



UWL REPOSITORY

repository.uwl.ac.uk

Lignin modified PVDF membrane with antifouling properties for oil filtration

Zakaria, N.A., Hussin, M. Hazwan, Ahmad, A.L., Leo, C.P., Poh, Phaik Eong, Behzadian, Kourosh
ORCID: <https://orcid.org/0000-0002-1459-8408>, Akinwumi, Isaac I., Moghayedi, Alireza and
Diazsolano, Joaquin (2021) Lignin modified PVDF membrane with antifouling properties for oil
filtration. *Journal of Water Process Engineering*, 43. p. 102248.

<http://dx.doi.org/10.1016/j.jwpe.2021.102248>

This is the Accepted Version of the final output.

UWL repository link: <https://repository.uwl.ac.uk/id/eprint/8498/>

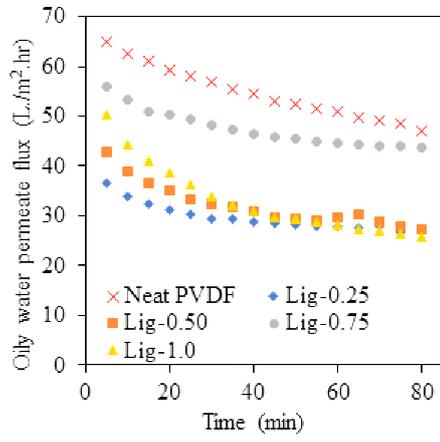
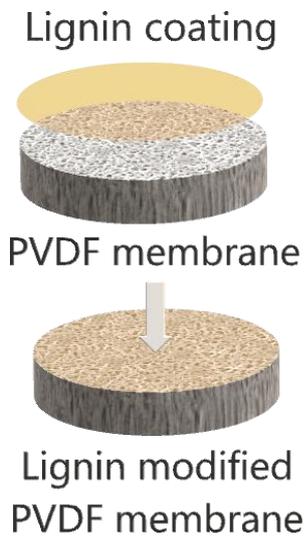
Alternative formats: If you require this document in an alternative format, please contact:
open.research@uwl.ac.uk

Copyright: Creative Commons: Attribution-Noncommercial-No Derivative Works 4.0

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy: If you believe that this document breaches copyright, please contact us at open.research@uwl.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.

Graphical Abstract



1 **Lignin modified PVDF membrane with antifouling properties for oil**
2 **filtration**

3 **N.A. Zakaria¹, M. Hazwan Hussin², A.L. Ahmad¹, C.P. Leo^{1,*} Phaik Eong Poh³,**
4 **Kourosh Behzadian⁴, Isaac I. Akinwumi⁵, Alireza Moghayedi⁶, Joaquin**
5 **Diazsolano⁷**

6 *¹School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300*
7 *Nibong Tebal, Pulau Pinang, Malaysia*

8 *²Lignocellulosic Research Group, School of Chemical Sciences, Universiti Sains Malaysia,*
9 *11800, Minden, Penang, Malaysia*

10 *³Chemical Engineering Discipline, School of Engineering, Monash University Malaysia, Jalan*
11 *Lagoon, 47500 Bandar Sunway, Selangor, Malaysia*

12 *⁴School of Engineering and Computing, University of West London, St. Mary's Rd, London,*
13 *W55RF, UK*

14 *⁵Department of Civil Engineering, College of Engineering, Covenant University, Ota, Ogun*
15 *State, Nigeria*

16 *⁶Faculty of Engineering and Built Environment, University of Cape Town, 7700, Cape Town,*
17 *South Africa*

18 *⁷Tekmann, SA de CV, Cda de Profr Miguel F. Trommer lote 5, 42950, Tlaxcoapan, Hidalgo,*
19 *México*

20 **ABSTRACT**

21 Lignin is a sustainable chemical that can be extracted from a wide range of
22 lignocellulosic biowaste. It was blended into polymeric membranes to improve
23 membrane morphology for filtration. **Lignin dissolved in NaOH solution can be coated**
24 **on different substrates to improve the surface hydrophilicity.** In this work, the
25 polyvinylidene fluoride (PVDF) membrane was coated with lignin to improve the
26 filtration of oily water. Lignin was dissolved in NaOH solution with varied alkaline

27 concentration (0.25-1.50 wt.%) and lignin concentration (0.25-1.00 wt.%). The PVDF
28 membrane degraded in the highly alkaline solution, but the increasing lignin content
29 reduced the membrane pore size for the effective rejection of oil emulsion. The PVDF
30 membrane modified with 0.75 wt% of lignin in 0.5 wt% of NaOH solution attained a
31 permeate flux about $70 \text{ L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$, but a slightly lower permeate flux of $55 \text{ L}\cdot\text{m}^{-2}\cdot\text{hr}^{-1}$
32 was recorded after immersed in alkaline solution 12 h. The lignin modified membrane
33 rejected up to 99.30% of oil, while the neat PVDF membrane only rejected 83.30% of
34 oil. The lignin modified membrane showed slightly lower but stable flux than the neat
35 PVDF membrane due to the reduction of membrane fouling.

36 *Keywords:* lignin; membrane; microfiltration; oil

37 1. Introduction

38

39 Lignin is a biopolymer that can be isolated from a wide range of lignocellulosic
40 waste, representing near to 30% of lignocellulosic waste [1]. It consists of
41 phenylpropanoids such as coniferyl, sinapyl and coumaryl alcohols at a varied ratio and
42 a small amount of lignols, depending on the plant source. More than 50 million tons of
43 lignin and lignin-related chemicals were produced annually [2]. Their emerging
44 applications as bioplastics, adsorbents, anticorrosion coating, adhesive, and more have
45 been extensively reported.

46 For wastewater treatment, lignin has been developed into flocculant,
47 adsorbents, and membrane filters. The lignin-based flocculants are efficient in the
48 removal of dyes, heavy metals, chemical oxygen demand (COD), phosphate in
49 wastewater after amination, carboxymethylation, crosslinking, sulfonation, and
50 grafting [3]. The lignin-based adsorbent could be prepared through the mentioned
51 modification strategies to remove heavy metal ions in water [4] similarly to porous
52 adsorbents [5]. The adsorption of heavy metals on lignin through ion-exchange could
53 be further improved by increasing the surface area. Lignin derivatives also adsorbed
54 dyes [6] and drugs [7], likewise the porous adsorbents [8–10].
55 Glycidyltrimethylammonium chloride was used to modify lignin to remove 80% of
56 anionic viruses through flocculation followed by filtration [11]. Polyurathane/lignin
57 composite foam with lignin content up to 50 wt.% was produced through blending
58 followed by polymerization [12]. The hydrophobic polyurethane foam was transformed
59 into the hydrophilic composite foam after incorporating lignin. The adsorption of oil
60 from water into the composite foam increased, and the composite foam showed
61 excellent reusability.

62 Lignin-modified membranes were studied in recent years due to the continued
63 demand for hydrophilic modification agents in membrane fabrication. Membranes
64 made of hydrophobic polymers could be easily fouled [13]. Yong et al. [14] reported
65 on the blending of lignin into polyvinyl chloride (PVC) dope solution before phase
66 inversion to form an antifouling membrane for the ultrafiltration of oily solution. A
67 high lignin content promoted the increment of the glass transition temperature, as
68 shown in the thermogravimetric spectra with only a single phase. X-ray diffraction
69 spectra also confirmed the compatibility between lignin and PVC due to the interaction
70 between the hydroxyl groups of lignin and the chlorine groups of PVC, as proven in
71 Fourier-transform infrared spectra. Membrane pore size and porosity were slightly
72 increased, but the surface hydrophilicity was significantly improved for promoting
73 water permeation more than 3 times. Oil rejection, chemical oxygen demand (COD)
74 reduction, and suspended solid removal of PVC membrane was also greatly enhanced
75 beyond 83.92% after lignin incorporation. Using lignin as the additive in the fabrication
76 of polyethersulfone (PES) membrane, Shamaei et al. [15] observed an increment in the
77 underwater oil contact angle and negative surface charge. The lignin modified PES
78 membrane attained about 270% higher water permeability than PES membrane, but
79 rejection of organic pollutants dropped about 9% due to pore size enlargement was
80 reported. The blending of lignin into the dope solution containing polybenzoxazine, the
81 dense membrane formed with the hydrophilic surface [16]. Phenol and tertiary amine
82 groups of polybenzoxazine were released from the hydrogen bondings network
83 constructed between polybenzoxazine and lignin. The water permeation in
84 pervaporation for the dehydration THF and isopropanol aqueous solution increased
85 more than 2-folds. Lavanya and Balakrishna [17] further blended the peanut shell
86 power, which comprises of cellulose, hemicellulose and lignin, into polysulfone (PSf)

87 membrane dope solution prior phase inversion. Pore formation was greatly enhanced,
88 resulting in large pores and finger-like channels. The lignocellulose modified PSf
89 membrane achieved higher water permeability than PSf membrane due to the
90 improvement of porous structure and surface hydrophilicity. It rejected more BSA and
91 exhibited less fouling even though the negative surface charge increased.

