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Lignin modified PVDF membrane with antifouling properties for oil filtration

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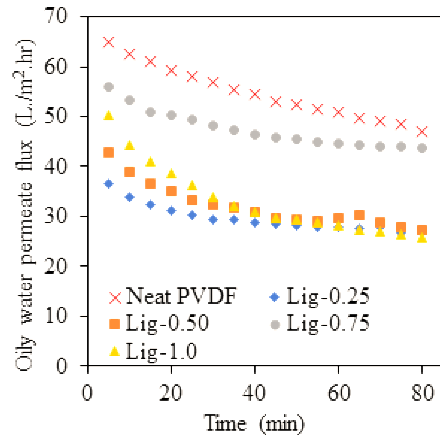
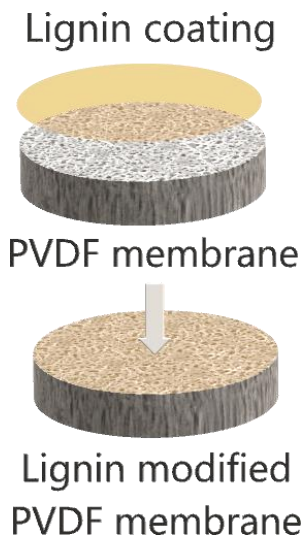
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**Graphical Abstract**



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

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20 **ABSTRACT**

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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.

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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 (H<sub>3</sub>PO<sub>4</sub>) (> 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.%), H<sub>3</sub>PO<sub>4</sub> (3 wt.%), and LiCl<sub>2</sub> (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  $\mu\text{m}$  (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<sup>-1</sup> to 3,800cm<sup>-1</sup> 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 cm<sup>2</sup> were tested in the  
174 pressure range of 0.2-1.0 bar after compaction using nitrogen gas. The permeation flux  
175 ( $J$ , L·m<sup>2</sup>·h<sup>-1</sup>) 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  $\mu\text{m}$  was reduced to be smaller

236 than 0.30  $\mu\text{m}$  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  $\text{CH}_2$  wagging vibration within 1401 – 1406.39  $\text{cm}^{-1}$  and C-C bonding within 1165 -  
250 1171  $\text{cm}^{-1}$ . These samples also displayed C-F and C-C-C symmetrical stretching  
251 vibration peaks within the range of 838 – 840  $\text{cm}^{-1}$  and 876-878  $\text{cm}^{-1}$ , 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  $\text{cm}^{-1}$   
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  $\text{cm}^{-1}$ ) and S bands (1330, 1115 and 819.94  $\text{cm}^{-1}$ ) could not  
258 be identified due to overlapping with PVDF characteristic peaks. The appearance of  
259 G band at 1275  $\text{cm}^{-1}$  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

