Current work

386 ^a Initial flux

387

388 **4. Conclusion**

389 For the treatment of saline oily water by DCMD, an eco-friendly and inexpensive
390 PAN/SAN membrane was fabricated. In order to boost the production rate, the electroblowing
391 process was implemented using a low-toxic DMSO solvent to fabricate a dual-layer PAN/SAN
392 membrane. Then, through a simple hot-pressing process, the membrane characteristics including
393 a decrease in surface hydrophobicity and an increase in the LEP value were manipulated in a way
394 to meet the demands of the MD process. Interaction between oil and the hydrophobic surface was
395 mitigated by a layer of PAN nanofibers. As the PAN layer of the hot-pressed PAN/SAN membrane
396 became underwater superoleophobic, nearly complete salt rejection without any considerable
397 increase in EC value was measured while for the hot-pressed single-layer SAN membrane, the
398 wetting started from the beginning of the DCMD process. It is hopeful that the anti-wetting and
399 anti-fouling properties of the fabricated membrane can address the challenging issue of saline oily
400 water treatment in a more scalable, eco-friendly, and cost-efficient manner.

401

402 **Declaration of competing interest**

403 The authors declare that they have no known competing financial interests or personal
404 relationships that could have appeared to influence the work reported in this paper.

405

406 **Acknowledgment**

407 This work is dedicated to my father (Bahram Sallakh Niknejad) who backed me a lot during the
408 past years. He is the sole provider of my published papers (11 papers) and I enjoy having him on
409 my side.

410

411 **Appendix A. Supplementary data**

412 Cross-sectional morphology of sonicated H-PAN/SAN membrane is also provided in [Fig S1](#). A
413 video showing the nonstick character of the H-PAN/SAN membrane against gasoline was also
414 provided in [video S1](#).

415

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