92 Lignin is an anion polyelectrolyte, and it could be paired with the cationic
93 polyelectrolyte to modify polymeric membranes with a negatively charged surface.
94 Through layer-by-layer assembly, lignin/poly(diallyldimethylammonium
95 chloride) bilayers were coated on the PES ultrafiltration membrane [18]. The water
96 permeability was reduced after coating, while the molecular weight cut-off of PES
97 membrane reduced from 19 kDa to 2 kDa. Gu et al. [19] coated
98 lignin/polyethyleneimine (PEI) bilayers on polysulfone membrane. Increasing the
99 coating numbers reduce surface hydrophobicity and protein adsorption. Although
100 showing the reduced fouling in the filtration of bovine serum albumin (BSA) solution,
101 changes in membrane pore size, rejection, and permeability were not reported.

102 Alkaline extraction of lignin has been commonly reported. The lignin in
103 alkaline solution was successfully applied as the food coating [20] and packaging
104 materials [21]. Similarly, lignin in the alkaline solution is expected to form a
105 hydrophilic coating on the hydrophobic PVDF membrane to reduce fouling in filtration.
106 In this work, lignin was dissolved in NaOH solution to modify the polyvinylidene
107 fluoride (PVDF) membrane for the improvement of surface hydrophilicity and oily
108 water filtration. Unlike blending, surface modification using lignin allows the
109 improvement of membrane properties without affecting the existing membrane
110 formulation. The effects of NaOH concentration and lignin loading on membrane

111 morphology and other properties were studied. The modified membranes were further
112 tested in the filtration of oily water.

113

114 **2. Materials and methods**

115

116 *2.1. Materials*

117

118 PVDF (Solef® 6010 PVDF) from Solvay Solexis (France) was dried at 100 °C
119 before preparing the membrane dope solution. The solvent, N-methyl-2-pyrrolidone
120 (NMP) (> 99.5%) was supplied by Merck (Darmstadt, Germany), while the other
121 additives such as ortho-phosphoric acid (H₃PO₄) (> 85 %), lithium chloride (LiCl) and
122 acetone were acquired from Merck (Darmstadt, Germany). Ethanol acquired from
123 Merck (> 99.9 %, Darmstadt, Germany) was used as the coagulation bath. Lignin in the
124 form of dry powder was provided by the School of Chemical Sciences, Universiti Sains
125 Malaysia. NaOH from Sigma Aldrich (ACS reagent, ≥99.0%, pellets) was used in the
126 pH adjustment of an aqueous solution for preparing lignin solution. Corn cooking oil
127 from ACH Food Companies, Inc and Tween 80 from Merck were used to prepare oily
128 water for the filtration test.

129

130 *2.2. Synthesis and modification of membrane*

131

132 PVDF membranes were first prepared as described in the previous work [22].
133 PVDF (13 wt.%) was dissolved into NMP solvent (77 wt.%) containing acetone (5
134 wt.%), H₃PO₄ (3 wt.%), and LiCl₂ (2 wt.%) that work as the non-solvent additives. The
135 dope solution was stirred at 50 °C for 1 day. After degassing, the dope solution was cast

136 on the woven support on a glass plate at a casting gap of 400 μm (XB320D, Beijing
137 Jiahang Technology Co. Ltd., China). The wet film was immersed into the ethanol bath
138 for 20 min, followed by the water bath for 1 day to form a PVDF membrane through
139 phase inversion.

140 Lignin solution was prepared by dissolved the lignin into NaOH solution with
141 varied concentration (0.25%, 0.5%, 1.0% and 1.5%). Lignin dissolves in alkaline-based
142 aqueous system such as NaOH solution [23]. The dissolution is affected by the cation
143 size and increases drastically above pH 9. A stable coating could be formed after
144 immersing the membrane into lignin solution and rinsing with water. PVDF
145 membranes were modified via surface coating by fully immersed into the lignin
146 solution for 1 day. The modified membranes (NaOH-0.25, NaOH-0.5, NaOH-1.00,
147 NaOH-1.50) were then rinsed with distilled water and kept in distilled water for
148 characterization and filtration test. The lignin concentration was then adjusted between
149 0.25 wt.% and 1.0 wt% in the NaOH solution with concentration which caused
150 minimum changes on membrane morphology. The samples were designated as Lig-
151 0.25, Lig-0.50, Lig-0.75, Lig-1.0.

152

153 2.3. Membrane characterization

154

155 The lignin modified PVDF membranes were rinsed with deionized water and
156 dried for 24 h before characterization. The cross-section of membranes modified using
157 lignin solution with varied NaOH concentration was studied using a scanning electron
158 microscope (SEM) (HITACHI S-3000N, Hitachi Ltd., Japan). The cross-section and
159 top surface of membranes modified using lignin solution with varied lignin
160 concentration were studied using a field emission SEM (FE-SEM, Hitachi SU8010

161 model, Japan). The mean pore size of membranes was measured using a porometer
162 (Porolux 1000, IB-FT GmbH, Germany). For pore size measurement, membrane
163 samples were wetted with Porefil for 30 min before the test. The membrane samples
164 from 600 cm⁻¹ to 3,800cm⁻¹ were analyzed using Fourier transformed infrared (FT-IR)
165 spectroscopy (Nicolet iS10, Thermo Scientific, USA) to study the chemical properties
166 of membrane samples. The oil adhesion on the membranes was studied using Lauda
167 surface analyzer LSA200.

168

169 2.4. *Oil-water emulsion preparation and separation test*

170

171 The water permeate flux of membranes was determined using a dead-end stirred
172 cell, Sterlitech HP4750 (Sterlitech Corporation, WA) and distilled water at room
173 temperature. The membranes with an effective area of 14.6 cm² were tested in the
174 pressure range of 0.2-1.0 bar after compaction using nitrogen gas. The permeation flux
175 (J , L·m²·h⁻¹) was calculated using the following equation.

$$176 \quad J = \frac{V}{A \times t} \quad (1)$$

177 where V is the volume of the permeate, A is the effective area of the membrane, and t
178 is the filtration time. The water permeability was further determined from the graph of
179 water permeate flux versus pressure through linear regression. The oily water was
180 prepared by mixing oil and distilled water with a volume ratio of 1:100. Tween-80
181 (0.5mg/mL) was added to form the stable emulsion. The oil-water emulsion was
182 ultrasonicated for 15 min before feeding into the dead-end stirred cell for separation
183 test [24]. The membranes were tested at 1.0 bar and the oil rejection was calculated
184 using:

$$185 \quad r = \left(1 - \frac{c_p}{c_f}\right) \times 100\% \quad (2)$$

186 where C_p is the oil concentration in the permeate, and C_f is the oil concentration in the
187 feed solutions. The oil concentration in the permeate sample was determined using a
188 UV-visible spectrophotometer (Genesys 20, Thermo Fisher Scientific) at 225 nm [25].
189 The oil concentration was determined using a calibration curve of 0.0068-0.0543 mol/L
190 ($y = 39.94x$, $r^2 = 0.8452$). The lignin modified PVDF membrane with the highest oil
191 rejection was immersed in NaOH solution (2 wt.%) for 12 h to understand its' stability.
192 The separation performance of alkaline treated membrane in oily water filtration was
193 tested, as mentioned before.

194

195

196 3. Results and discussion

197

198 3.1. Membrane characteristics

199

200 Fig. 1 shows the cross-section morphology of the neat PVDF and PVDF
201 membrane modified with 1 wt.% of lignin dissolved in NaOH solution with varied
202 concentration. The unmodified PVDF membrane showed spongy structure with
203 interconnected pores as reported in our recent works [26], [27] and other works [28].
204 The porous structure, pore size and surface roughness are greatly affected by the solvent
205 exchange rate in the coagulating baths. The solvent exchange rate is lower in the ethanol
206 bath compared to the water bath, resulting in a spongy structure. PVDF is less soluble
207 in ethanol, reducing the precipitation rate to form a spongy structure as well [29]. The
208 SEM images in Fig. 1 (b), (c) and (d) shows that the porous structure was not
209 significantly affected after lignin coating except when NaOH solution with 1.5 wt%
210 was used. The membrane sample, NaOH-1.50 turned into a dense membrane after

211 lignin coating, as shown in Fig. 1 (e). Lignin from different plant sources and processing
212 routes is commonly soluble in alkaline solution [30], but PVDF membrane is
213 susceptible to the morphology changes in alkaline solution [31].