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339

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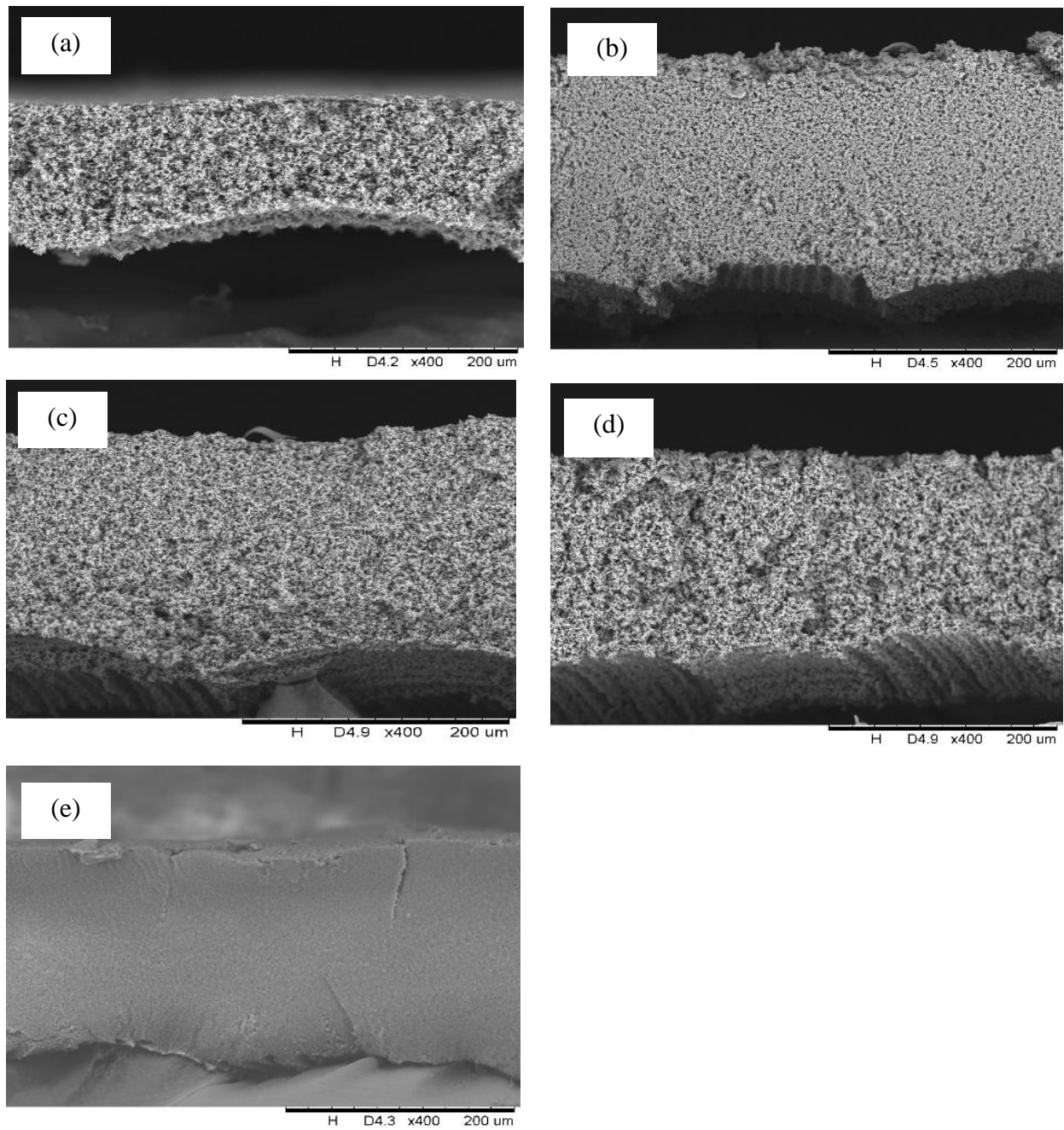
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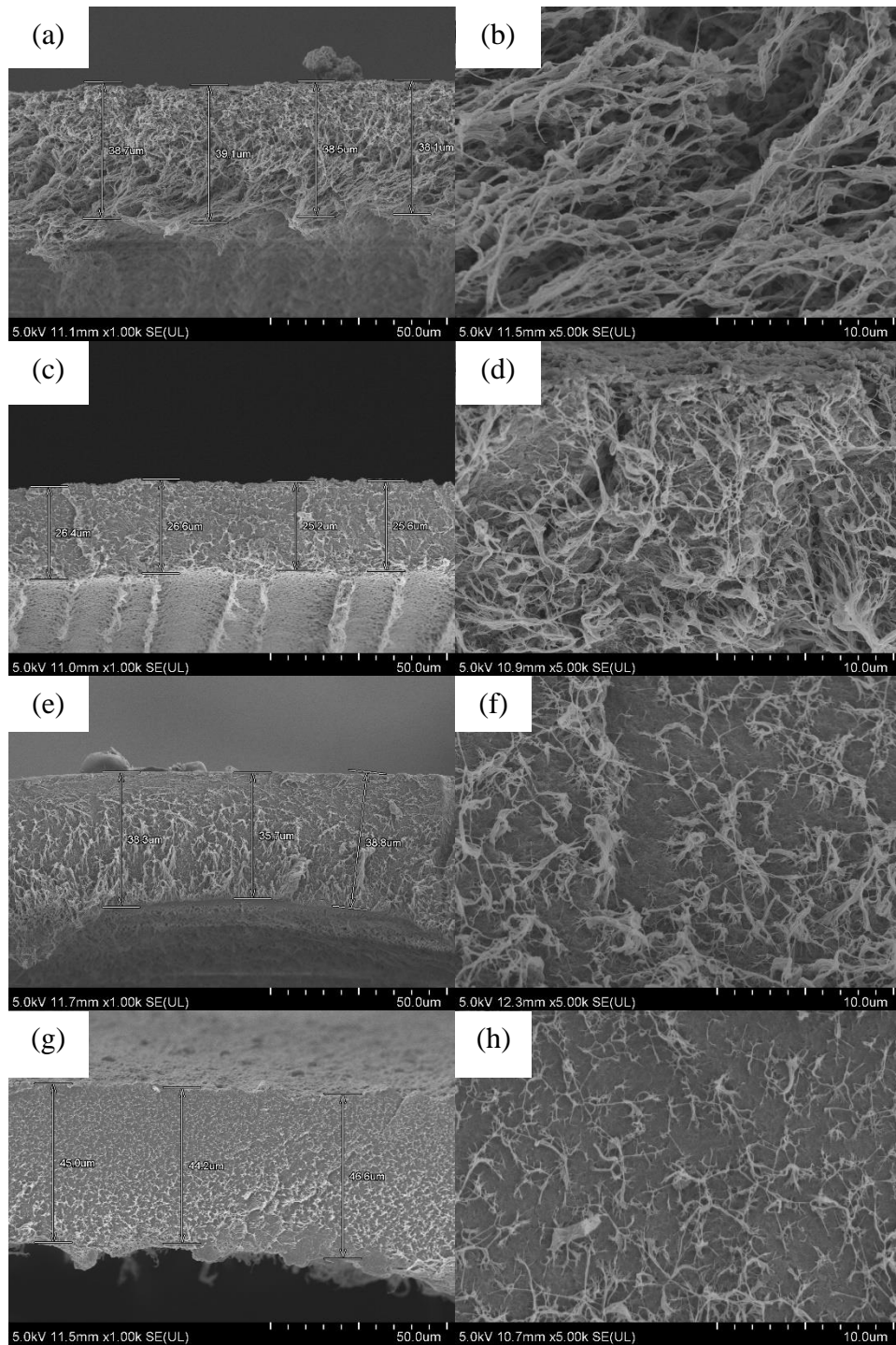
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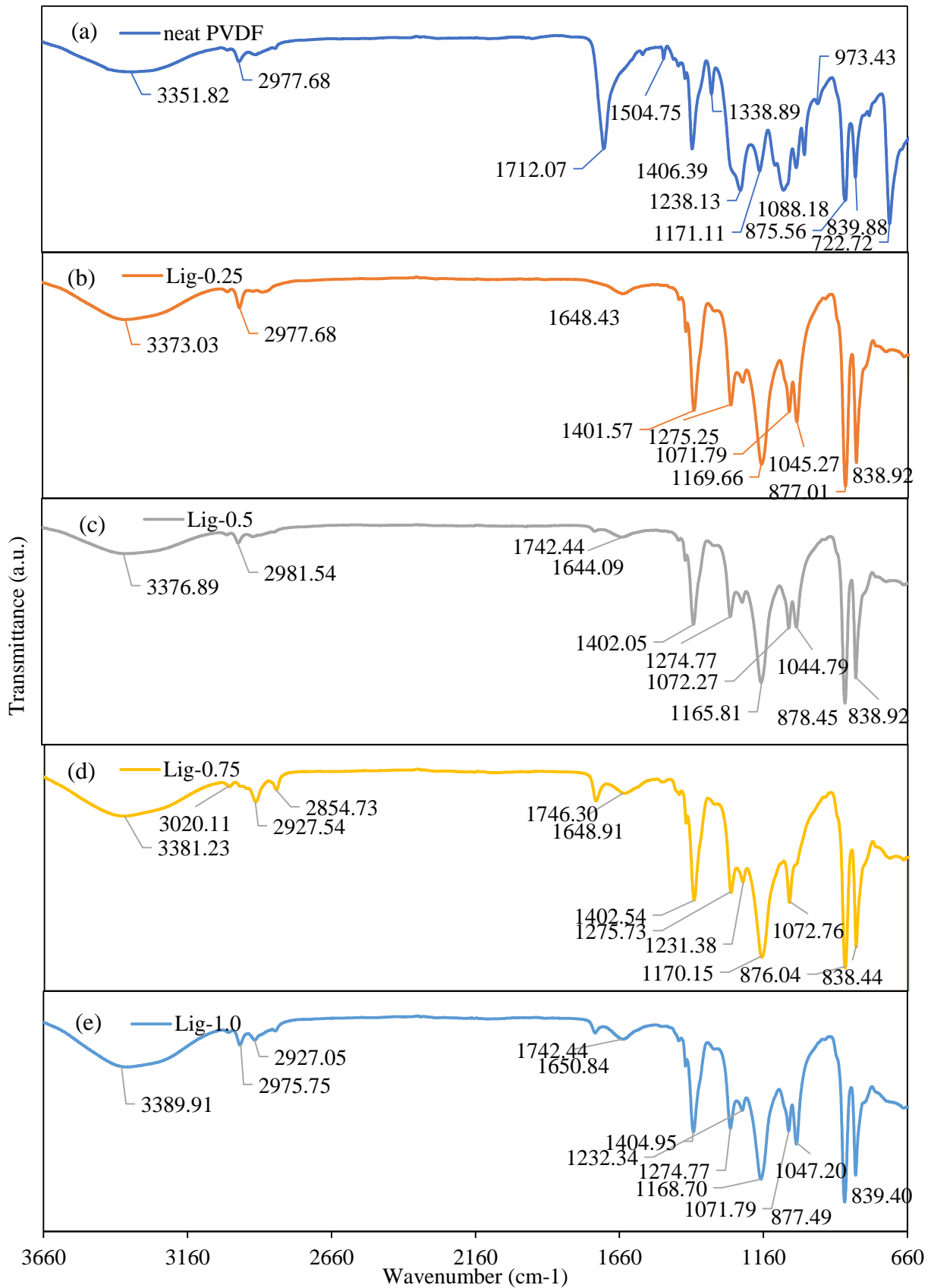


**Fig. 1.** SEM images of (a) PVDF membrane and PVDF membrane modified with 1 wt.% of lignin in NaOH solution with (b) 0.25 wt.%, (c) 0.5 wt.%, (d) 1.0 wt.%, and (e) 1.5 wt.% concentration.

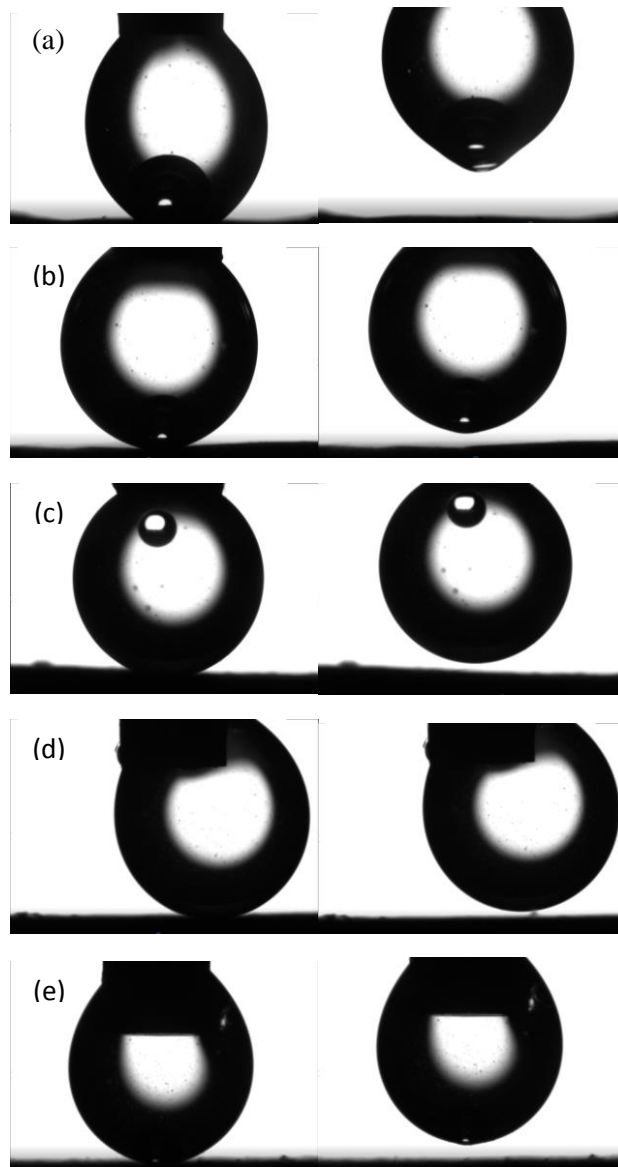




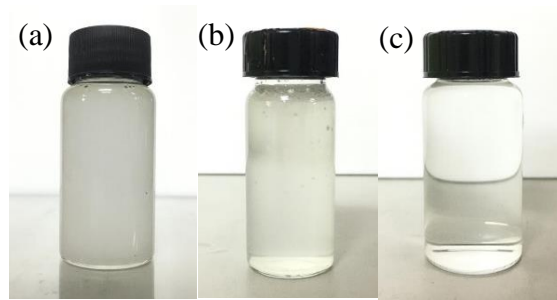
**Fig. 2.** SEM images of (a) PVDF membrane modified with 0.25 wt.% (Lig-0.25), (b) 0.50 wt.% (Lig-0.50), (c) 0.75 wt.% (Lig-0.75) and (d) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.



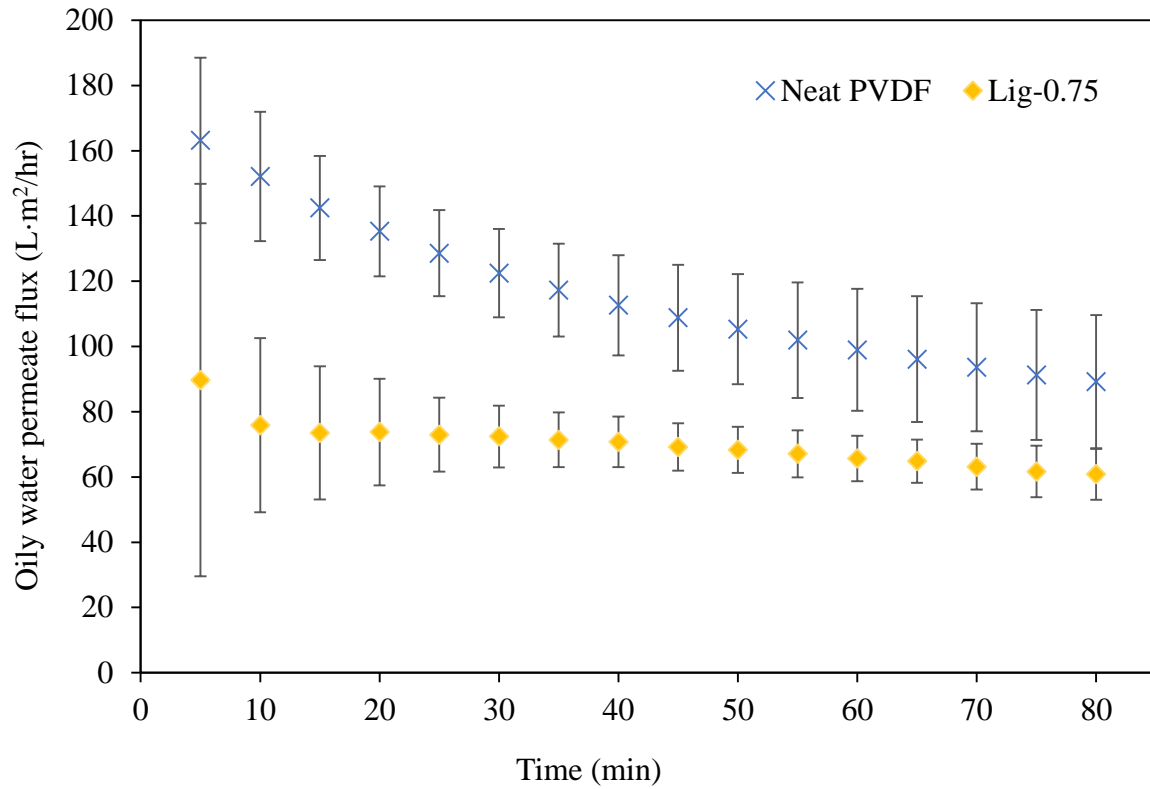
**Fig. 3.** FTIR spectra of (a) neat PVDF membrane and PVDF membrane modified with (b) 0.25 wt.% (Lig-0.25), (c) 0.50 wt.% (Lig-0.50), (d) 0.75 wt.% (Lig-0.75) and (e) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.



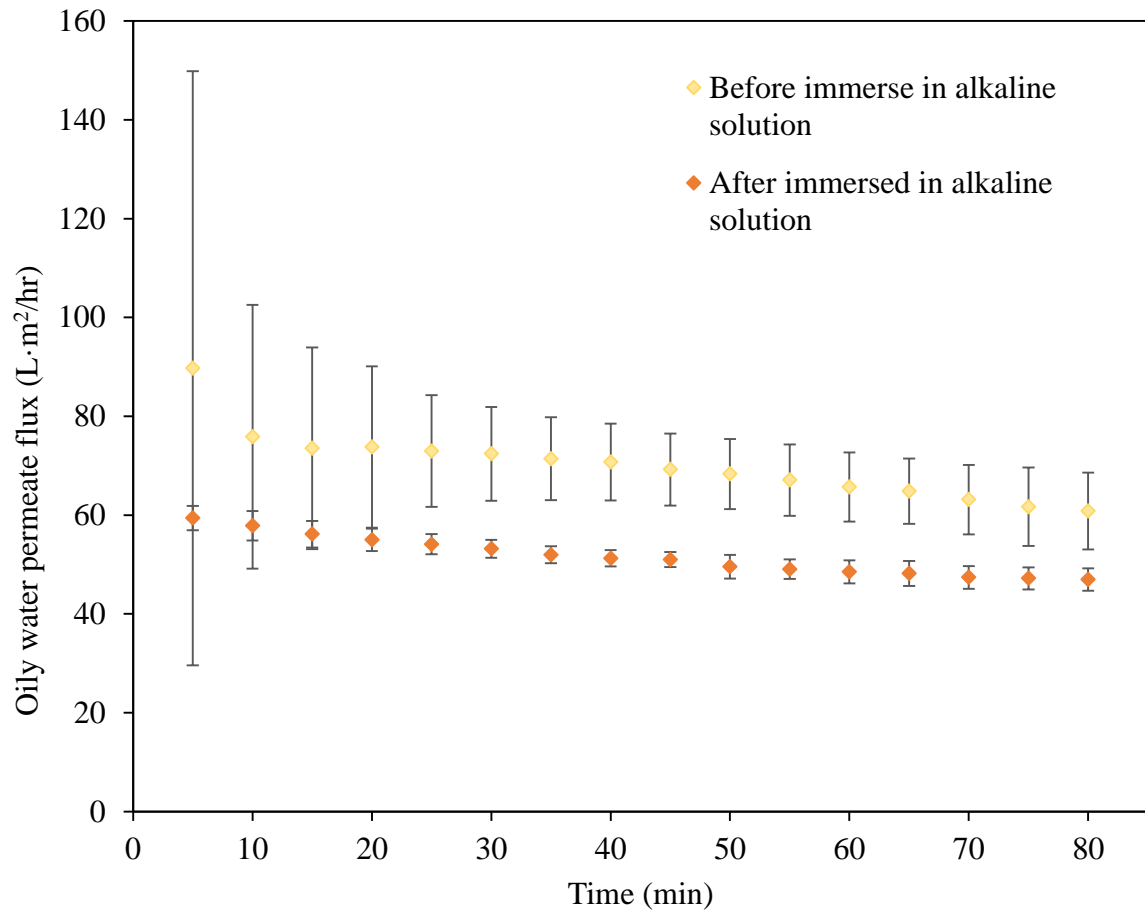
**Fig. 4.** Underwater oil droplets placed on (a) neat PVDF membrane and PVDF membrane modified with (b) 0.25 wt.% (Lig-0.25), (c) 0.50 wt.% (Lig-0.50), (d) 0.75 wt.% (Lig-0.75) and (e) 1.0 wt.% (Lig-1.0) of lignin in 0.5 wt.% of NaOH solution.



**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 ( $\mu\text{m}$ )
Neat PVDF	0	$0.41 \pm 0.22$
Lig-0.25	0.25	$0.28 \pm 0.18$
Lig-0.50	0.50	$0.30 \pm 0.01$
Lig-0.75	0.75	$0.22 \pm 0.13$
Lig-1.0	1.00	$0.37 \pm 0.27$

**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	$525.99 \pm 16.28$
NaOH-0.25	1	0.25	$408.49 \pm 20.93$
NaOH-0.50	1	0.50	$522.44 \pm 12.56$
NaOH-1.00	1	1.00	$296.03 \pm 15.89$
NaOH-1.50	1	1.50	$245.73 \pm 19.07$



**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	$525.99 \pm 16.28$
Lig-0.25	0.25	0.50	$595.06 \pm 21.94$
Lig-0.50	0.50	0.50	$607.98 \pm 10.74$
Lig-0.75	0.75	0.50	$1102.60 \pm 13.47$
NaOH-0.5 or Lig-1.00	1.00	0.50	$624.78 \pm 24.08$

**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 <sup>-2</sup> .h <sup>-1</sup> .bar <sup>-1</sup> )	
Tannic acid (TA)/ethylenediaminetetraacetic acid disodium salt (EDTA-2Na)	In-situ extraction	0	>150	99.99	2671.60 <sup>-1</sup>	[39]
TA - Titanium (Ti)	Facile layer-by-layer self-assembly	0	>150	99.35	689.6 <sup>1</sup>	[40]
Phytic Acid (PA)@Polyethyleneimine (PEI)	Surface depositing	37	154.9 ± 0.42	>98.5	12203.6	[41]
Tannic acid (TA)/sodium periodate (NaIO <sub>4</sub> )	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: