

22 **Abstract**

23 Ultrafiltration (UF) membrane is extensively utilized in water treatment for the removal of
24 colloidal particles, dissolved organic matters and microorganisms. These colloidal particles and
25 organic matters are prone to being adsorbed on membrane surface known as membrane fouling,
26 which increases operational costs and lowers down membrane efficiency. In this work, a group
27 of synthesized hydrophilic random copolymers and homopolymer were utilized to enhance PES
28 UF membrane performance by a simple deposition of a thin layer. Despite the increased intrinsic
29 resistance as a result of the thin modification layer, higher pure water permeability and recovery
30 rate were observed for the modified Polyethersulfone (PES) membrane during Bovine Serum
31 Albumin (BSA) fouling test in comparison to the virgin membrane. Moreover, the stability of
32 the adsorbed polymer layers was evaluated by a cyclic fouling test and chemical cleaning
33 endurance assessment. The membrane surface morphology and topography were characterized
34 by field emission scanning electron microscopy (FESEM) and atom force microscope (AFM).
35 The chemical composition before and after cyclic fouling test and chemical cleaning were
36 studied with attenuated total reflectance fourier transform infrared (ATR-FTIR) spectroscopy.
37 The results show that the random copolymer modified membrane exhibited average 26% rises
38 in water permeability compared with the virgin PES UF membrane when 0.5 wt % BSA solution
39 was used as feed. The stable permeability and flux recovery rate during the cyclic study with
40 chemical cleaning suggest good affinity of the newly synthesized random copolymer with the
41 PES membrane and water. This strategy successfully enhanced the UF membrane anti-fouling
42 performance.

43

44 **Keywords:** Ultrafiltration; copolymer; anti-fouling; adsorption.

45 **Research Highlights:**

46

- 47 • Synthesized polymers were robustly deposited on PES UF membrane surface.
- 48 • PES UF membrane antifouling performance was enhanced by the polymer deposition.
- 49 • The polymer increased intrinsic membrane resistance but reduced total resistance during
50 fouling.
- 51 • The stability of the polymer layer during BSA fouling test and chemical cleaning were
52 investigated.

53 **1. Introduction**

54 Membrane technologies play a vital role in the water treatment industry due to its high efficiency,
55 small footprint, and low energy requirement for operation [1-3]. Ultrafiltration (UF) membranes
56 allow the removal of colloidal particles, microorganisms and a considerable amount of
57 dissolved organic matters especially those with the sizes in the micrometer range to purify water
58 [4-6]. These membranes have been extensively utilized as an alternative technology to
59 conventional water purification methods [7, 8]. However, UF membranes frequently hindered
60 by membrane fouling, resulting from the undesirable deposition of organic matters on to the
61 membrane surface and pores clogging, which in turn reduces the membrane efficiency, shortens
62 membrane lifespan and increases operation cost [7, 9, 10]. Thus, the development of membranes
63 with anti-fouling properties, easy cleaning, and high water productivity has become a matter of
64 high priority in membrane technology.

65

66 It is well recognized that a membrane with hydrophobic, rough, highly positively charged
67 surface exhibits high adsorption tendency to protein [11]. Therefore, modification of membrane
68 surfaces to induce hydrophilic, smooth and negatively charged characteristics has been a
69 significant focus for development of fouling-resistant membranes. So far, two major types of
70 methodologies have been exploited to increase the hydrophilicity of UF membranes: (1)
71 Antifouling materials are grafted onto membrane surfaces via a variety techniques including
72 chemical posttreatment [12], UV irradiation [13] and plasma treatment; (2) Blending polymer
73 materials with a more hydrophilic inorganic nanomaterials, polymers and amphiphilic
74 copolymers [14-17] is another strategy to improve membrane hydrophilicity. Although the
75 membrane's hydrophilicity can be enhanced for antifouling modification, these procedures
76 usually are aggressive, tedious or incapable of large-scale production[18].

77

78 UF membrane fouling usually appears in a combination of mechanisms such as adsorption, pore
79 blocking, and cake or gel formation [4, 19-21]. Adsorption of proteins and humic acids is a
80 common problem encountered and often irreversible [10]. It is challenging to recover the
81 membrane's water flux causing by internal fouling where the foulants are trapped inside porous

82 sublayers [22]. A more effective way to prevent or reduce fouling is to avoid the foulant from
83 trapping into the membrane sublayer. The membrane separation process is a surface
84 phenomenon where the skin/selective layer plays a pivotal role in retaining foulants. Thus, it is
85 a natural option to alter the surface chemistry or topography of membranes for fouling control
86 [23]. Among various approaches, a thin hydrophilic layer generated on membrane surface via
87 deposition is a practical solution attributing to its simple procedure, low cost, easy to scale-up
88 and its presence on the surface. This inert deposition layer could act as a prefilter to screen out
89 those matters with a high propensity to cause membrane fouling [9, 10]. However, in most
90 situations, the deposited material may leach out or be washed off after long time filtration or
91 frequent chemical cleaning. The development of a robust antifouling deposition layer is
92 therefore important for practical applications.

93

94 Methyl acrylate was found to be hydrophilic and has demonstrated its antifouling property when
95 grafted on polysulfone membrane via UV (ultraviolet-visible) irradiation [13]. Ethylene glycol
96 derivatives were reported to be less adhesive to protein and natural organic matters [24-26].
97 Blending low molecular ethylene glycol derivatives into the polymer for membrane fabrication
98 [17, 26] or grafting via UV [13] have been extensively studied, but both methods either have
99 potential risks of leakage of modifiers with low molecular weights and reducing membrane
100 mechanical strength, or rely on the harsh and complicated reaction conditions.

101

102 In this work, a group of synthesized hydrophilic polymers including one type of random
103 copolymer and two types of homopolymer were deposited onto the PES membrane surface. It
104 is expected to use these polymer-based modifiers to improve the membrane hydrophilicity via
105 the water affinitive unit of glyceryl monomethacrylate (GLMMA), and to strengthen the
106 interaction with PES membrane surface via the membrane affinitive unit of poly(ethylene glycol)
107 methyl ether acrylate (PEGA). The membrane surface chemistry, surface charge, and
108 topography were characterized using ATR-FTIR, zeta-potential, FESEM and AFM, respectively.
109 The fouling behaviors of the modified membranes were evaluated in a cross-flow filtration
110 system using 0.5 wt % Bovine Serum Albumin (BSA) solutions. Subsequently, a long-term

111 cyclic fouling test was conducted to assess their stability during filtration and chemical cleaning.
112 The results demonstrated the feasibility of as-synthesized copolymer in reducing organic
113 fouling for UF membrane applications.

114

115 **2. Methodology**

116 **2.1 Materials and chemicals**

117 Polyethersulfone resins (PES, Ultrason® E6020P, BASF) and N, N-Dimethylformamide (DMF,
118 Merck) were used to prepare dope solutions for membrane substrates. Bovine Serum Albumin
119 (BSA, CAS number 9048-46-8) and Sodium hydroxide (CAS number 1310-73-2) were
120 purchased from Sigma Aldrich to represent organic foulant and using as cleaning chemical,
121 respectively.

122

123 **2.2 Synthesis of random copolymer GP2, homopolymer AM2, and homopolymer GL2**

124 The copolymer (GP2) and homo-polymer (AM2 and GL2) were synthesized by Nippon
125 Shokubai Co., Ltd. The chemical structures of the three macromolecules are listed in Table 1.
126 AM 2, GL2 and GP2 are synthesized from 100% PEGA, 100% GLMMA, and a mixture of
127 GLMMA and PEGA (molar ratio 80% to 20%), respectively. In brief, Pure water (50.7 g) was
128 charged in a flask under a nitrogen atmosphere and the solution was preheated at 80 °C in an
129 oil bath. Then, glycerol monomethacrylate (GLMMA) (4.8 g, 30 mmol), poly(ethylene glycol)
130 methyl ether acrylate (PEGA) (57.9 g, 150 mmol), 35 wt % sodium hydrogensulfite aqueous
131 solution (0.9 g, 3 mmol), and pure water (20 g) were constantly fed into the reaction flask for 3
132 h and 2 wt % sodium peroxodisulfate aqueous solution (22.5 g, 2 mmol) was fed for 3.5 h,
133 generating GP2. Similarly, AM2 was synthesized using PEGA, and GL2 was synthesized using
134 GLMMA. Molecular weight was measured by gel permeation chromatography. In current
135 condition, the amount of residual monomer in the final reaction solution, measured by gas
136 chromatography and liquid chromatography, is zero. So, the chemical composition of the final
137 polymer is the same as the ratio of initial monomers.

138

139 **2.3 Fabrication of UF membranes**

140 The PES hollow fiber UF membranes was obtained following the dry-jet wet spinning
141 method, which was depicted in our previous work [27]. The obtained membrane has a
142 molecular weight cut-off (MWCO) around 60,000 Dalton.

143

144 **2.4 Deposition of polymer modifiers onto PES hollow fiber UF membrane surfaces**

145 Membrane modules were prepared according to our previous work [28]. Each module consists
146 of 6 pieces fibers with an active membrane area of $\sim 46 \text{ cm}^2$. The pure water permeability (PWP)
147 was measured before conducting the modification, and only the membrane modules with similar
148 PWP were selected for further modification. The polymer solution (2 g/L) was vacuumed into
149 a hollow fiber module by a syringe and stayed in contact with the membrane for 24 hours. The
150 modification is designed to occur on the lumen side of the hollow fibers. Then the excess
151 solution was purged off and cleaned with DI water for several times. The modified modules
152 were kept in DI water until further use.

153

154 **2.5 Membrane characterization**

155 All the membrane samples were freeze-dried for at least 12 hours before characterization. For
156 surface characterizations, the hollow fiber membrane was cut open and fixed on a flat tape with
157 the inner surface faced up properly. The surface and cross-section morphologies of the
158 membranes, coated with a thin layer of platinum, were observed by a Field-emission scanning
159 electron microscopy (JSM-7600F) from JEOL. The surface roughness was estimated by atomic
160 force microscope technology (AFM, Park XE-100) in a non-contact mode.

161

162 Attenuated total reflection-Fourier transform infrared spectra (ATR-FTIR) of the membranes
163 were characterized by an infrared spectrometer (Shimadzu Prestige-21, Japan). The water
164 contact angle of the membrane surfaces was measured using a goniometer (Contact Angle
165 System OCA, Data Physics Instruments GmbH, Singapore). The data reported are based on 8
166 replicate samples. The zeta potentials of membrane skin layer were characterized using an
167 electro-kinetic analyzer (SurPASSTM 3, Anton Paar) with 10 mM NaCl aqueous solution acting
168 as the background electrolyte solution [29].

169

170 2.6 Membrane fouling tests

171 BSA fouling tests were conducted at constant pressure mode in a typical cross-flow filtration
172 setup as mentioned elsewhere [6]. In brief, a membrane module was mounted in a circulated
173 testing loop. Deionized water was pumped to permeate through the membrane at a surface flow
174 velocity of $\sim 0.8 \text{ m}\cdot\text{s}^{-1}$ at a constant pressure of 1 bar. The initial pure water flux of the module,
175 labelled as J_{BF} , was recorded. Then, the feed water was replaced with a BSA solution (0.5 wt %)
176 for fouling tests at the same mode. Water flux during the fouling tests, J_F , of each membrane
177 module was calculated and was recorded periodically for 120 minutes. After the 120-min
178 fouling test, the membrane was on-line washed with DI water for 15 mins and then cleaned with
179 a NaOH solution (0.2 wt %) for 15 min. The Flux after chemical cleaning, denoted as J_{AF} , was
180 tested and recorded. One complete testing loop of J_{BF} , J_F , J_{AF} is counted as one cycle. For the
181 cyclic fouling tests, three continuously cycles were conducted.

182 Flux recovery (FR) and membrane resistances were calculated as follows to appraise the fouling
183 performance of membranes [30, 31]:

$$184 \quad \text{FR (\%)} = J_{AF}/J_{BF} * 100\% \quad (1)$$

185 Intrinsic membrane resistance (R_m):

$$186 \quad R_m = \frac{TMP}{\mu \times J_{BF}} \quad (2)$$

187

188 Irreversible resistance (R_{ir}):

$$189 \quad R_{ir} = \frac{TMP}{\mu \times J_{AF}} - R_m \quad (3)$$

190 Reversible resistance (R_r):

$$191 \quad R_r = \frac{TMP}{\mu \times J_F} - R_m - R_{ir} \quad (4)$$

192 Total resistance (R_t):

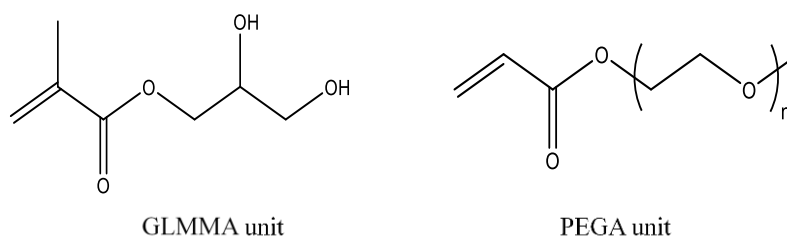
$$193 \quad R_t = R_m + R_{ir} + R_r \quad (5)$$

194 where TMP is transmembrane pressure (100 kPa) and μ is the viscosity of permeate.

195 **3. Results and discussion**

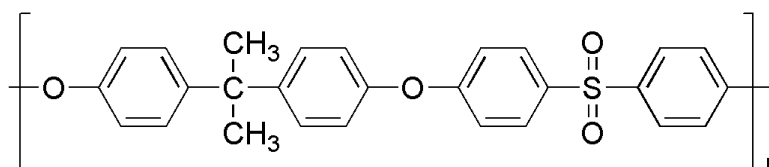
196 **3.1 Chemistry of random copolymer and homopolymers**

197 The Chemical structures of the repeat units in polymer modifiers and PES formula are shown
 198 in Figure 1. The composition of polymer modifiers and their intrinsic hydrophilicity are
 199 summarized in Table 1. Two homopolymers (GL2 and AM2) and one random copolymer (GP2)
 200 were synthesized with the molecular weight ranging from 43,000 to 54,000 Dalton. The
 201 synthesized polymer, GL2, is much more hydrophilic than PES, as indicated by its lower contact
 202 angle value, $\sim 44^\circ$. It is expected to assemble these polymers on PES UF membrane surface to
 203 improve membrane surface hydrophilicity and thus mitigate membrane fouling.



204
205
206

(a)



207
208

(b)

209 Figure 1. (a) Chemical structure of two monomers used for polymer synthesis; (b) chemical
 210 structure of Polyethersulfone (PES).

211

212

Table 1. Polymer composition and hydrophilicity

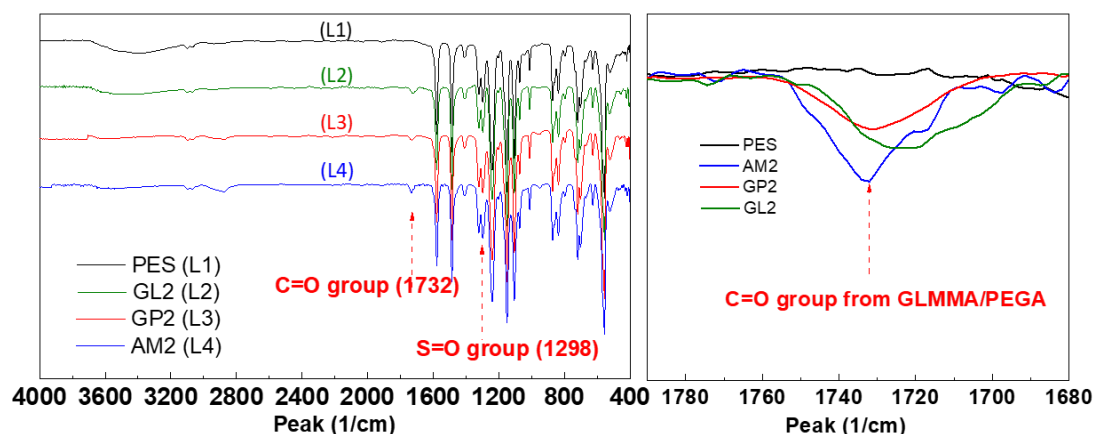
Polymer modifier	Composition (mol.%)	Molecular Weight (Mw)	Contact angle ($^\circ$) ⁽¹⁾
GL2	GLMMA=100	47000	44.0 \pm 1.2
GP2	GLMMA/PEGA=20/80 (random copolymer)	54000	-
AM2	PEGA=100	43000	-

213 Note: (1) The polymer was coated on a glass plate and was dried at 60° for 6 hours before water contact
 214 angle tests. GP2 and AM2 are viscous liquid and can dissolve in water quickly, thus do not have a water
 215 contact angle.

216

217 3.2 Membrane surface properties and morphologies

218 Three types of polymer modifiers with the same chemical segment and different molar ratio
219 were deposited onto three PES membrane surfaces, respectively. These membrane surfaces
220 were characterized via ATR-FTIR as illustrated in Figure 2. The peak at 1298 cm^{-1} corresponds
221 to S=O from PES UF membrane. Compared to the pristine membrane, a new peak can be
222 observed for all three modified membrane surfaces at 1732 cm^{-1} assigned to C=O group from
223 GLMMA and PEGA segments in polymer modifiers, which verifies the existence of the
224 modifiers on the PES surface.

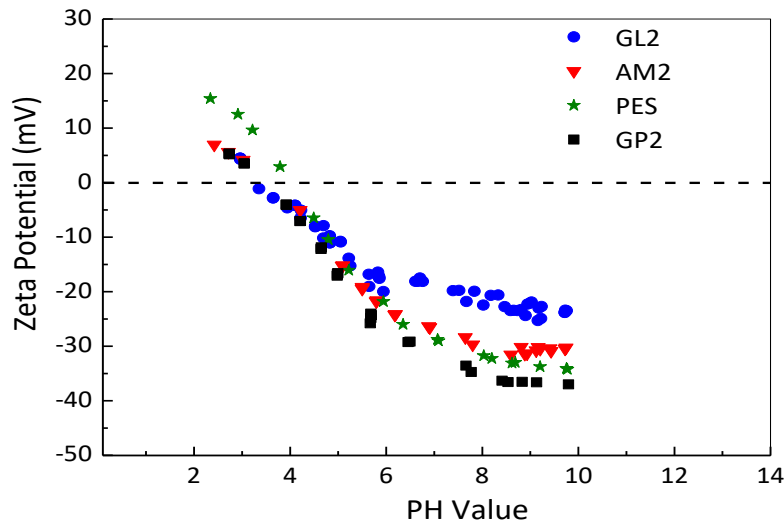


225

226 Figure 2. ATR-FTIR spectra of the control membrane and copolymers/homo-polymer modified
227 membrane. (a) Full spectra FTIR results; (b) enlarged spectra of the target specific peaks. Lines
228 (1)-(4) stand for the PES, GL2, GP2, AM2 adsorbed PES membranes, respectively.

229

230 The surface charge was characterized by Zeta potential as shown in Figure 3. All the membranes
231 show a similar charge profile in the pH values ranging from 2 to 10. It is noted that GL2 (100%
232 GLMMA unit) has a higher zeta potential value than AM2 (100% PEGA unit) in the pH range
233 of 4 to 10. It reveals that the segment unit GLMMA is more positively charged than the PEGA
234 unit in the basic pH range which may due to R-OH group in GLMMA unit can accept a proton
235 (H^+) to form R-OH_2^+ .



236

237 Figure 3. Zeta Potential as a function of pH of control PES membrane and modified membranes.

238

239 Figure 4 presents the surface images of PES membrane, GL2, GP2, AM2 modified PES

240 membranes, respectively. The surface of the membranes coated with polymer modifiers is less

241 porous than that of control PES membrane due to the deposition of the modifiers on the surface

242 and the covering of the large pores. The inserted images show the water contact angles of the

243 modified membranes and control membrane. The data of the water contact angles follow the

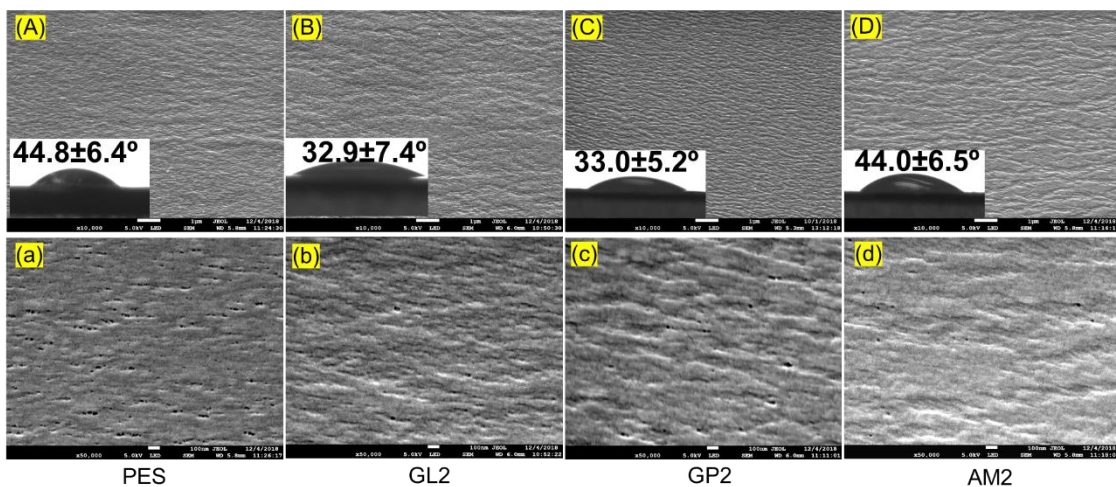
244 trend as $GL2 < GP2 < AM2/PES$, which is attributed to the portion of hydrophilic GLMMA unit.

245 The GL2 with 100% GLMMA unit has the lowest contact angle, and the GP2 has a moderate

246 low contact angle with 20% GLMMA unit. It is expected that these deposited hydrophilic

247 polymers are stable enough and can reduce the membrane contamination with organic foulants.

248



249

250 Figure 4. FESEM images of membrane surface (A) PES, (B) GL2, (C) GP2, and (D) AM2. The

251 scale bar in the first row stands for 1 μ m and 100 nm in the second row.

252

253 AFM was utilized to characterize the surface roughness after surface modification. It is
 254 observed from Table 2 that the root mean square roughness (R_q), mean roughness (R_a) and
 255 maximum peak-to-valley distance (R_z) of the GP2 are lower than those of the control PES, AM2,
 256 and GL2, indicating the more smooth surface of the GP2 membrane. It is expected that GP2
 257 and GL2 membrane could benefit from this reduced roughness when foulants exist in feed
 258 solution during filtration.

259

260 Table 2. Roughness of the control membrane and polymer-coated membranes.

Polymer modifier	R_q (nm)	R_a (nm)	R_z (nm)
PES	7.2±2.2	5.9±1.9	49.4±12.8
GL2	4.5±0.6	3.6±0.5	35.9±5.3
GP2	3.7±0.3	2.8±0.3	46.0±1.9
AM2	7.2±0.2	5.8±0.1	58.8±13.4

261

262 3.3. UF membrane intrinsic permeability and fouling study

263 The pure water permeability (PWP) of membranes is presented in Table 3. The absolute initial
 264 PWP of the GL2, GP2 and AM2 decreases ~60% after the modification from 253 LMH/bar to
 265 ~100 LMH/bar, due to the mass transfer resistance induced by the additional polymer layer. The
 266 additional layer may cover some visible large surface pores according to the FESEM images in
 267 Figure 4, resulting in the decrease in PWP. The decrement in MWCO in Table 3 further verifies
 268 that the pore size was narrowed when the polymer adsorbed onto PES UF membranes.

269

270 Table 3. Intrinsic permeability of the control membrane and the modified membranes.

Membrane code	<i>PWP</i> (LMH/bar)	<i>MWCO</i> (Normalized, %) ⁽¹⁾	<i>BSA fouling</i> flux (LMH)⁽²⁾
PES	253±48	100	58±3
GL2	101±21	98	59±15
GP2	104±10	79	73±7

AM2

103±11

70

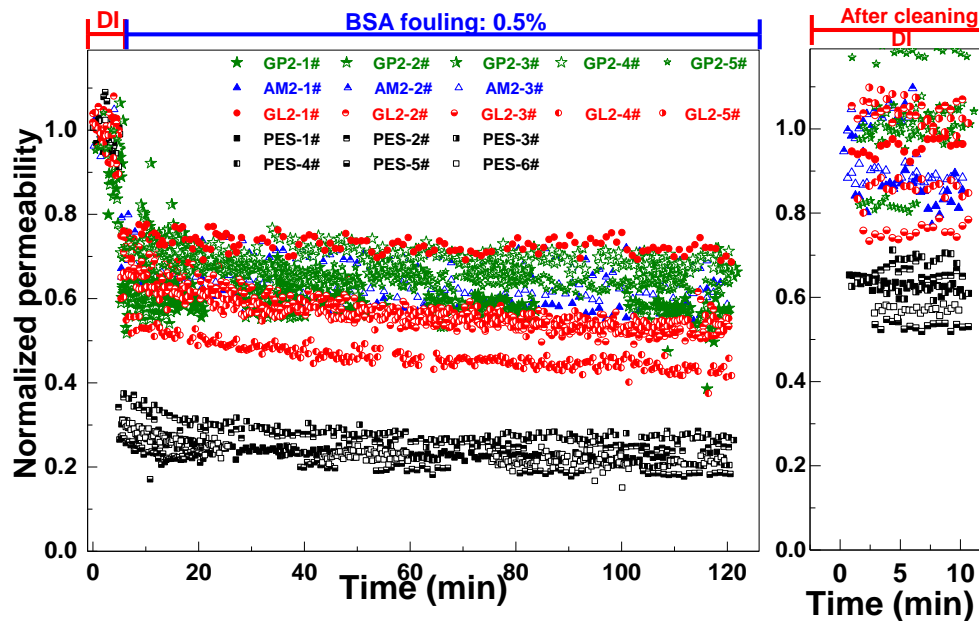
66±3

271 Note: (1) The MWCO of the modified membranes were tested and normalized with the MWCO
 272 of control PES membrane; (2) BSA fouling flux means the water flux using 0.5 wt % BSA
 273 solution under the pressure of 1 bar, the reported flux is the average data of the last 30 minutes
 274 in the 2-hour BSA fouling test.

275

276 On the other hand, the modified membranes perform better in terms of normalized permeability,
 277 absolute permeability, and flux recovery rate during the BSA fouling tests according to Figure
 278 5 and Figure 6. The values of normalized permeability, absolute permeability, and recovery rate
 279 are in the order of GP2> AM2> GL2>PES. As indicated in Figure 5 (Left), PES UF membrane
 280 deposited with GP2, GL2 and AM2 maintain 50% to 85% of their initial permeability during
 281 BSA fouling tests, while PES control membrane loss ~70% of its initial permeability. Flux
 282 recovery rate is an excellent index to evaluate membrane antifouling performance. The modified
 283 membranes show a higher flux recovery rate as compared with control PES membrane. The
 284 typical flux recovery rate is 95%, 85%, 60% for GP2, AM2 and control PES, respectively.

285



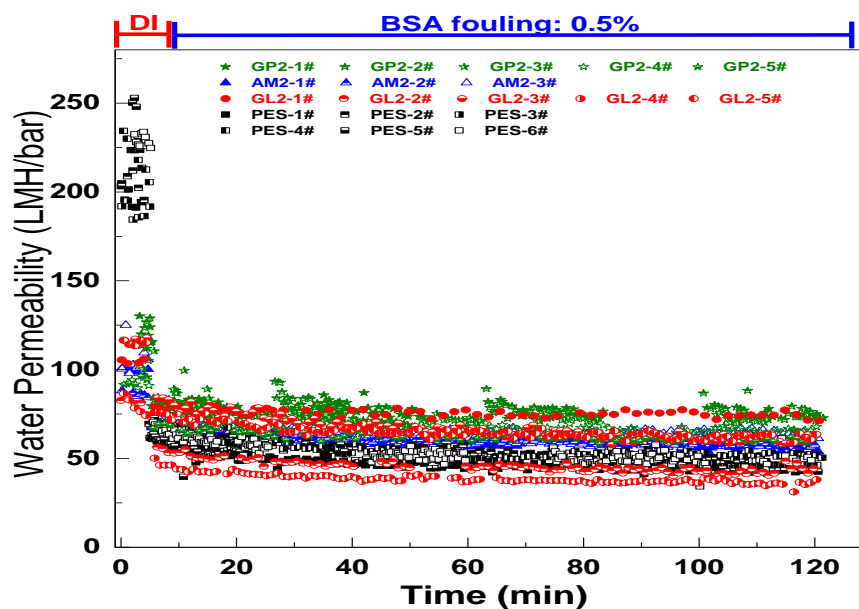
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287 Figure 5. Normalized water permeability of as-prepared membranes under high concentration
 288 foulant. Testing conditions: constant pressure at 1 bar; Time 0-5min, DI water as feed; Time 6-
 289 120min, 0.5% BSA solution as feed. The numbers in the legends mean the replicate fouling
 290 tests of each membrane type.

291

292 It is noted in Table 3 that the initial pure water permeability of the modified membrane is
293 obviously lower than that of the control PES membrane. The absolute permeability during BSA
294 fouling test, a good indicator of membrane energy consumption, is also studied in this work and
295 the results are shown in Figure 6. Generally, membrane fouling took place immediately when
296 the membrane contacts with foulants, indicated by the sudden water permeability decline.
297 Subsequently, a continuous gradual reduction of water flux was observed for the rest of the
298 testing period. Although the modified membranes show a lower initial permeability, they
299 outperform the control membrane in treating water containing foulants. The values of the water
300 permeability follow the sequence of GP2>AM2>PES. The results suggest that the PES UF
301 membrane modified with a hydrophilic thin layer of copolymers (GP2) is a practical and
302 straightforward way to reduce membrane fouling with the benefits of simple modification
303 procedures, high water permeability and good flux recovery rate. In addition, these copolymer
304 layers are highly stable after cleaning with a 0.2 wt % NaOH aqueous solution for three times
305 in the cyclic fouling test, indicated by the unchanged water permeability.

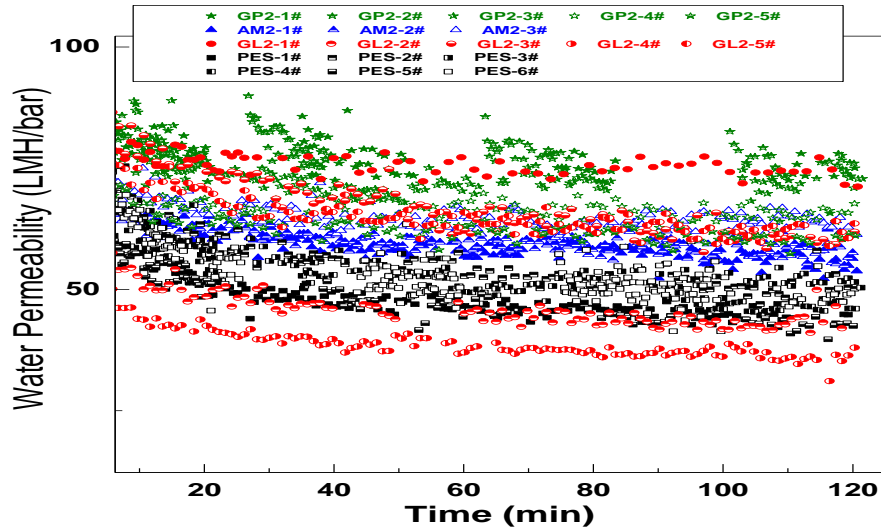
306



307

308

(a)



(b)

309

310

311 Figure 6. (a) full profile view and (b) enlarged view of the permeability dependence on testing
 312 time of control membrane and polymer modified membranes. The numbers in the legends mean
 313 the replicate fouling tests of each membrane type.

314

315 The membrane resistance profiles are summarized in Table 4. It reveals that the modified
 316 membranes have a higher intrinsic membrane resistance than the control PES membrane due to
 317 the additional polymer layer. The irreversible resistance, reversible resistance and total
 318 resistance of modified membranes, especially GP2 membrane, are lower than those of control
 319 PES membrane during fouling testing.

320

321

Table 4. Membrane resistance profiles

Membrane code	$R_m (\times 10^{11} \text{ m}^{-1})$	$R_{ir} (\times 10^{11} \text{ m}^{-1})$	$R_r (\times 10^{11} \text{ m}^{-1})$	$R_t (\times 10^{11} \text{ m}^{-1})$
GL2	42.3±8.0	3.6±4.7	32.5±19.8	78.5±24.4
GP2	37.7±4.4	0.7±1.6	19.9±2.5	58.4±5.0
AM2	42.0±4.3	5.1±3.2	22.3±2.9	69.4±5.5
PES	19.0±2.6	11.7±2.4	49.8±4.9	80.4±5.8

322

Note: R_m , R_{ir} , R_r , and R_t represents the intrinsic membrane resistance, irreversible resistance,

323 reversible resistance, and total resistance, respectively.

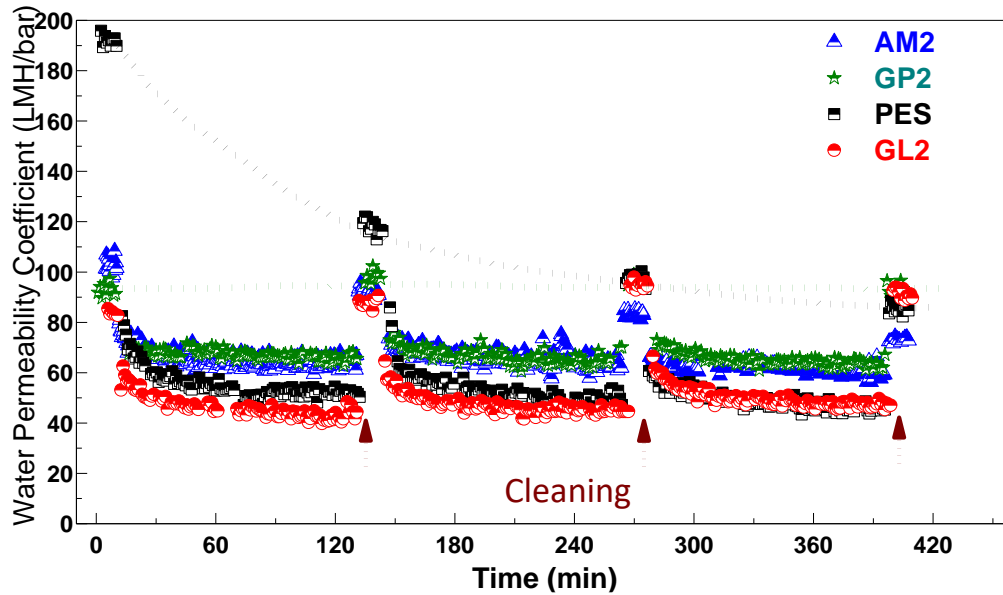
324

325 **3.4 Evaluation of the stability of the deposition layer**

326 **3.4.1 Cyclic fouling tests**

327 Cyclic fouling tests were conducted to evaluate the deposition layer's stability during the
328 chemical cleaning, which is a necessary step in practical applications. Figure 7 shows the cyclic
329 fouling test results of modified membranes. In general, the modified membrane's pure water
330 permeability was supposed to increase to a comparable value as of PES membrane if the
331 deposition layer is removed from the membrane surface. The unchanged PWP and recovery rate
332 of all the modified membranes at the initial stage of all three cycles indicates that the deposition
333 layers are firmly attached on the membrane surface throughout the cyclic fouling test and
334 chemical cleaning. The dotted green and black lines were depicted to project the trend of pure
335 water permeability of the GP2 and PES membranes in long-term service. Although the GP2
336 membrane shows a significant lower pure water permeability than that of PES control
337 membrane, the GP2 membrane excels PES membrane in BSA filtration process. The pure water
338 permeability of the GP2 membrane is almost maintained around 95 LMH/bar, while PES
339 membrane dropped from 200 LMH/bar to 85 LMH/bar, which is below that of the GP2
340 membrane after three cycles of fouling test. To summarize, the GP2 exhibits better performance
341 than the other three membranes in view of the stability, fouling filtration permeability, and flux
342 recovery rate.

343



344

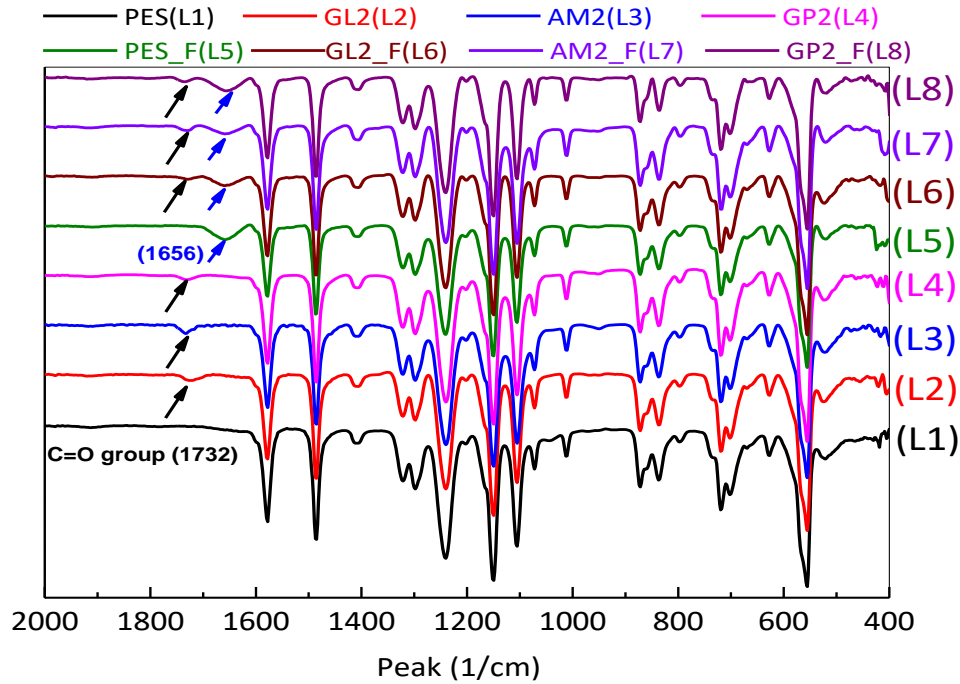
345 Figure 7. Long-term cyclic fouling test of a representative sample of each type of membrane.
 346 The membranes were cleaned with DI water and 0.2 wt % NaOH solution during each fouling
 347 cycle. The dotted angles point out the time of cleaning, and dotted lines were drawn to
 348 illustrating the trend of pure water permeability of the control membrane and GP2 modified
 349 membrane.

350

351 3.4.2 Membrane surface chemistry after cyclic fouling test

352 Figure 8 shows the ATR-FTIR spectra of the pristine membranes (L1-L4) and chemical cleaned
 353 membranes after three cyclic fouling testing (L5-L8). Compared to the corresponding pristine
 354 membranes, an additional peak is shown in the fouled membranes at 1656 cm^{-1} which is the
 355 characteristic peak of BSA protein due to the C=O stretching mode of amide I [32]. The
 356 existence of BSA peak even after chemical cleaning indicates that the membrane even modified
 357 with polymer can not permanently avoid fouling, but the decreased peak area project that these
 358 modifier can reduce the degree of fouling. The peak at 1732 cm^{-1} , characteristic peak of C=O
 359 group in modifier, evidenced by ATR-FTIR even covered with BSA foulant layer after chemical
 360 cleaning in the cyclic fouling testing confirms the existence of the assembled modified layer.

361



362

363 Figure 8. FTIR spectra of clean membranes (L1-L4) and chemical cleaned membrane after BSA
 364 fouling test (L5-L8). Here, the sample label ended with _F means the chemical cleaned
 365 membrane after fouling test.

366

367 4. Conclusions

368 Three types of synthesized polymer modifiers were utilized to enhance anti-fouling property of
 369 PES UF membrane via direct coating and their response to BSA foulant were evaluated. The
 370 membranes' stability in fouling and chemical cleaning were evaluated as well in the current
 371 study. Several findings can be concluded as follows:

372 (1) The chemical composition, hydrophilicity and molecular weight of the synthesized polymer
 373 were characterized. These macromolecules are hydrophilic and have a molecule weight of
 374 43000, 47000 and 54000 for AM2, GL2 and GP2, respectively.

375 (2) The morphology, water permeability, pore size and chemistry of the control PES and
 376 polymer-modified PES UF membranes were systemically investigated. It was found that
 377 these polymers can deposit on the lumen side of hollow fiber membrane and reduce the
 378 membrane's pure water permeability and pore size.

379 (3) The modified membranes show an average 26% increment of water permeability during
 380 BSA fouling testing as well as higher flux recovery rate compared with the control PES
 381 membrane although the modified membranes exhibit a lower initial pure water permeability.

382 The random copolymer synthesised from two monomers shows a good chemical stability
383 and antifouling effect during the fouling test.

384 (4) The cyclic fouling testing and FTIR characterization demonstrated the stability of the
385 deposited polymer layers in long-term testing and chemical cleaning. The promising result
386 suggests the feasibility of using this group of hydrophilic polymers in developing
387 antifouling UF membranes.

388

389

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394

395 **References**

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397 [1] M.R. Chowdhury, J. Steffes, B.D. Huey, J.R. McCutcheon, 3D printed polyamide
398 membranes for desalination, *Science*, 361 (2018) 682-686.

399 [2] M. Elimelech, W.A. Phillip, The future of seawater desalination: energy, technology, and the
400 environment, *Science*, 333 (2011) 712-717.

401 [3] J. Lin, W. Ye, M.-C. Baltaru, Y.P. Tang, N.J. Bernstein, P. Gao, S. Balta, M. Vlad, A. Volodin,
402 A. Sotto, Tight ultrafiltration membranes for enhanced separation of dyes and Na₂SO₄ during
403 textile wastewater treatment, *Journal of Membrane Science*, 514 (2016) 217-228.

404 [4] W. Gao, H. Liang, J. Ma, M. Han, Z.-l. Chen, Z.-s. Han, G.-b. Li, Membrane fouling control
405 in ultrafiltration technology for drinking water production: A review, *Desalination*, 272 (2011)

406 1-8.

407 [5] W.J. Lau, P.S. Goh, A.F. Ismail, S.O. Lai, Ultrafiltration as a pretreatment for seawater
408 desalination: A review, *Membr Water Treat*, 5 (2014) 15-29.

409 [6] H. Lee, G. Amy, J. Cho, Y. Yoon, S.-H. Moon, I.S. Kim, Cleaning strategies for flux recovery
410 of an ultrafiltration membrane fouled by natural organic matter, *Water Research*, 35 (2001)
411 3301-3308.

412 [7] A. Brehant, V. Bonnelye, M. Perez, Comparison of MF/UF pretreatment with conventional
413 filtration prior to RO membranes for surface seawater desalination, *Desalination*, 144 (2002)
414 353-360.

415 [8] W. Yuan, A.L. Zydney, Humic Acid Fouling during Ultrafiltration, *Environmental Science
416 & Technology*, 34 (2000) 5043-5050.

417 [9] C. Güell, P. Czekaj, R.H. Davis, Microfiltration of protein mixtures and the effects of yeast
418 on membrane fouling, *J Membrane Sci*, 155 (1999) 113-122.

419 [10] X. Shi, G. Tal, N.P. Hankins, V. Gitis, Fouling and cleaning of ultrafiltration membranes:
420 A review, *Journal of Water Process Engineering*, 1 (2014) 121-138.

421 [11] S.P. Beier, A.D. Enevoldsen, G.M. Kontogeorgis, E.B. Hansen, G. Jonsson, Adsorption of
422 Amylase Enzyme on Ultrafiltration Membranes, *Langmuir*, 23 (2007) 9341-9351.

423 [12] X. Ma, Y. Su, Q. Sun, Y. Wang, Z. Jiang, Enhancing the antifouling property of
424 polyethersulfone ultrafiltration membranes through surface adsorption-crosslinking of
425 poly(vinyl alcohol), *J Membrane Sci*, 300 (2007) 71-78.

426 [13] H. Hua, N. Li, L. Wu, H. Zhong, G. Wu, Z. Yuan, X. Lin, L. Tang, Anti-fouling
427 ultrafiltration membrane prepared from polysulfone-graft-methyl acrylate copolymers by UV-

428 induced grafting method, *Journal of Environmental Sciences*, 20 (2008) 565-570.

429 [14] B. Fang, Q. Ling, W. Zhao, Y. Ma, P. Bai, Q. Wei, H. Li, C. Zhao, Modification of
430 polyethersulfone membrane by grafting bovine serum albumin on the surface of
431 polyethersulfone/poly(acrylonitrile-co-acrylic acid) blended membrane, *J Membrane Sci*, 329
432 (2009) 46-55.

433 [15] W. Chen, J. Peng, Y. Su, L. Zheng, L. Wang, Z. Jiang, Separation of oil/water emulsion
434 using Pluronic F127 modified polyethersulfone ultrafiltration membranes, *Sep Purif Technol*,
435 66 (2009) 591-597.

436 [16] Z. Xu, J. Liao, H. Tang, J.E. Efoeme, N. Li, Preparation and antifouling property
437 improvement of Tröger's base polymer ultrafiltration membrane, *Journal of Membrane Science*,
438 561 (2018) 59-68.

439 [17] A. Asatekin, S. Kang, M. Elimelech, A.M. Mayes, Anti-fouling ultrafiltration membranes
440 containing polyacrylonitrile-graft-poly (ethylene oxide) comb copolymer additives, *J*
441 *Membrane Sci*, 298 (2007) 136-146.

442 [18] L.Y. Ng, A. Ahmad, A.W. Mohammad, Alteration of polyethersulphone membranes
443 through UV-induced modification using various materials: A brief review, *Arabian Journal of*
444 *Chemistry*, 10 (2017) S1821-S1834.

445 [19] M.F.A. Goosen, S.S. Sablani, H. Al-Hinai, S. Al-Obeidani, R. Al-Belushi, D. Jackson,
446 Fouling of Reverse Osmosis and Ultrafiltration Membranes: A Critical Review, *Separation*
447 *Science and Technology*, 39 (2005) 2261-2297.

448 [20] K.J. Howe, M.M. Clark, Fouling of Microfiltration and Ultrafiltration Membranes by
449 Natural Waters, *Environmental Science & Technology*, 36 (2002) 3571-3576.

- 450 [21] A.R. Costa, M.N. de Pinho, M. Elimelech, Mechanisms of colloidal natural organic matter
451 fouling in ultrafiltration, *Journal of Membrane Science*, 281 (2006) 716-725.
- 452 [22] K. Kimura, Y. Hane, Y. Watanabe, G. Amy, N. Ohkuma, Irreversible membrane fouling
453 during ultrafiltration of surface water, *Water Research*, 38 (2004) 3431-3441.
- 454 [23] D. Rana, T. Matsuura, Surface modifications for antifouling membranes, *Chemical reviews*,
455 110 (2010) 2448-2471.
- 456 [24] W. Zhao, C. He, H. Wang, B. Su, S. Sun, C. Zhao, Improved Antifouling Property of
457 Polyethersulfone Hollow Fiber Membranes Using Additive of Poly(ethylene glycol) Methyl
458 Ether-b-Poly(styrene) Copolymers, *Industrial & Engineering Chemistry Research*, 50 (2011)
459 3295-3303.
- 460 [25] S. Yin, L. Ren, Y. Wang, Plasma graft of poly(ethylene glycol) methyl ether methacrylate
461 (PEGMA) on RGP lens surface for reducing protein adsorption, *Plasma Science and Technology*,
462 19 (2017) 015501.
- 463 [26] Z. Zhou, S. Rajabzadeh, A.R. Shaikh, Y. Kakihana, W. Ma, H. Matsuyama, Effect of
464 surface properties on antifouling performance of poly(vinyl chloride-co-poly(ethylene
465 glycol)methyl ether methacrylate)/PVC blend membrane, *J Membrane Sci*, 514 (2016) 537-546.
- 466 [27] R. Wang, L. Shi, C.Y. Tang, S. Chou, C. Qiu, A.G. Fane, Characterization of novel forward
467 osmosis hollow fiber membranes, *J Membrane Sci*, 355 (2010) 158-167.
- 468 [28] Y. Chen, C.H. Loh, L. Zhang, L. Setiawan, Q. She, W. Fang, X. Hu, R. Wang, Module
469 scale-up and performance evaluation of thin film composite hollow fiber membranes for
470 pressure retarded osmosis, *Journal of Membrane Science*, 548 (2018) 398-407.
- 471 [29] Y. Liao, S. Goh, M. Tian, R. Wang, A.G. Fane, Design, development and evaluation of

472 nanofibrous composite membranes with opposing membrane wetting properties for extractive
473 membrane bioreactors, *J Membrane Sci*, 551 (2018) 55-65.

474 [30] A. Razmjou, J. Mansouri, V. Chen, The effects of mechanical and chemical modification
475 of TiO₂ nanoparticles on the surface chemistry, structure and fouling performance of PES
476 ultrafiltration membranes, *J Membrane Sci*, 378 (2011) 73-84.

477 [31] D.J. Miller, S. Kasemset, D.R. Paul, B.D. Freeman, Comparison of membrane fouling at
478 constant flux and constant transmembrane pressure conditions, *J Membrane Sci*, 454 (2014)
479 505-515.

480 [32] I.M. Tang, N. Krishnamra, N. Charoenphandhu, R. Hoonsawat, W. Pon-On, Biomagnetic
481 of Apatite-Coated Cobalt Ferrite: A Core-Shell Particle for Protein Adsorption and pH-
482 Controlled Release, *Nanoscale research letters*, 6 (2010) 19-19.

483