214 The membrane was further modified using lignin with a varied concentration in
215 NaOH solution with a low concentration of 0.5 wt.%. The morphology of membrane
216 cross-section and surface could be observed from Fig. 2. The porous surface of Lig-
217 0.25, Lig-0.5, Lig-0.75, and Lig-1.0 membranes was filled up with lignin. A very dense
218 surface was observed from the SEM image of Lig-1.0 membrane modified with 1 wt.%
219 of lignin in NaOH solution with a concentration of 0.5 wt.%. However, the surface
220 remains rough. The morphology changes observed in this work are different from the
221 morphology of PES membrane blended with lignin reported by Shamaei et al. [15]. The
222 blending promoted precipitation and the demixing rate. They caused the enlargement
223 of pore size but the reduction of the dense sublayer. On the other hand, the layer-by-
224 layer coating of poly (diallyldimethylammonium chloride) and lignin on PES
225 membrane resulted in a smooth surface [18]. The thickness of membranes without
226 fabric support was measured using SEM images as shown in Fig. 2 (a), (c), (e), and (g).
227 The membrane thickness only reduced greatly when lignin concentration was adjusted
228 to 0.25 wt.%. The anionic lignin solution at low concentration could penetrate into the
229 PVDF membrane with a negative surface charge and densified the membrane after
230 NaOH removal. Hence, the membrane thickness reduced significantly during drying
231 due to severe shrinkage. Yeo et al. [32] commented that the polymer shrinkage was
232 significantly affected by the microvoid formation after incorporating lignin.

233 The membrane pore size after modification using the varied concentration of
234 lignin solution was further measured. The changes in pore size are summarized in Table
235 1. The large pore size of the neat PVDF membrane at 0.41 μm was reduced to be smaller

236 than 0.30 μm when the lignin concentration was varied between 0.25 wt.% to 0.75
237 wt.%. However, such pore size reduction was not observed for Lig-1.0 sample
238 modified using 1 wt.% of lignin in NaOH solution with a concentration of 0.5 wt.%.
239 The lignin solution is anionic [33], and it was expected to be physically coated on PVDF
240 with a negative surface charge [34]. The high concentration of lignin solution is
241 expected to raise the electrostatic repulsion between lignin and PVDF membrane.
242 Hence, the penetration of lignin into the membrane could be greatly reduced. The lignin
243 coating tends to densify on the membrane surface after removing NaOH in the solvent
244 exchange step, as shown in Fig. 2 (c), (e), and (g). The pore size reduction could be
245 related to the polymer shrinkage caused by microvoid absence [32].

246 FTIR spectra of the neat PVDF membrane and the PVDF membranes modified
247 using lignin solution containing varied lignin concentration in NaOH solution (0.5
248 wt.%) are shown in Fig. 3. All the PVDF membrane samples exhibited the bands related
249 to CH_2 wagging vibration within 1401 – 1406.39 cm^{-1} and C-C bonding within 1165 -
250 1171 cm^{-1} . These samples also displayed C-F and C-C-C symmetrical stretching
251 vibration peaks within the range of 838 – 840 cm^{-1} and 876-878 cm^{-1} , respectively [35].
252 Syringyl (S), guaiacyl (G) and p-hydroxyphenyl (H) bands are commonly observed in
253 the FTIR spectra of lignin extracted from the alkaline pulping process [36]. Lig-0.25,
254 Lig-0.50, Lig-0.75, and Lig-1.0 samples only showed an additional peak at 1275 cm^{-1}
255 in their FTIR spectra compared to the neat PVDF membrane. The addition peak can be
256 correlated to the stretching vibration of guaiacyl rings. However, the other characteristic
257 peaks of the G band (1029 cm^{-1}) and S bands (1330, 1115 and 819.94 cm^{-1}) could not
258 be identified due to overlapping with PVDF characteristic peaks. The appearance of
259 G band at 1275 cm^{-1} and the absence of S bands could be induced by demethoxylation

260 reaction in the alkaline pulping process. This reaction transformed S groups to G groups
261 with higher stability in the lignin.

262 The water contact angle on the modified membrane samples could not be
263 measured due to the fast penetration of water droplet into the membrane sample with
264 large pores and hydrophilic surface. The oil droplet could not be placed on the
265 membrane surface for underwater contact angle measurement. Hence, the adhesion of
266 the oil droplet on the membrane surface was studied. Fig. 4 shows that the oil droplets
267 did not adhere to the membrane surface either the membrane samples have been
268 modified with lignin solution or not. Unlike our previous works [27, 37] the neat PVDF
269 membrane had not been dried before the oil adhesion test in this work. The neat PVDF
270 membrane with a rough surface could capture a water layer within the hierarchical
271 structure formed using an ethanol bath in phase inversion. The water layer captured by
272 hierarchical structure prevents fouling, as reported by others [38]. The lignin coating
273 further improved the surface hydrophilicity, and oil adhesion was not observed on the
274 lignin modified membrane samples (Lig-0.25, Lig-0.5, Lig-0.75, and Lig-1.0).

275

276 3.2. *Water permeation and oil emulsion rejection test*

277

278 The water permeability of the neat PVDF membrane and the lignin modified
279 PVDF membrane using NaOH with varied concentration (NaOH-0.25, NaOH-0.50,
280 NaOH-1.00, NaOH-1.50) was determined. As stated in Table 2, the water permeability
281 was significantly reduced when the PVDF membrane was modified using lignin
282 solution with a high NaOH concentration of 1.50 wt.%. The pore rupture observed in
283 SEM images (Fig. 1(e)) could be the main reason. Hence, the subsequent modification
284 of PVDF membrane was conducted using lignin solution with a NaOH concentration

285 of 0.50 wt.%. NaOH-0.5 membrane showed the least reduction of water permeability
286 compared to the neat PVDF membrane. By adjusting the lignin concentration to 0.75
287 wt.% in the NaOH solution with a concentration of 0.50 wt.%, the membrane
288 permeability could be significantly enhanced, about 110% (Table 3). The lignin
289 concentration of 0.75 wt.% was preferred as it also resulted in the membrane with the
290 rejection of oil emulsion up to 99.25%. The milky feed was purified into crystal clear
291 water, as shown in Fig. 5. With an underwater oil contact angle larger than 150 °, the
292 PVDF membranes modified by other researchers [39-42] also rejected more than 98%
293 of oil in water, as shown in Table 4. The neat PVDF membrane only rejected 83.30%
294 of oil emulsion in the feed. However, the permeate flux of oily water through the lignin
295 modified membranes is lower than the permeate flux of oily water through the neat
296 PVDF membrane as displayed in Fig. 6. The oily water permeate flux of Lig-0.75
297 membrane stabilized after 1 h, but the oily water permeate flux of the neat PVDF
298 membrane reduced continuously. The unrejected oil emulsion could penetrate into the
299 pores of the neat PVDF membrane and fouled the membrane through pore condensation
300 [43]. After being immersed in NaOH solution for 12 h, the lignin modified PVDF
301 membrane (Lig-0.75) could still reject 99.00% oil emulsion. A stable but lower
302 permeate flux was recorded, as shown in Fig. 7.

303

304 4. Conclusions

305

306 PVDF membrane was successfully coated with lignin solution with varied
307 NaOH and lignin concentration. The lignin coated membrane showed slight changes in
308 morphology, but great improvement in separation performance. The excessive NaOH
309 caused the pore collapse due to the instability of PVDF in the highly alkaline solution.

310 The lignin penetrated into the porous membrane and caused the reduction of pore size.
311 The rough surface was not fully demolished after lignin coating. The FTIR spectra
312 confirmed the existence of guaiacyl groups of lignin on the PVDF membrane. The
313 hydrophilic lignin and rough surface could cause the formation of the water layer on
314 the membrane surface. Hence, the adhesion of the oil droplet on the lignin coated
315 membrane immersed in water was prevented. The increasing lignin content enhanced
316 the water permeability and oil rejection of the lignin modified membranes. Although
317 at lower permeate flux, the lignin coated membranes rejected more oil than the neat
318 PVDF membrane with minimum fouling.

319

320 **CRedit authorship contribution statement**

321

322 **N.A. Zakaria:** Investigation, Writing – original draft. **Hoi-Fang Tan:**
323 Investigation. **M. Hazwan Hussin:** Investigation. **A.L. Ahmad:** Supervision, Writing
324 – review & editing. **C.P. Leo:** Conceptualization, Methodology, Writing - review &
325 editing, Supervision. **Phaik Eong Poh:** Investigation, Conceptualization, Writing –
326 review & editing. **Kourosh Behzadian:** Fund acquisition, Writing – review & editing.
327 **Isaac I. Akinwumi:** Fund acquisition, Writing – review & editing. **Alireza**
328 **Moghayedi:** Fund acquisition, Writing – review & editing. **Joaquin Diazsolano:** Fund
329 acquisition, Writing – review & editing.

330

331 **Declaration of Competing Interest**

332 The authors declare no conflict of interest.

333

334 **Acknowledgements**

335

336 The authors would like to acknowledge the Royal Academy of Engineering for the
337 financial support (Frontiers of Engineering for Development Contract, FoE2021\9\2)
338 to conduct this work.

339

340 **References**

341 [1] M. Hazwan Hussin, A. A. Aziz, A. Iqbal, M. N. M. Ibrahim, N. H. A. Latif,
342 Development and characterization novel bio-adhesive for wood using kenaf core
343 (Hibiscus cannabinus) lignin and glyoxal, *Int. J. Biol. Macromol.*, 122 (2019)
344 713–722, <https://doi.org/10.1016/j.ijbiomac.2018.11.009>.

345 [2] M. Norgren and H. Edlund, Lignin: Recent advances and emerging applications,
346 *Curr. Opin. Colloid Interface Sci.*, 19 (5) (2014) 409–416,
347 <https://doi.org/10.1016/j.cocis.2014.08.004>.

348 [3] B. Wang, S.F. Wang, S.S. Lam, C. Sonne, T.Q. Yuan, G.Y. Song, R.C. Sun, A
349 review on production of lignin-based flocculants: Sustainable feedstock and low
350 carbon footprint applications, *Renew. Sustain. Energy Rev.*, 134 (2020) 110384,
351 <https://doi.org/10.1016/j.rser.2020.110384>.

352 [4] W. Zhang, H. Duo, S. Li, Y. An, Z. Chen, Y. Ren, S. Wang, X. Zhang, X. Wang,
353 An overview of the recent advances in functionalization biomass adsorbents for
354 toxic metals removal, *Colloids Interface Sci. Commun.*, 38, (2020) 100308,
355 <https://doi.org/10.1016/j.colcom.2020.100308>.

356 [5] T. M. Albayati, A.A. Sabri, D. B. Abed, Adsorption of binary and multi heavy
357 metals ions from aqueous solution by amine functionalized SBA-15 mesoporous
358 adsorbent in a batch system, *Desalin. Water Treat.*, 151 (2019) 315-321,
359 <https://doi.org/10.5004/dwt.2019.23937>.

- 360 [6] Y. Ma, D. Zheng, Z. Mo, R. Dong, X. Qiu, Magnetic lignin-based carbon
361 nanoparticles and the adsorption for removal of methyl orange, *Colloid. Surface*
362 *A*, 559 (2018) 226-234, <https://doi.org/10.1016/j.colsurfa.2018.09.054>.
- 363 [7] B. Gao, P. Li, R. Yang, A. Li, H. Yang, Investigation of multiple adsorption
364 mechanisms for efficient removal of ofloxacin from water using lignin-based
365 adsorbents, *Sci. Rep.*, 9 (2019) 637, [https://doi.org/10.1038/s41598-018-37206-](https://doi.org/10.1038/s41598-018-37206-1)
366 [1](https://doi.org/10.1038/s41598-018-37206-1).
- 367 [8] T.M. Albayati, Application of nanoporous material MCM-41 in a membrane
368 adsorption reactor (MAR) as a hybrid process for removal of methyl orange,
369 *Desalin. Water Treat.*, 151 (2019) 138-144,
370 <https://doi.org/10.5004/dwt.2019.23878>.
- 371 [9] A. M. Alkafajy, T. M. Albayati, High performance of magnetic mesoporous
372 modification for loading and release of meloxicam in drug delivery
373 implementation, 23 (2020) 100890,
374 <https://doi.org/10.1016/j.mtcomm.2019.100890>.
- 375 [10] T. M. Albayati, A.A.A. Jassam, Synthesis and characterization of mesoporous
376 materials as a carrier and release of prednisolone in drug delivery system, *J Drug.*
377 *Deliv. Sci. Tec.*, 53 (2019) 101176, <https://doi.org/10.1016/j.jddst.2019.101176>.
- 378 [11] G. N. Rivière, A. Korpi, M. H. Sipponen, T. Zou, M. A. Kostianen, M.
379 Österberg, Agglomeration of viruses by cationic lignin particles for facilitated
380 water purification, *ACS Sustain. Chem. Eng.*, 8 (10) (2020) 4167–4177,
381 <https://doi.org/10.1021/acssuschemeng.9b06915>.
- 382 [12] O. S. H. Santos, M. Coelho da Silva, V. R. Silva, W. N. Mussel, M. I. Yoshida,
383 Polyurethane foam impregnated with lignin as a filler for the removal of crude
384 oil from contaminated water, *J. Hazard. Mater.*, 324 (2017) 406–413,

- 385 <https://doi.org/10.1016/j.jhazmat.2016.11.004>.
- 386 [13] A. Abdel-Karim, H. Elhaes, A.S. El-Kalliny, M.I. Badawy, M. Ibrahim, T.A.
387 Gad-Allah, Probing protein rejection behavior of blended PES-based flat-sheet
388 ultrafiltration membranes: A density functional theory (DFT) study,
389 *Spectrochim. Acta A*, 238 (2020) 118399.
- 390 [14] M. Yong, Y. Zhang, S. Sun, W. Liu, Properties of polyvinyl chloride (PVC)
391 ultrafiltration membrane improved by lignin: Hydrophilicity and antifouling, *J.*
392 *Memb. Sci.*, 575 (2019) 50–59, <https://doi.org/10.1016/j.memsci.2019.01.005>.
- 393 [15] L. Shamaei, B. Khorshidi, M. A. Islam, M. Sadrzadeh, Development of
394 antifouling membranes using agro-industrial waste lignin for the treatment of
395 Canada's oil sands produced water, *J. Memb. Sci.*, 611 (2020) 118326,
396 <https://doi.org/10.1016/j.memsci.2020.118326>.
- 397 [16] Y. T. Chen, Y. L. Liao, Y. M. Sun, C. C. Hu, J. Y. Lai, Y. L. Liu, Lignin as an
398 effective agent for increasing the separation performance of crosslinked
399 polybenzoxazine based membranes in pervaporation dehydration application, *J.*
400 *Memb. Sci.*, 578 (2019) 156–162,
401 <https://doi.org/10.1016/j.memsci.2019.02.036>.
- 402 [17] C. Lavanya and R. Geetha Balakrishna, Naturally derived polysaccharides-
403 modified PSF membranes: A potency in enriching the antifouling nature of
404 membranes, *Sep. Purif. Technol.*, 230 (2020) 115887,
405 <https://doi.org/10.1016/j.seppur.2019.115887>.
- 406 [18] L. Shamaei, B. Khorshidi, M. A. Islam, M. Sadrzadeh, Industrial waste lignin as
407 an antifouling coating for the treatment of oily wastewater: Creating wealth from
408 waste, *J. Clean. Prod.*, 256 (2020) 120304,
409 <https://doi.org/10.1016/j.jclepro.2020.120304>.

- 410 [19] L. Gu, M.Y. Xie, Y. Jin, M. He, X.Y. Xing, Y. Yu, Q.Y. Qu, Construction of
411 antifouling membrane surfaces through layer-by-layer self-assembly of
412 lignosulfonate and polyethyleneimine, *Polymers (Basel)*, 11 (11) (2019) 9–11,
413 <https://doi.org/10.3390/polym11111782>.
- 414 [20] W. Jonglertjunya, T. Juntong, N. Pakkang, N. Srimarut, C. Sakdaronnarong,
415 Properties of lignin extracted from sugarcane bagasse and its efficacy in
416 maintaining postharvest quality of limes during storage, *LWT - Food Sci.*
417 *Technol.*, 57 (1) (2014) 116–125, <https://doi.org/10.1016/j.lwt.2013.11.042>.
- 418 [21] A. Javed, H. Ullsten, P. Rättö, L. Järnström, Lignin-containing coatings for
419 packaging materials, *Nord. Pulp Pap. Res. J.*, 33 (3) (2018) 548–556,
420 <https://doi.org/10.1515/npprj-2018-3042>.
- 421 [22] N. Hamzah and C. P. Leo, Fouling prevention in the membrane distillation of
422 phenolic-rich solution using superhydrophobic PVDF membrane incorporated
423 with TiO₂ nanoparticles, *Sep. Purif. Technol.*, 167 (2016) 79–87,
424 <https://doi.org/10.1016/j.seppur.2016.05.005>.
- 425 [23] E. Melro, A. Filipe, D. Sousa, A.J.M. Valente, A. Romano, F.E. Antunes, B.
426 Medrohno, Dissolution of kraft lignin in alkaline solutions, *Int. J. Biol.*
427 *Macromol.*, 148 (2020) 688–695.
428 <https://doi.org/10.1016/j.ijbiomac.2020.01.153>.
- 429 [24] J. Cui, Z. Zhou, A. Xie, Q. Wang, S. Liu, J. Lang, C. Li, Y. Yan, J. Dai, Facile
430 preparation of grass-like structured NiCo-LDH/PVDF composite membrane for
431 efficient oil–water emulsion separation, *J. Memb. Sci.*, 573 (2019) 226–233,
432 <https://doi.org/10.1016/j.memsci.2018.11.064>.
- 433 [25] A. L. Ahmad, T. A. Otitoju, B. S. Ooi, Optimization of a high performance 3-
434 aminopropyltriethoxysilane-silica impregnated polyethersulfone membrane

435 using response surface methodology for ultrafiltration of synthetic oil-water
436 emulsion, *J. Taiwan Inst. Chem. Eng.*, 93 (2018) 461–476,
437 <https://doi.org/10.1016/j.jtice.2018.08.021>.

438 [26] H. F. Tan, W. L. Tan, N. Hamzah, M. H. K. Ng, B. S. Ooi, C. P. Leo, Membrane
439 distillation crystallization using PVDF membrane incorporated with TiO₂
440 nanoparticles and nanocellulose, *Water Sci. Technol. Water Supply*, 20 (5)
441 (2020) 1629–1642, <https://doi.org/10.2166/ws.2020.068>.

442 [27] H. Tan, W. Tan, B. S. Ooi, C. P. Leo, Superhydrophobic PVDF /microfibrillated
443 cellulose membrane for membrane distillation crystallization of struvite, *Chem.*
444 *Eng. Res. Des.*, 170, (2021) 54–68, <https://doi.org/10.1016/j.cherd.2021.03.027>.

445 [28] A. Hai, A. A. Durrani, M. Selvaraj, F. Banat, M. A. Haija, Oil-water emulsion
446 separation using intrinsically superoleophilic and superhydrophobic PVDF
447 membrane, *Sep. Purif. Technol.*, 212 (2019) 388–395,
448 <https://doi.org/10.1016/j.seppur.2018.10.001>.

449 [29] P. Sukitpaneemit and T. S. Chung, Molecular elucidation of morphology and
450 mechanical properties of PVDF hollow fiber membranes from aspects of phase
451 inversion, crystallization and rheology, *J. Memb. Sci.*, 340 (1–2) (2009) 192–
452 205, <https://doi.org/10.1016/j.memsci.2009.05.029>.

453 [30] S. Maitz, W. Schlemmer, M. A. Hobisch, J. Hobisch, and M. Kienberger,
454 Preparation and characterization of a water-soluble kraft lignin, *Adv. Sustain.*
455 *Syst.*, 4 (8) (2020) 2000052, <https://doi.org/10.1002/adsu.202000052>.

456 [31] M. F. Rabuni, N. M. Nik Sulaiman, M. K. Aroua, N. A. Hashim, Effects of
457 alkaline environments at mild conditions on the stability of PVDF membrane:
458 An experimental study, *Ind. Eng. Chem. Res.*, 52 (45) (2013) 15874–15882,
459 <https://doi.org/10.1021/ie402684b>.

- 460 [32] J. S. Yeo, J. H. Lee, S. H. Hwang, Effects of lignin on the volume shrinkage and
461 mechanical properties of a styrene/unsaturated polyester/lignin ternary
462 composite system, *Compos. Part B Eng.*, 130 (2017) 167–173,
463 <https://doi.org/10.1016/j.compositesb.2017.07.084>.
- 464 [33] Z. Wang, N. Bo, Y. Liu, G. Yang, Y. Liu, Y. Zhao, Preparation of lignin-based
465 anion exchangers and their utilization for nitrate removal, *BioResources*, 8 (3)
466 (2013) 3505–3517, <https://doi.org/10.15376/biores.8.3.3505-3517>.
- 467 [34] Y. Kakihana, L. Cheng, L.F. Fang, S.Y. Wang, S. Jeon, D. Saeki, S. Rajabzadeh,
468 H. Matsuyama, Preparation of positively charged PVDF membranes with
469 improved antibacterial activity by blending modification: Effect of change in
470 membrane surface material properties, *Colloids Surfaces A Physicochem. Eng.*
471 *Asp.*, 533 (2017) 133–139, <https://doi.org/10.1016/j.colsurfa.2017.08.039>.
- 472 [35] H. Bai, X. Wang, Y. Zhou, L. Zhang, Preparation and characterization of
473 poly(vinylidene fluoride) composite membranes blended with nano-crystalline
474 cellulose, *Prog. Nat. Sci. Mater. Int.*, 22 (3) (2012) 250–257,
475 <https://doi.org/10.1016/j.pnsc.2012.04.011>.
- 476 [36] N. A. Aziz, A.F.A. Latip, C.P. Leo, N.H.A. Latif, N. Brosse, R. Hashim, M.H.
477 Hussin, Reinforced lignin-phenol-glyoxal (LPG) wood adhesives from coconut
478 husk, *Int. J. Biol. Macromol.*, 141 (2019) 185–196,
479 <https://doi.org/10.1016/j.ijbiomac.2019.08.255>.
- 480 [37] N. Hamzah and C. P. Leo, Membrane distillation of saline with phenolic
481 compound using superhydrophobic PVDF membrane incorporated with TiO₂
482 nanoparticles: Separation, fouling and self-cleaning evaluation, *Desalination*,
483 418 (2017) 79–88, <https://doi.org/10.1016/j.desal.2017.05.029>.
- 484 [38] J. Ju, T. Wang, Q. Wang, Superhydrophilic and underwater superoleophobic

485 PVDF membranes via plasma-induced surface PEGDA for effective separation
486 of oil-in-water emulsions, *Colloids Surfaces A Physicochem. Eng. Asp.*, 481
487 (2015) 151–157, <https://doi.org/10.1016/j.colsurfa.2015.01.041>.

488 [39] J. Gao, M. Cai, Z. Nie, J. Zhang, Y. Chen, Superwetting PVDF membrane
489 prepared by in situ extraction of metal ions for highly efficient oil/water mixture
490 and emulsion separation, *Sep. Purif. Technol.*, 275 (2021) 119174, [https://doi:
491 10.1016/j.seppur.2021.119174](https://doi.org/10.1016/j.seppur.2021.119174).

492 [40] J. Wu, Z. Hou, Z. Yu, J. Lang, J. Cui, J. Yang, J. Dai, C. Li, Y. Yan, A. Xie.,
493 Facile preparation of metal-polyphenol coordination complex coated PVDF
494 membrane for oil/water emulsion separation, *Sep. Purif. Technol.*, 258 (2021)
495 118022, [https://doi: 10.1016/j.seppur.2020.118022](https://doi.org/10.1016/j.seppur.2020.118022).

496 [41] X. Zeng, J. Lin, W. Cai, Q. Lu, S. Fu, J. Li, X. Yan, X. Wen, C. Zhou, M. Zhang,
497 Fabrication of superhydrophilic PVDF membranes by one-step modification
498 with eco-friendly phytic acid and polyethyleneimine complex for oil-in-water
499 emulsions separation, *Chemosphere*, 264 (2021) 128395, [https://doi:
500 10.1016/j.chemosphere.2020.128395](https://doi.org/10.1016/j.chemosphere.2020.128395).

501 [42] B. Jiang, K. Cheng, N. Zhang, N. Yang, L. Zhang, Y. Sun, One-step modification
502 of PVDF membrane with tannin-inspired highly hydrophilic and underwater
503 superoleophobic coating for effective oil-in-water emulsion separation, *Sep.
504 Purif. Technol.*, 255 (2021), 117724, [https://doi: 10.1016/j.seppur.2020.117724](https://doi.org/10.1016/j.seppur.2020.117724).

505 [43] I. N. H. M. Amin, A. W. Mohammad, M. Markom, C.P. Leo, N. Hilal, Flux
506 decline study during ultrafiltration of glycerin-rich fatty acid solutions, *J. Memb.
507 Sci.*, 351 (1–2) (2010) 75–86, 2010,
508 <https://doi.org/10.1016/j.memsci.2010.01.033>.

509

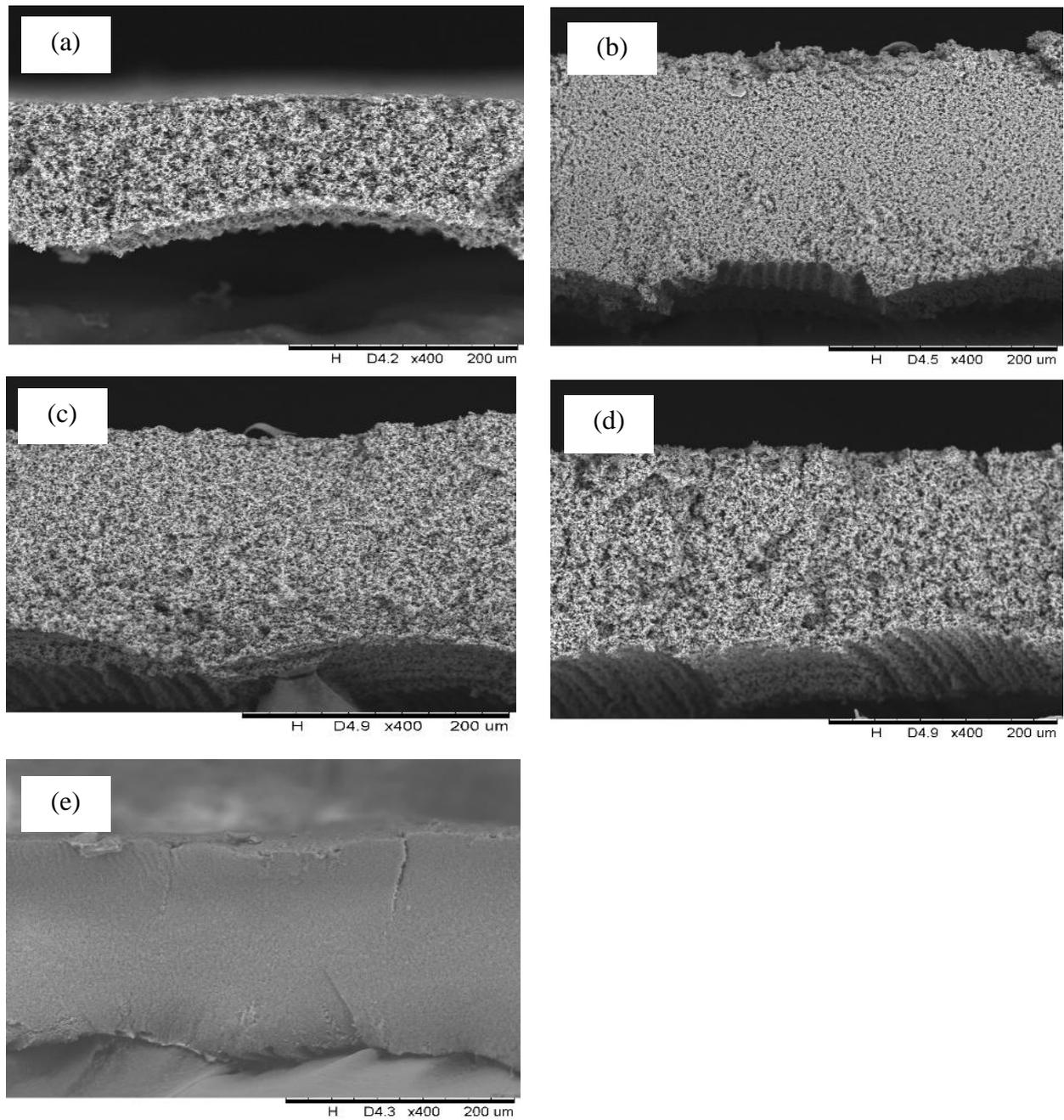


Fig. 1. SEM images of (a) PVDF membrane and PVDF membrane modified with 1 wt.% of lignin in NaOH solution with (b) 0.25 wt.%, (c) 0.5 wt.%, (d) 1.0 wt.%, and (e) 1.5 wt.% concentration.

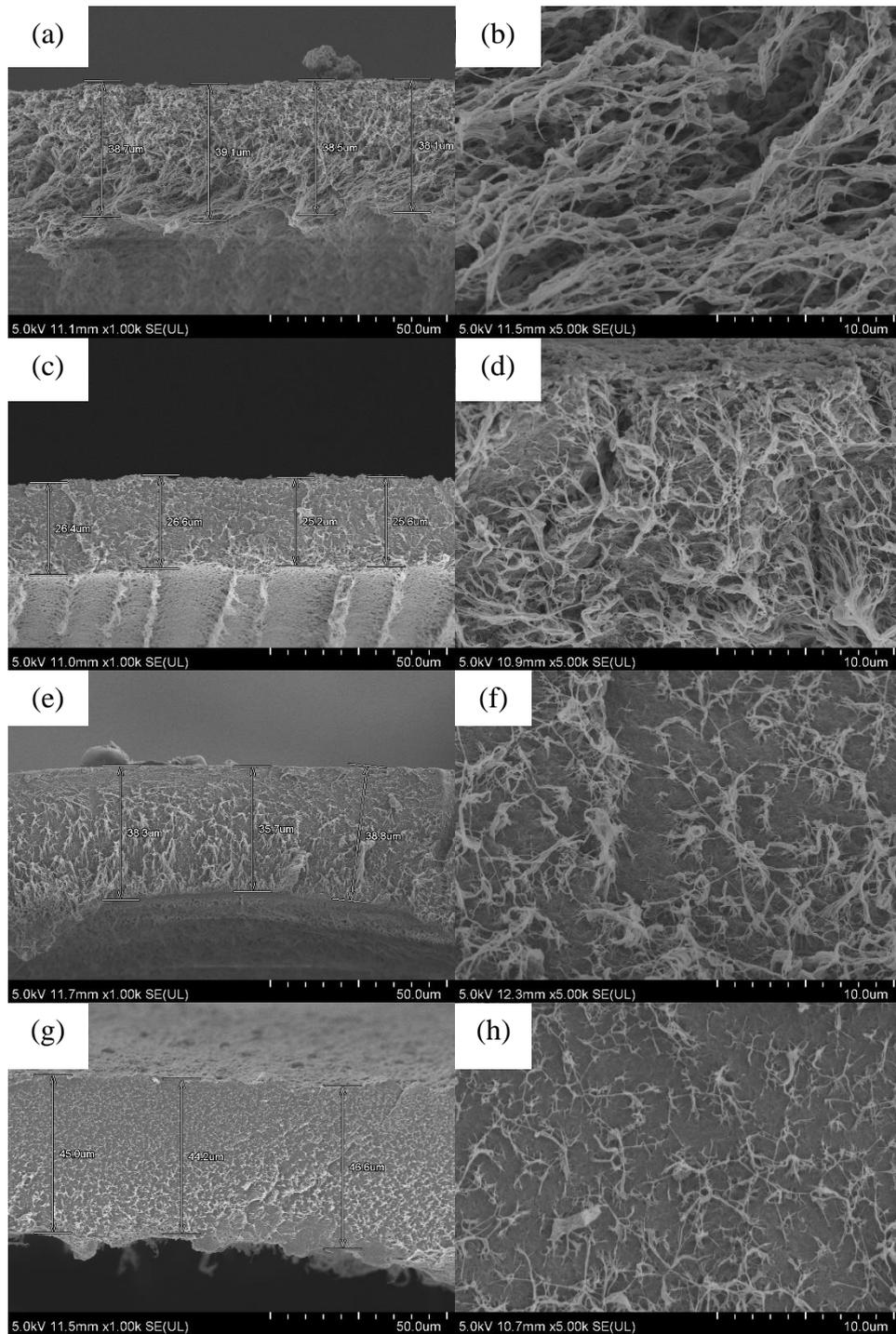


Fig. 2. SEM images of (a) PVDF membrane modified with 0.25 wt.% (Lig-0.25), (b) 0.50 wt.% (Lig-0.50), (c) 0.75 wt.% (Lig-0.75) and (d) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.

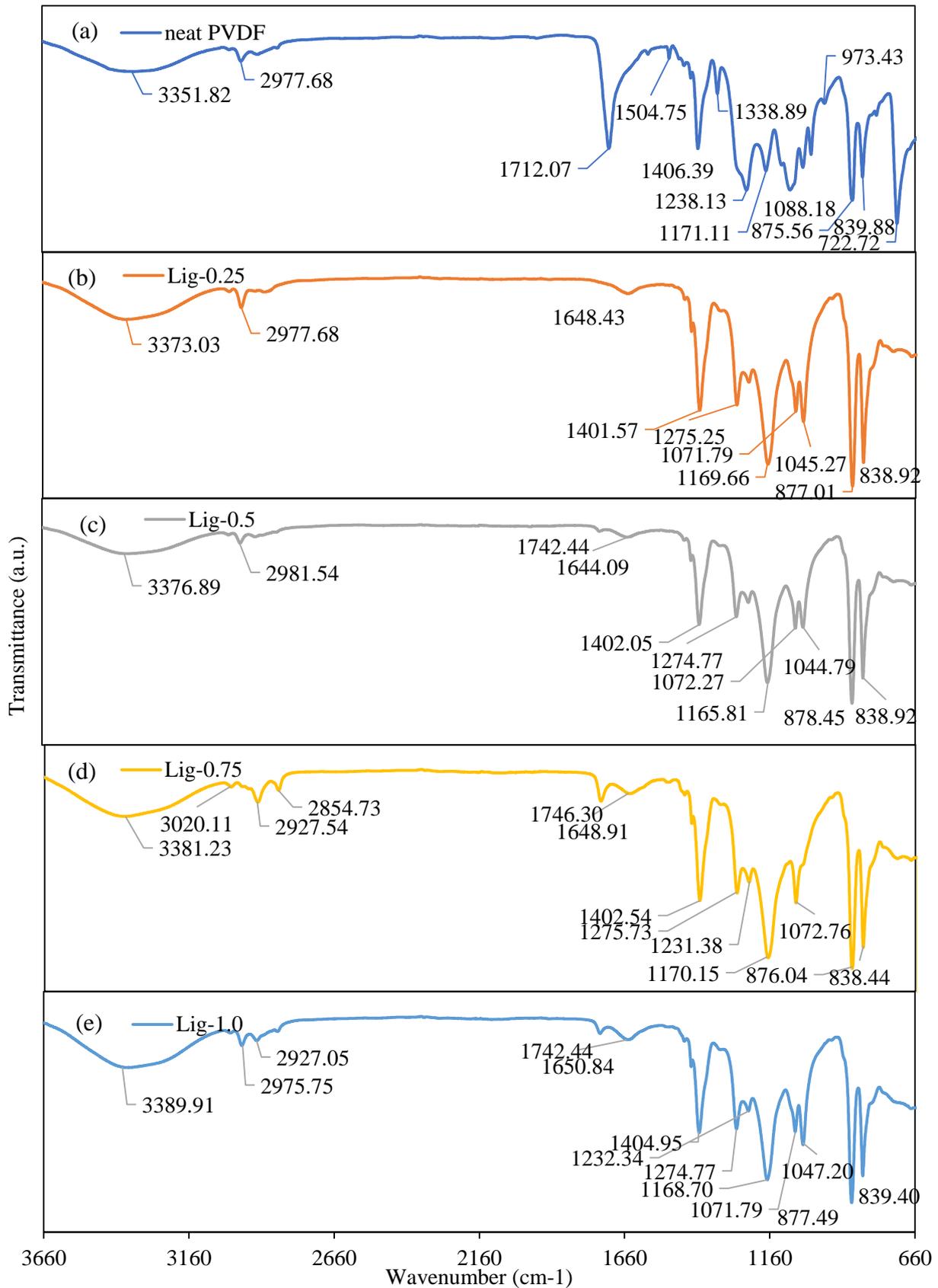


Fig. 3. FTIR spectra of (a) neat PVDF membrane and PVDF membrane modified with (b) 0.25 wt.% (Lig-0.25), (c) 0.50 wt.% (Lig-0.50), (d) 0.75 wt.% (Lig-0.75) and (e) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.

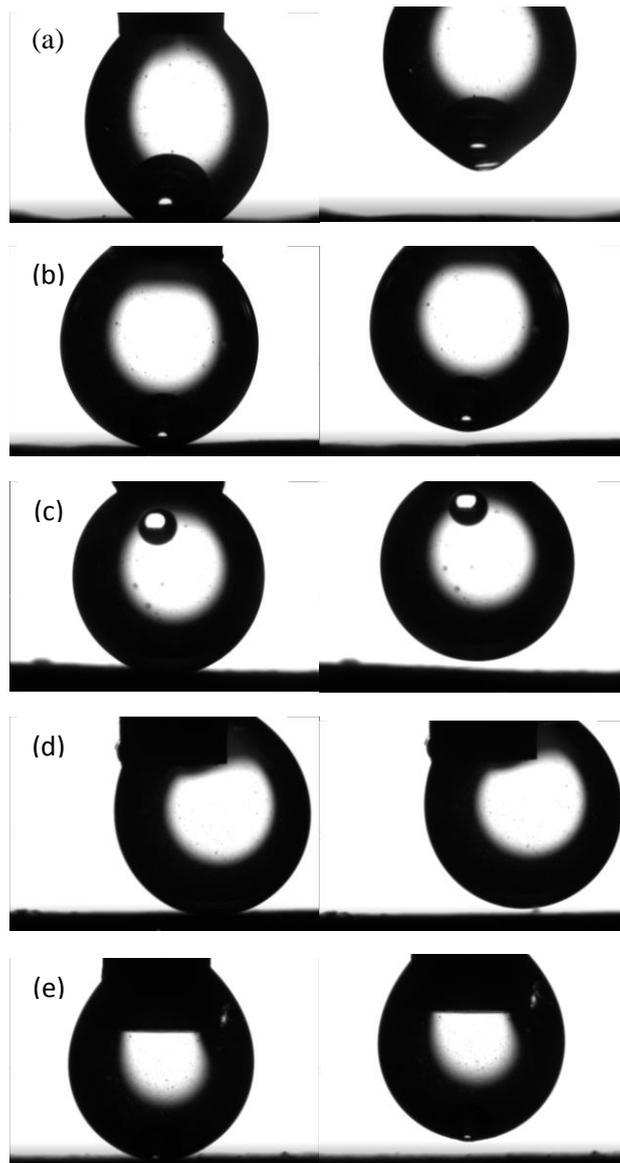


Fig. 4. Underwater oil droplets placed on (a) neat PVDF membrane and PVDF membrane modified with (b) 0.25 wt.% (Lig-0.25), (c) 0.50 wt.% (Lig-0.50), (d) 0.75 wt.% (Lig-0.75) and (e) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.

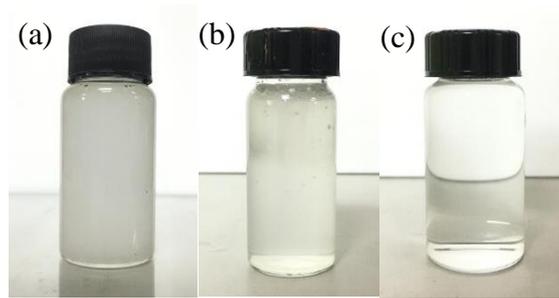


Fig. 5. The feed sample and the permeate samples of oily water filtration using b) the neat PVDF membrane and (b) the PVDF membrane modified with 0.75 wt.% (Lig-0.75) and (e) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.

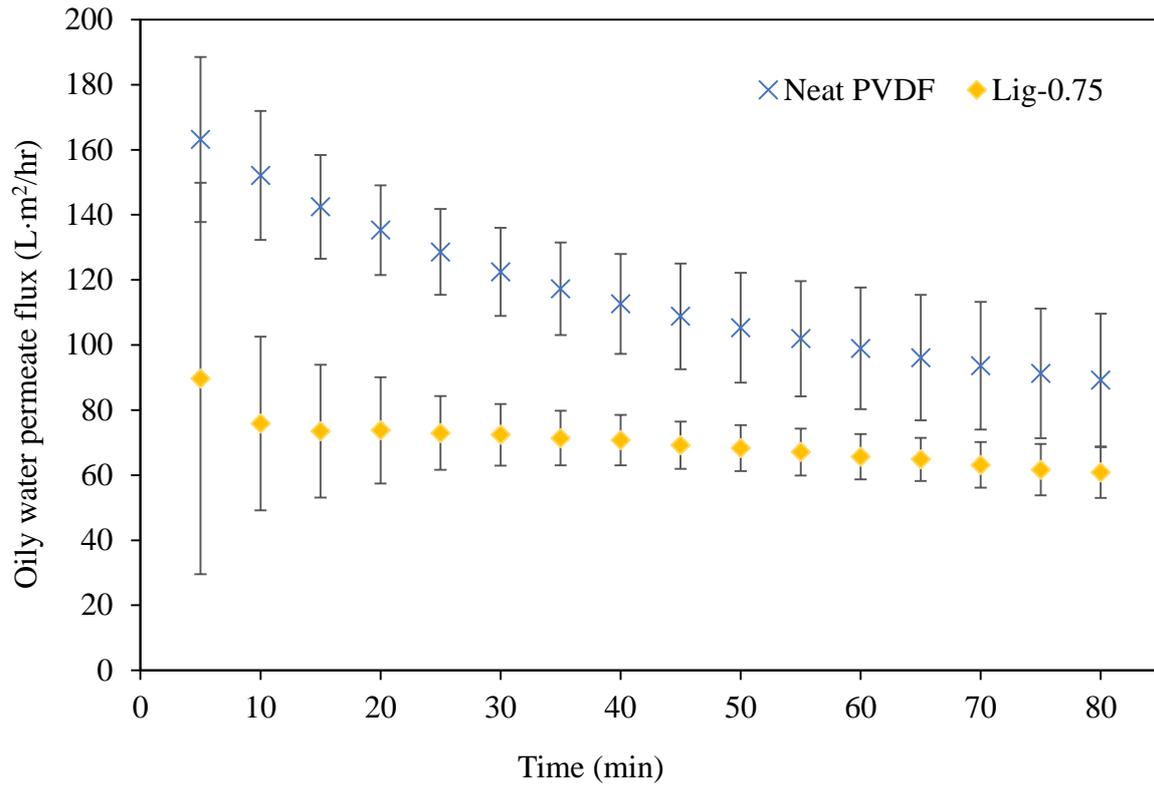


Fig. 6. The permeate flux of oily water filtration using the neat PVDF membrane and the PVDF membrane modified with 0.75 wt.% (Lig-0.75) of lignin in 0.5 wt.% of NaOH solution.

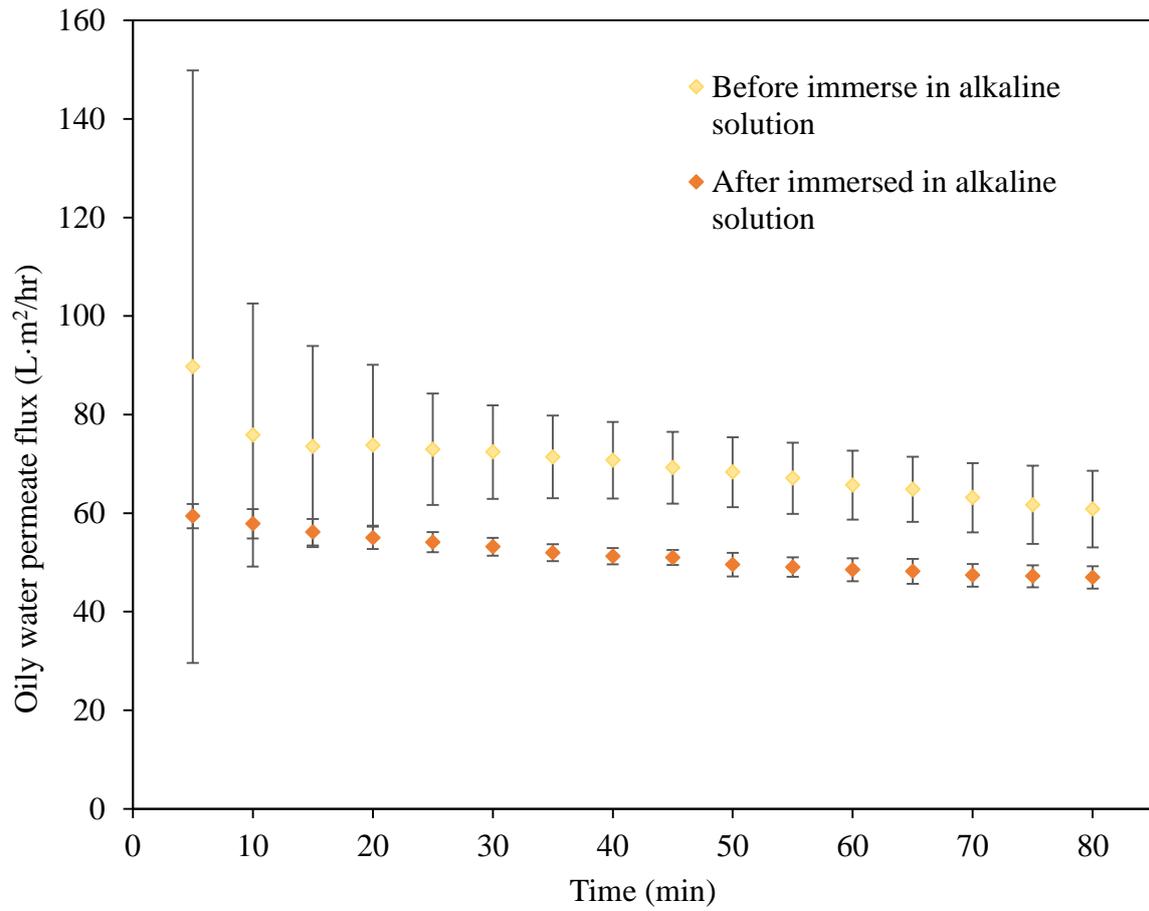


Fig. 7. The permeate flux of oily water filtration using PVDF membrane modified with 0.75 wt.% (Lig-0.75) of lignin in 0.5 wt.% of NaOH solution before and after immersed in alkaline solution.

Table 1

The pore size of the neat PVDF membrane and the PVDF membranes modified with lignin in NaOH solution.

Membrane	Lignin content (wt%)	Pore size (μm)
Neat PVDF	0	0.41 ± 0.22
Lig-0.25	0.25	0.28 ± 0.18
Lig-0.50	0.50	0.30 ± 0.01
Lig-0.75	0.75	0.22 ± 0.13
Lig-1.0	1.00	0.37 ± 0.27

Table 2

The pure water permeability of the neat PVDF membrane and the PVDF membrane modified with 1 wt.% of lignin in NaOH solution with varied concentration.

Membrane	Lignin content (wt.%)	NaOH concentration (wt.%)	Water Permeability ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)
PVDF	0	0	525.99 ± 16.28
NaOH-0.25	1	0.25	408.49 ± 20.93
NaOH-0.50	1	0.50	522.44 ± 12.56
NaOH-1.00	1	1.00	296.03 ± 15.89
NaOH-1.50	1	1.50	245.73 ± 19.07

Table 3

The pure water permeability of the neat PVDF membrane and the PVDF membrane modified with varied lignin content in 0.5 wt.% NaOH solution with varied concentration.

Membrane	Lignin content (wt.%)	NaOH concentration (wt.%)	Water Permeability ($\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)
PVDF	0	0	525.99 ± 16.28
Lig-0.25	0.25	0.50	595.06 ± 21.94
Lig-0.50	0.50	0.50	607.98 ± 10.74
Lig-0.75	0.75	0.50	1102.60 ± 13.47
NaOH-0.5 or Lig-1.00	1.00	0.50	624.78 ± 24.08

Table 4**Comparison to other works reporting on the modified PVDF membranes with underwater oil contact angle larger than 150 °.**

Modifier	Preparation techniques	Wetting properties		Performances		Ref
		Water contact angle (°)	Oil contact angle (°)	Oil rejection (%)	Water Permeability (L.m ⁻² .h ⁻¹ .bar ⁻¹)	
Tannic acid (TA)/ethylenediaminetetraacetic acid disodium salt (EDTA-2Na)	In-situ extraction	0	>150	99.99	2671.60 ⁻¹	[39]
TA - Titanium (Ti)	Facile layer-by-layer self-assembly	0	>150	99.35	689.6 ¹	[40]
Phytic Acid (PA)@Polyethyleneimine (PEI)	Surface depositing	37	154.9 ± 0.42	>98.5	12203.6	[41]
Tannic acid (TA)/sodium periodate (NaIO ₄)	Dip-coating	32	162	>98	>2400	[42]
PVDF-lignin/sodium hydroxide (NaOH)	Surface coating	-	>150	99.25	1102.60 ± 13.47	Present work

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: