

1 **Mitigation of reverse osmosis membrane fouling by electrochemical-microfiltration-**

2 **activated carbon pretreatment**

3 Submitted to

4 ***Journal of Membrane Science***

5 Xiaolei Zhang ¹, Jialin Huang ¹, Xiaoying Cheng ¹, Huihui Chen ¹, Qiang Liu ^{1*}, Ping Yao ²,

6 Hao H. Ngo ³, and Long D. Nghiem ^{3*}

7
8 ¹. *School of Environmental & Chemical Engineering, Shanghai University, No. 99 Shangda*
9 *Road, Shanghai 200444, China*

10 ². *School of Textile clothing & Arts Media, Suzhou Institute of Trade and Commerce, No. 287*
11 *Xuefu Road, Suzhou 215009, China*

12 ³. *Centre for Technology in Water and Wastewater, School of Civil and Environmental*
13 *Engineering, University of Technology Sydney, Sydney, NSW 2007, Australia*

14

15

16

17

18

19 *Corresponding to Qiang Liu*

20 *School of Environmental and Chemical Engineering, Shanghai University, No. 99 Shangda Road*

21 *Shanghai 200444, China, qliu@shu.edu.cn*

22 *Long D. Nghiem*

23 *Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering,*

24 *University of Technology Sydney, Sydney, NSW 2007, Australia, DucLong.Nghiem@uts.edu.au*

25 **Abstract**

26 In this study, a hybrid electrochemical-microfiltration-granular activated carbon adsorption (e-
27 MF-GAC) pretreatment process was developed and demonstrated for controlling reverse
28 osmosis (RO) fouling. Compared to ultrafiltration (UF), e-MF-GAC pretreatment resulted in
29 30% higher permeate flux. Results in this study show the complementarity among individual
30 treatment processes of e-MF-GAC for removing inorganic/organic foulants and small organic
31 molecules, leading to superior performance over conventional UF pretreatment. This
32 hypothesis is validated by systematic feed water and foulant composition analysis as well as
33 fluorescence excitation-emission matrix and X-ray diffraction spectroscopic characterization
34 of the organic and inorganic foulants on the membrane surface, respectively. Organic foulants
35 on the membrane were mostly protein-like compounds and their disposition onto the membrane
36 surface was much lower after pretreatment using e-MF-GAC compared to UF. Similarly, after
37 e-MF-GAC-RO pretreatment, organic content in the RO concentrate was lower than that after
38 UF pretreatment. Results in this study provide the basis for further research at pilot scale to
39 assess the economic viability of the proposed e-MF-GAC process as an alternative to
40 conventional UF pretreatment for mitigating RO membrane fouling.

41 **Key words:** Reverse osmosis, fouling, electrochemical, microfiltration, activated carbon.

42 1. Introduction

43 Water reuse has been increasingly applied around the world for a secured water supply [1].
44 With outstanding permeate quality, efficient energy consumption and small footprints, reverse
45 osmosis (RO) is the most commonly used technology for water reuse [2]. The RO process is
46 especially effective and efficient at removing micropollutants of concern for water reuse
47 applications [3, 4]. However, membrane fouling, which could lead to significant flux decline
48 and deteriorated permeate quality, remains a critical bottleneck to RO applications [5].

49 RO fouling can be categorized into inorganic scaling, organic fouling and biofouling. As
50 the RO feed was generally pretreated by the microfiltration (MF) or ultrafiltration (UF) and
51 preconditioned with anti-scalants and chloramine, membrane scaling and biofouling could be
52 reduced to some extent [5-7]. However, small organic molecules that could not be removed by
53 MF or UF can eventually cause severe organic fouling [8, 9]. In addition, multivalent cations
54 such as Ca^{2+} and Mg^{2+} can complex with these small organic molecules to exacerbate membrane
55 fouling [10, 11]. As such, an effective pretreatment technique to remove small organic
56 molecules is essential for the sustainable RO filtration of reclaimed water.

57 To alleviate the organic fouling of RO, several pretreatment technologies (e.g., MF, UF,
58 coagulation, activated carbon adsorption and oxidation) have been investigated for eliminating
59 organics in the feed water [12, 13]. Amongst these technologies, MF/UF is mostly used for
60 removing turbidity and suspended solids, where their capacity for removing dissolved organics
61 was limited [14]. Coagulation and granular activated carbon (GAC) adsorption have been
62 proven to be capable of removing organic matter and subsequently reducing the fouling of RO
63 [15, 16]. However, coagulation generally produces significant amounts of sludge and the GAC

64 adsorption requires frequent regeneration [17, 18]. One example of oxidation method is pre-
65 ozonation to alter characteristics (e.g., charge and hydrophilicity) of organic molecules in the
66 feed water and subsequently reduce the affinities of organic matter towards the membrane [19].
67 However, it is noteworthy that the RO fouling may be aggravated by ozonation when high
68 concentration of divalent ions (e.g., Ca^{2+}) and polysaccharides were coexisted in the feed water
69 [19]. As a result, developing effective oxidation method for sustainable fouling control is still
70 required. Electrochemical process has recently emerged as a potentially effective advanced
71 oxidation processes for organic removal. Electrochemical pretreatment has been successfully
72 integrated with the membrane filtration processes [20, 21]. The electrochemical process
73 generates strong oxidants (e.g., reactive oxygen species (ROS) and reactive chlorine species
74 (RCS)) with the presence of chloride or oxygen contained in the bulk solution, which could
75 decompose the organic matter or alter their physical properties (e.g., surface charge and
76 hydrophilicity) [13]. Compared to ozonation, the electrochemical process has several
77 advantages including: chemical free, effective in organic decomposition and low operation cost
78 [22]. Several studies have achieved efficient fouling reductions in the membrane bioreactors
79 with the application of electric field, where the fouling was significantly inhibited due to the
80 removal of high fouling potential organic matters (e.g., biopolymers) and enhanced electrostatic
81 repulsion between the foulants and the membrane surface [23-25]. Mameda et al. [26] observed
82 that MF membrane fouling was significantly reduced after electrochemical pretreatment.
83 However, the application of electrochemical pretreatment for controlling RO fouling has not
84 yet been studied.

85 It is noted that most commercially available RO membranes (e.g., polyamide) could be

86 significantly damaged on contacting the RCSs [27]. This suggests the electro-generated RCSs
87 should be removed if the electrochemical approach were applied as the RO pretreatment. To
88 eliminate the RCSs, GAC adsorption has proven to be a valid approach which was widely
89 applied in water treatment process [28]. However, the information regarding to the coupling
90 electrochemical process and GAC for RO fouling control is lacking.

91 As such, this study proposed a hybrid electrochemical process based pretreatments
92 approaches to control the fouling of RO during the treatment of a biological treated industrial
93 wastewater. The electrochemical process was coupled with the submerged ceramic MF process
94 and activated carbon adsorptions, where the MF was used to remove the large particles and the
95 activated carbon was employed to eliminate the RCS in the effluent to avoid the damage of RO
96 membrane by the RCS. The effects of different electric fields on the treatment performances
97 and membrane fouling control of RO were investigated and compared with those using
98 conventional UF pretreatment. The detailed characterization of the organic transformation,
99 foulant layer during the entire treatment was carried out for an in depth understanding of the
100 mechanism associated with the fouling reduction.

101 **2. Materials and methods**

102 **2.1. Feed wastewater**

103 Biologically treated effluent from a wastewater treatment plant (WWTP) which receives
104 the wastewater from an industrial complex in Shanghai was used as the feedwater. The
105 industrial complex is mainly composed of the chemical and petrochemical processing
106 incorporates, which produces a great amounts of high strength wastewaters. Key characteristics

107 of the feed water are summarized in Table 1.

108 Table 1: Key characteristics of the raw wastewater.

Parameter	TDS	COD	TN	TP	pH	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Na ⁺	K ⁺
Value (mg L ⁻¹)	3554.8	52.1	8.4	0.3	7.5	50.4	31.4	195.2	524.5	57.5

109

110 2.2. Pretreatment rig

111 The e-MF-GAC process was carried out in a custom-made unit (Fig.1). For the
112 electrochemical device, two flat IrO₂/Ti electrodes with the dimension of 10 cm × 10 cm were
113 vertically placed 1.5 cm apart in a 2 L reactor. These electrodes were connected to a DC power
114 regulator. The feed water was continuously pumped into the reactor and a level sensor was used
115 to regulate the water level in the reactor. The water was thoroughly mixed using a magnetic
116 stirrer. A flat sheet ceramic MF membrane made of ZrO₂ (nominal pore size of 0.1 μm and
117 effective membrane surface of 0.02 m²) was submerged in the reactor. The ceramic membrane
118 has a dimension of 10 cm × 12 cm × 0.5 cm. The membrane surface was hydrophilic since
119 ZrO₂-based membranes usually have a contact angle less than 20°, and was negatively charged
120 under the experimental conditions (i.e., at ~pH 7) [29]. The membrane module was vertically
121 placed between the two electrodes, where the distance between the membrane and anode or
122 cathode electrode was the same. The MF flux was regulated at 55 LMH corresponding to a
123 hydraulic retention time (HRT) of 6 h. The permeate was transferred from the membrane
124 permeate outlet to an activated carbon column for quenching any residual chlorine prior to the
125 RO membrane. The activated carbon column was made of polymethyl methacrylate with length
126 and diameter of 60 cm and 4 cm, respectively. The column was packed with GAC of 0.18-0.30

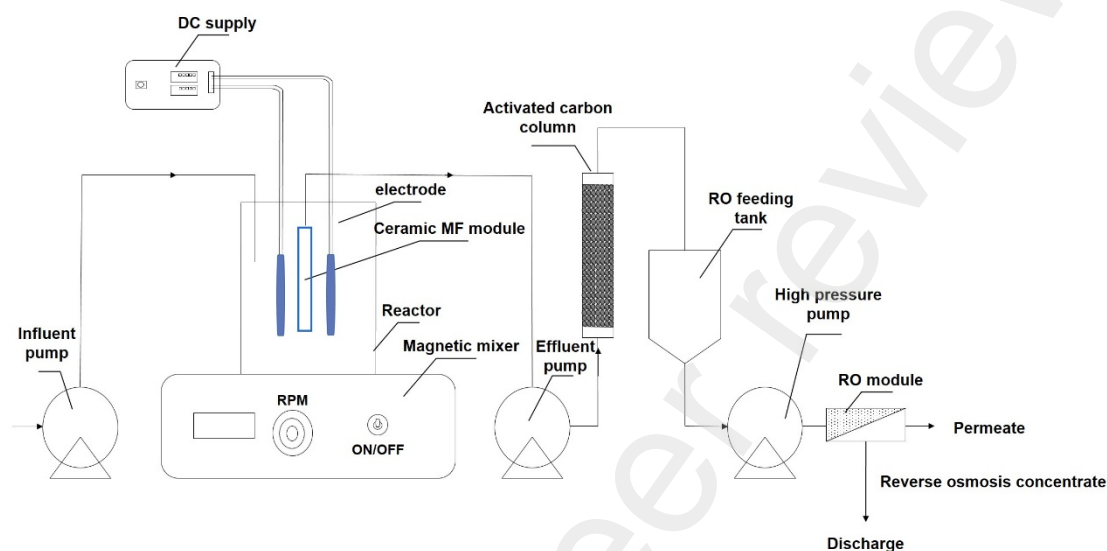
127 mm in size. The GAC has a specific surface area of about 1039 m² g⁻¹ and iodine value of 800
128 mg g⁻¹. Prior to packing into the column, the granular activated carbon was sieved and cleaned
129 using deionized water. The filtration rate for the operation of activated carbon was about 1.2 m
130 h⁻¹ (Empty bed contact time of 30 min). Fresh activated carbon was packed into the column
131 after each pretreatment experiment.

132 A lab-scale RO filtration rig was used. The rig was equipped with a polyamide spiral
133 wound membrane (Shandong Bolong Pty Ltd, China) with an effective size of 0.3 m² and a
134 nominal NaCl rejection rate of 99.5% and a high pressure pump that deliver 2.8 MPa of pressure
135 at 24 °C. The rig was operated at cross flow filtration mode and the crossflow velocity was set
136 at 2 m s⁻¹. To accelerate membrane fouling, the initial flux for the RO was set at 14 LMH. The
137 reverse osmosis concentrate was discharged during the filtration. The RO feed volume for UF,
138 e-MF(1 V)-GAC, e-MF(3 V)-GAC and e-MF(6 V)-GAC was 24, 16, 13 and 12 L, respectively.
139 The permeate was collected through the permeate line and weighed using a digital balance. The
140 filtration of all experiments was 7 hours. The permeate sample was collected at the end of each
141 filtration experiment. After each experiment, the fouled membrane was removed from the
142 module and cut into small pieces. The fouled membrane samples were then soaked in 100 mL
143 of 10 mM NaOH to extract the foulants for further analysis.

144 To evaluate the performance of electrochemical-MF-activated carbon adsorption
145 pretreatment, conventional UF pretreatment was conducted. The UF membrane has a contact
146 angle of ~70 °C and a negative surface charge of ~-10 mV under the experimental condition.
147 The UF module was equipped on the same rig as RO. The UF membrane was spiral wound
148 shaped and made of polyethersulfone (Shandong Bolong Pty Ltd, China), which has a nominal

149 pore size of 0.01 μm and effective surface area of 0.4 m^2 . The UF was conducted at crossflow
150 mode, where the constant pressure of about 0.2 MPa was applied. The collected UF permeate
151 was subjected to the following RO treatment.

152



153

154

155

Fig.1 The electrochemical-MF-adsorption pretreatment setup

156 2.3 Analytical methods

157 The COD of water sample was monitored using the standard method (US-EPA 5200D).

158 The content of total organic carbon in the solution was measured by a total organic carbon

159 (TOC) analyzer (N/C 2100, Analytik Jena AG, Germany). The metal concentration was

160 measured using an inductively coupled plasma spectrophotometer (ICP-AES, Leeman, Prodigy

161 7). The organic composition was characterised using the fluorescence excitation-emission

162 matrix spectra (EEMs) at a fluorophotometer (F97, Lengguang, China). The obtained EEMs

163 were calculated using parallel factor analysis (PARAFAC). The model calculation was carried

164 out using Matlab (R2012a) with the tool box (drEEM 0.64) according to the protocol reported

165 elsewhere [30, 31]. The particle size and zeta (ζ) potential of the samples were determined using

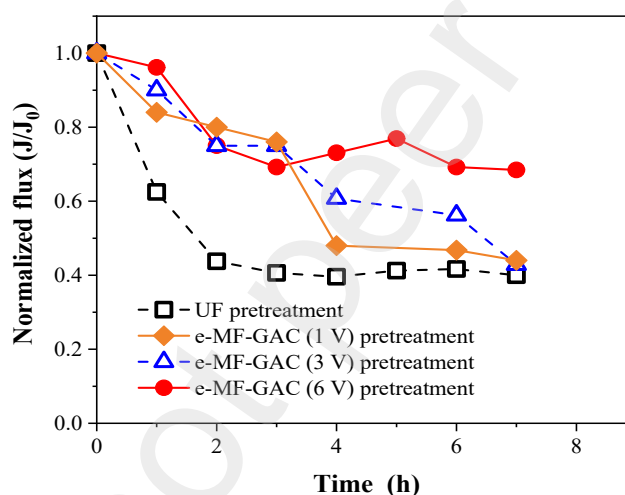
166 a Malvern Zetasizer Nano ZS (Malvern Instruments). The composition of organic and inorganic
167 foulants attached on the membrane was measured using a loss on ignition (LOI) analysis [32].
168 According to the protocol, the foulant attached on the membrane was completely washed from
169 the membrane with 100 mL of 10 mM NaOH, and the foulant solution was then filtered through
170 a pre-weighed GF/C filter. After filtering, the filtered paper was dried at 105 °C for more than
171 24 h and weighed again. Finally, the dried GF/C filter paper was combusted at 550 °C for 2 h.
172 The weight loss was considered as the mass of organic foulant, whereas the remaining mass
173 was considered as the inorganic foulant. Due to the high mass of cake layer, the weight of Na⁺
174 and the foulant dissolved in the detaching liquid which could pass through the filter paper was
175 considered as negligible. The crystal structure of the foulant layer on the membrane surface
176 was characterised using an X-ray diffraction spectroscopy (D/MAX2500 X-ray powder)
177 according to the previously reported protocol [33]. The active chlorine was measured using a
178 diethylphenylenediamine (DPD) colorimetric method according to the Standard Method 4500-
179 Cl.

180 **3. Results and discussions**

181 **3.1. Filtration performance of RO after various pretreatments**

182 The RO normalized flux profiles were evaluated after UF and e-MF-GAC pretreatments
183 and shown in Fig. 2. After UF pretreatment, a rapid flux decline by 60% during the first 2 hours
184 of RO filtration was observed and the flux was then stable for the rest of the experiment. After
185 e-MF-GAC with 1 and 3 V, similar flux profiles were observed and the flux decline was much
186 more gradual compared to that after UF pretreatment. However, at the end of the RO filtration

187 experiment, the final flux was the same with that after UF pretreatment, at 40% of the initial
188 flux. The flux of RO after e-MF-GAC with 6V voltage input has a similar profile but stable
189 after 3 hours of filtration at a much high final flux. Compared to UF pretreatment, the final flux
190 after pretreatment using 6V voltage input was enhanced by 25%. Results in Fig. 2 suggest that
191 e-MF-GAC pretreatment efficiency is dependent on energy input and a sufficiently high voltage
192 (i.e. 6 V) could achieve stably higher flux performance compared to conventional UF
193 pretreatment. Based on results in Fig. 2, all subsequent e-MF-GAC pretreatment experiments
194 were conducted at 6 V.

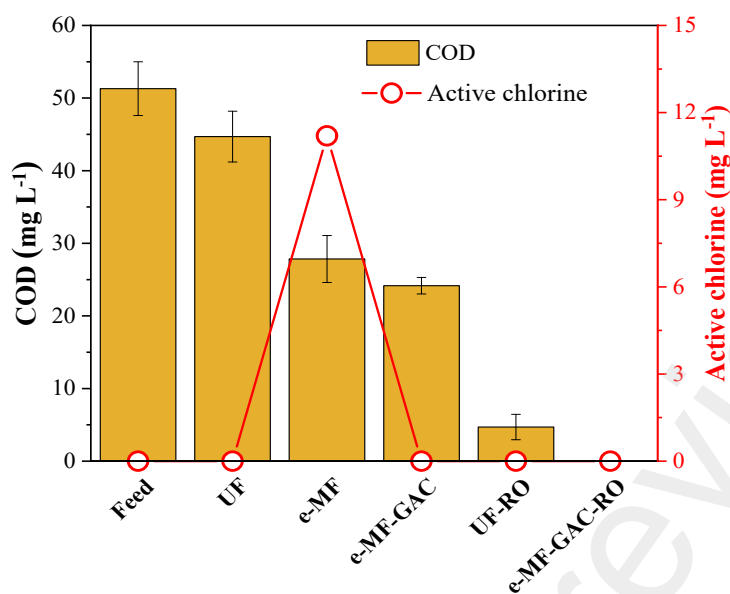


195
196 Fig.2 The comparison of UF and e-MF-GAC pretreatments with different electric input on the
197 flux decline of RO

198 3.2. Characterisation of the organics during various treatments

199 Changes in organic content and composition due to pretreatment were evaluated to
200 determine the underlying mechanisms. UF pretreatment did not significantly remove the
201 organic matter (measured as COD) from the feed water (Fig. 3). By contrast, organic removal
202 by a combination of electrochemical and MF pretreatment was >50% (Fig. 3). In this study, the

203 nominal pore size of the MF membrane was ten times larger than the UF membrane (section
204 2.2), thus, better pretreatment performance of the electrochemical MF hybrid process was
205 attributed to the oxidation of organics by electrochemical treatment. GAC adsorption only
206 resulted in a marginal increase in organic removal (Fig. 3). It is noteworthy that active chlorine
207 was detected in all the effluent samples after electrochemical and microfiltration pretreatment
208 (Supplementary Data, Table S1). The concentration of active chlorine also increased with
209 increasing voltage input. However, after the GAC adsorption, no active chlorine could be
210 detected, confirming the efficiency of the GAC column for chlorine quenching. The reason of
211 low COD removal by GAC in e-MF-GAC is unclear. However, due to the presence of the
212 electrochemical prior to the GAC adsorption, it could be speculated that the RCS produced by
213 electrochemical process could occupy the adsorption site on GAC grains leading to low organic
214 removal. These results are consistent with the designed purpose of the GAC column to remove
215 reactive chlorine prior to the RO membrane. The water quality was significantly improved by
216 UF-RO treatment compared with the UF alone, where the COD in the RO permeate was below
217 10 mg L⁻¹. The COD content was reduced to almost zero after a combination of e-MF-GAC
218 pretreatment and RO filtration and was significantly better than the UF-RO process. In addition,
219 RO concentrate (ROC) collected from UF-RO process contained a significantly higher COD
220 content compared with that of e-MF-GAC-RO (Supplementary data).



221

222 Fig. 3 The COD and active chlorine concentration variation in the raw wastewater and
 223 effluent after various treatment processes (error bars represent the standard deviation of for
 224 times of measurements).

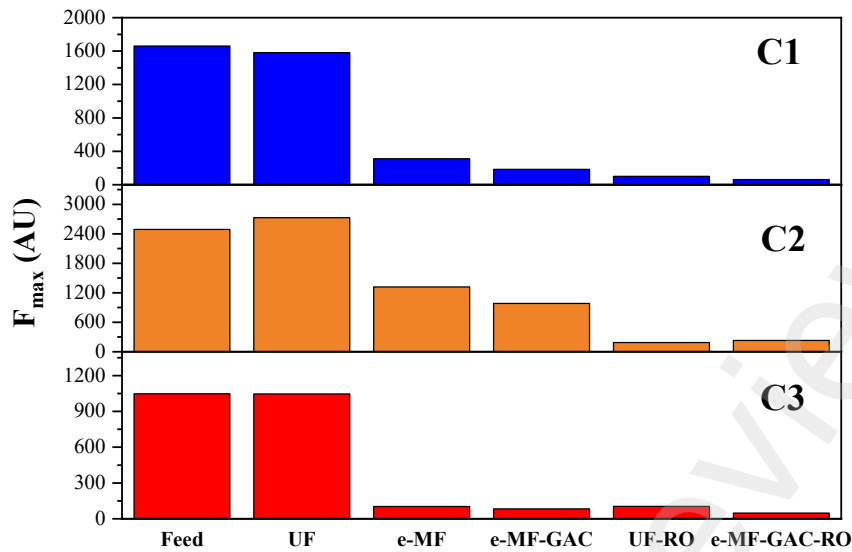
225 To characterise the organic matter removed by UF and e-MF-GAC pretreatment processes,
 226 the treated water by them was determined using EEM spectroscopy. Major peaks from EEMs
 227 analysis of all samples were further separated and quantified by PARAFAC analysis. Three
 228 components (C1-3) extracted from the EEMs of the raw wastewater, treated effluent by UF, e-
 229 MF, e-MF-GAC, UF-RO and e-MF-GAC-RO using PARAFAC are shown in Supplementary
 230 information (Fig.S1). Component 1 (C1) showing the peak at Em/Ex=400/320 nm and 3 (C3)
 231 showing the peaks at Em/Ex=460/350 nm and Em/Ex=460/290 nm were associated with humic
 232 acid and fulvic acid-like compounds, respectively [30, 34], whereas component 2 (C2) with the
 233 peak at Em/Ex=320/290 nm represented the protein-like substances [34, 35].

234 The maximum fluorescence (F_{\max}) values of each component in different samples are
 235 shown in Fig.4. The F_{\max} values of all EEMs components in the raw wastewater were not
 236 significantly reduced by UF. As for the e-MF process, the F_{\max} values of C1 and C3 were

237 reduced by 90% compared with those in the raw wastewater, suggesting the humics-like
238 materials were fairly susceptible to the electrochemical process. Besides, the F_{\max} of C2 was
239 eliminated by over 50% by the e-MF, suggesting protein-like compounds in the wastewater
240 could also be significantly removed by e-MF process. It was noticed that the GAC following
241 the e-MF gave a slight reduction of C1 and C2 components but no reduction in the content of
242 C3 component. This suggested that the GAC could only adsorbed very limited amounts of
243 fluorescent organics from the effluent of e-MF. Both UF-RO and e-MF-GAC-RO achieved
244 almost 100% removal of all the components, which was attributed to the effective organic
245 retention capacity of RO.

246 The EEMs of ROC was further characterised (Fig.S2 and S3, Supplementary data) to show
247 the peaks related to humics (C1 and C3) and protein-like compounds (C2) according to the
248 EEM-PARAFAC analysis for both UF and e-MF-GAC pretreatment methods. The F_{\max} values
249 for all the components of ROC for UF pretreatment were significantly higher compared with
250 that of e-MF-GAC pretreatment, suggesting the e-MF-GAC could significantly lower the
251 content of all organic components in the ROC compared with UF pretreatment.

252



253

254 Fig.4 The F_{\max} values of all components in the water samples calculated from EEMs-

255

PARAFAC analysis

256

3.3. Variation of Ca^{2+} and Mg^{2+} concentration during various treatments

257

Multivalent cations such as Ca^{2+} and Mg^{2+} and anions SO_4^{2-} are potential scalants and can

258

also aggravate organic fouling during RO filtration of reclaimed water. As a result, Ca^{2+} , Mg^{2+}

259

and SO_4^{2-} concentrations before and after pretreatment were monitored and shown in Fig.6.

260

Ca^{2+} , Mg^{2+} and SO_4^{2-} removal by UF, e-MF and e-MF-GAC from the raw wastewater was

261

insignificant. After e-MF-GAC or UF pretreatment, the RO feed contained similar Ca^{2+} , Mg^{2+}

262

and SO_4^{2-} contents (Fig, 5). These results suggest that the observed lower RO fouling after e-

263

MF-GAC pretreatment compared with UF was attributed to the reduction of organic content

264

rather than potential scalants such as Ca^{2+} , Mg^{2+} and SO_4^{2-} . Due to the significant presence of

265

the high scaling potential components in the feedwater and pre-treated feedwater. The scaling

266

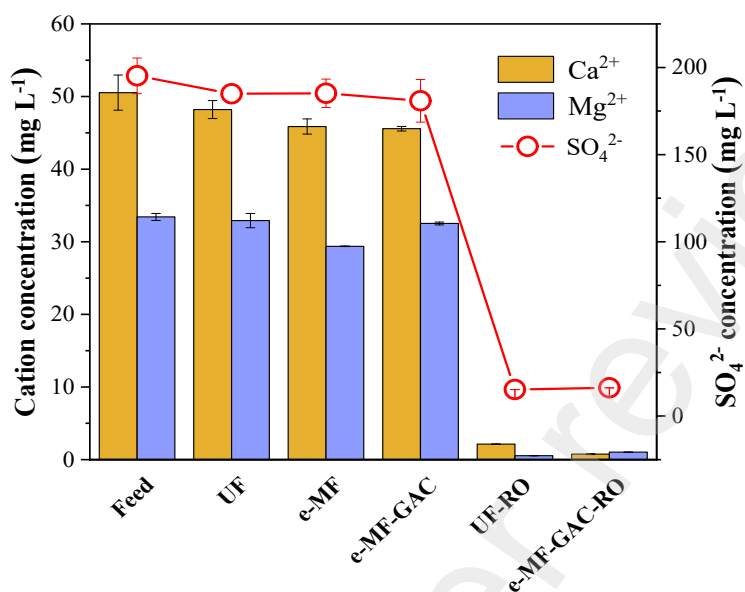
of RO could still occur, even if the UF and e-MF-GAC pretreatments were applied. However,

267

the enhancement of flux decline by e-MF-GAC suggested that the RO fouling could be

268 mitigated to some extent by reducing the organics, though the scaling was evitable.

269



270

271 Fig.5 The Ca²⁺, Mg²⁺ and SO₄²⁻ concentration in the raw wastewater and effluent after various
272 treatment processes (error bars represent the standard deviation of two replicate experiments).

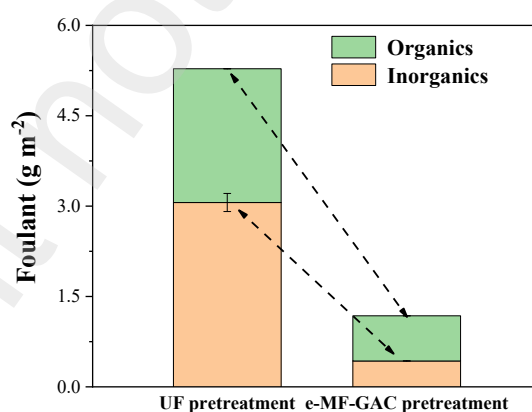
273

274 3.4. Fouling characterisation

275 3.4.1 Organic and inorganic distribution within the fouling layer

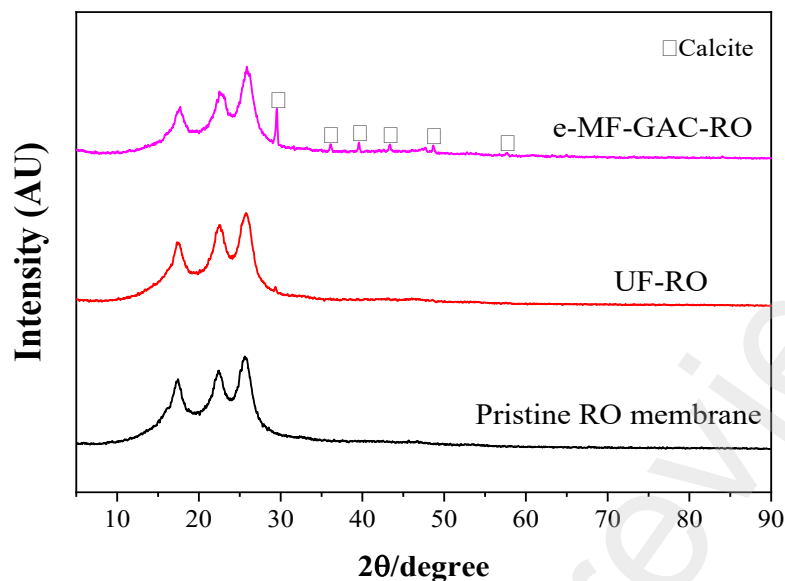
276 For further insight in to the mechanism of fouling retardation, the fouling layer on the RO
277 membrane surface after each test was extracted and characterised. Fig.6 shows the distribution
278 of the organic and inorganic constituents in the RO fouling layer. Organic (~3.0 g m⁻²) and
279 inorganic (~2.2 g m⁻²) foulants were present on the RO membrane surface after UF pretreatment.
280 After e-MF-GAC pretreatment, the amounts of both of the organic (~0.43 g m⁻²) and inorganic
281 (~0.75 g m⁻²) foulants on the RO membrane surface were significantly lower (Fig. 6). As
282 discussed above, e-MF-GAC pretreatment could only remove organics more effectively than

283 UF pretreatment. Ca^{2+} and Mg^{2+} contents were unaffected by both pretreatment methods
284 (section 3.3). Thus, results in Fig. 6 are consistent with the role of Ca^{2+} and Mg^{2+} to exacerbate
285 fouling to form a dense organic fouling layer. Here, effective removal of organics by e-MF-
286 GAC pretreatment could reduce their interactions and therefore prevent the formation of dense
287 cake layer [19]. This observation is further supported by the XRD analysis of the fouling layer
288 (Fig.7). As shown in the XRD spectra, only the RO membrane fouled by the effluent of e-MF-
289 GAC pretreatment gave significant peaks of calcites, where no significant peaks could be
290 observed on those for the UF pretreatment and pristine membrane. This was because the
291 inorganics after UF pretreatment ended up being trapped by the organics during the formation
292 of fouling layers on the RO membrane instead of directly crystallizing on the membrane surface.
293 However, it appears that e-MF-GAC pretreatment significantly removed organic matter, which
294 broke the associations between the organic and inorganics leading to some free inorganic ions
295 being attached on the membrane.



296
297 Fig.6 The distribution of the organic and inorganic component in the foulant layer of RO after
298 UF and e-MF-GAC pretreatment.

299

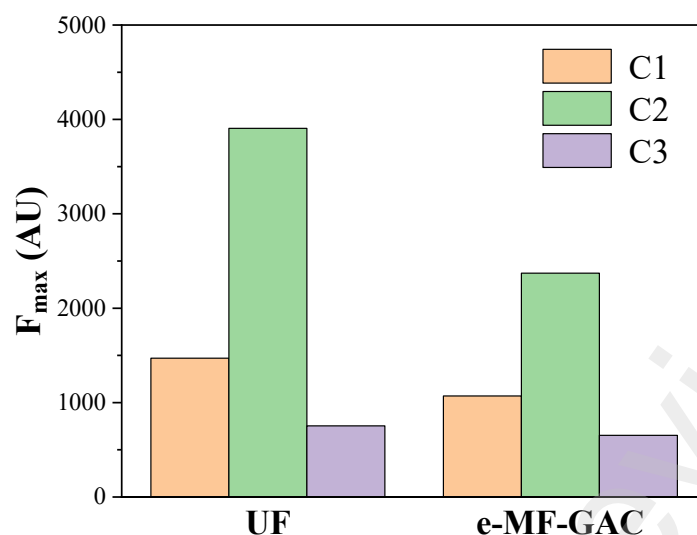


300

301 Fig.7 The XRD spectra of the pristine RO membrane and fouled RO membrane after UF and
 302 e-MF-GAC pretreatment.

303 3.4.2 Major organic components in the fouling layer

304 Fouling layers on the RO membrane surface after pretreatment were further characterised
 305 using EEM-PARAFAC analysis (Supplementary data , Fig.S1). It was found the F_{\max} value
 306 related to protein-like substances (C2) in the fouling layers obtained from the RO membrane
 307 (Fig. 8) was much higher than that of the other two components. This observation suggests that
 308 the protein-like component was the major organics deposited on the RO membrane surface.
 309 The F_{\max} of protein-like substances (C2) in the fouling layer with UF pretreatment was greater
 310 than that using e-MF-GAC pretreatment, which is consistent with the magnitude of their
 311 organic carbon content (2.6 g m⁻² for the sample with UF pretreatment, c.f., 0.25 g m⁻² for the
 312 sample with e-MF-GAC pretreatment). The results were also consistent with the results in Fig.4,
 313 where the e-MF-GAC was able to remove the protein-like compounds in the feed leading to
 314 less accumulation of these compounds on the membrane surface than UF pretreatment.



315

316 Fig.8 The EEM components in the foulant layer collected from the RO membrane after (a)

317

UF and (b) e-MF-GAC pretreatment.

318

3.4.3 Size and zeta potential

319

Size distributions of the organic content in the feed water, UF pretreated water and e-MF-

320

GAC pretreated water were measured and shown in Fig.9. The size of the molecules contained

321

in the feed water being detected ranged from 250-750 nm. After the UF pretreatment, the large

322

sized molecules were rejected by the UF membrane, where the majority of the molecules had

323

the size of 250-400 nm. The size range of the molecules contained in the e-MF-GAC pretreated

324

water was similar as those of UF pretreated water. However, it could be observed that the

325

proportion of small organic molecules (size <300 nm) in the e-MF-GAC pretreated water was

326

slightly higher than those of UF-pretreated water, but the content of large sized molecules (300-

327

400 nm) of them was less. The average size of the molecules in the effluent of e-MF-GAC was

328

slightly lower than that of UF. This result proved that the e-MF-GAC process could

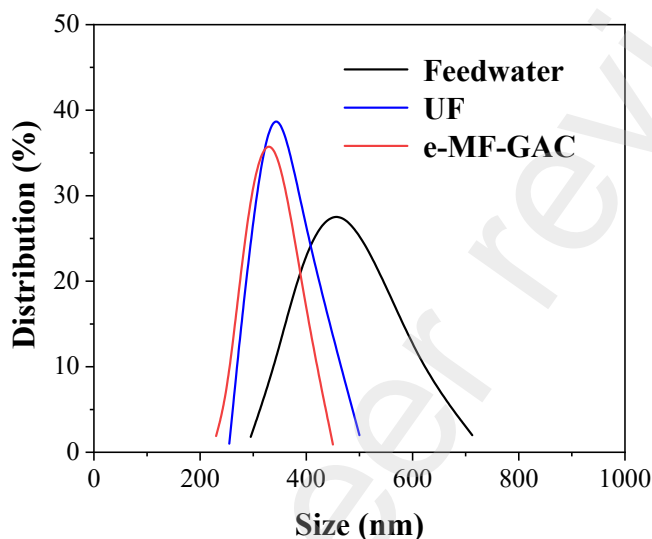
329

remove/decompose some of the organic molecules from the feed water and form smaller

330

molecule. It was reported that the larger sized molecules often could cause greater RO fouling,

331 as them could increase hydrodynamic drag and reduce the back-transport of these particles from
332 the membrane surface [36]. This suggested the overall smaller sized molecules resulting from
333 the e-MF-GAC than the UF was probably another reason for the more effective fouling
334 mitigation of RO by the e-MF-GAC.



335
336 Fig.9 The size distribution of the raw feedwater, UF pretreated water and e-MF-GAC
337 pretreated water.

338 The RO fouling could also be affected by the electrostatic interactions between the
339 components in the RO feed and the RO membrane. The polyamide membrane surface is
340 negatively charged, more negatively charged substances in the feed could be experienced
341 greater electrostatic repulsive forces during the filtration. As shown in Table S3
342 (Supplementary data), the ζ potential of effluent of UF pretreatment was similar as that of raw
343 wastewater, suggesting no significant alteration in organic characteristics was likely occurred
344 during the UF. As for the effluent of e-MF-GAC, the ζ potential was slightly higher than those
345 of raw wastewater and the effluent from UF pretreatment. This was likely because some of the
346 organics were decomposed by the e-MF process leading to less negative surface charge. The

347 slightly higher ζ potential for the effluent of e-MF-GAC pretreatment than UF pretreatment
348 suggested that the fouling reduction of RO by the e-MF-GAC was not attributed to the enhanced
349 electrostatic repulsion between the components in the RO feed and membrane.

350 **3.5. Implications**

351 The proposed e-MF-GAC hybrid process can replace convention UF pretreatment with
352 superior performance and potentially at a lower cost. The energy consumption by the UF-RO
353 and e-MF-GAC has been evaluated, where the UF-RO gave lower energy consumption
354 compared with the e-MF-GAC under 6 V of DC input (0.26 kW L⁻¹ for UF-RO, c.f., 0.48 kW
355 L⁻¹). Though, the additional e-MF process increased overall energy consumption, in addition to
356 fouling control, e-MF-GAC can offer several other benefits. Firstly, the results of this study
357 suggested that the COD removal level by e-MF-GAC-RO process was better than UF-RO and
358 equivalent to the UF-RO-RO process, suggesting the process could be possible to be an
359 alternative for UF-RO-RO process for water reuse. Secondly, the organic content in the ROC
360 was significantly reduced compared with the UF-RO process, which may reduce the difficulties
361 in ROC treatment. Several studies have reported that advanced oxidation process (e.g.,
362 electrochemical process) can also be used for ROC treatment [37-39]. As a result, the
363 application of electrochemical process as RO feed pretreatment could also save the steps for
364 the ROC treatment using advanced oxidation, where the cost for the whole water reuse
365 treatment system could be significantly reduced. Thirdly, due to the e-MF-GAC is a chemical
366 free process, the cost for frequent chemical addition could be lowered. The production of RCSs
367 by electrochemical process could enhance the bacterial inactivation efficiency, which could

368 reduce the risk of membrane biofouling [40].

369 **4. Conclusions**

370 Results from this study demonstrate the potential of a new hybrid e-MF-GAC system for
371 pretreating reclaimed wastewater to reduce RO fouling. Compare to UF pretreatment, e-MF-
372 GAC pretreatment resulted in significantly less RO fouling, reflected by lower flux decline.
373 The superior fouling mitigation by e-MF-GAC pretreatment was mainly due to the effective
374 removal of inorganic/organic foulants and small organic molecules (which could not be rejected
375 by UF) by the e-MF process. The GAC could eliminate the electrogenerated RCSs, which could
376 avoid the destruction of the membrane *via* the contact of RCS. Systematic feed water and
377 foulant composition analysis suggested that organic foulants on the membrane surface were
378 mainly protein-like compounds. The deposition of these organic foulants on the membrane
379 surface was much lower after e-MF-GAC compared to UF pretreatment. In addition, the
380 organic content in the permeate and RO concentrate was lower after e-MF-GAC-RO
381 pretreatment than that after UF pretreatment. This study proposed the e-MF-GAC process could
382 be a promising alternative to conventional UF pretreatment for mitigating RO membrane
383 fouling.

384 **Acknowledgment**

385 This study was financially supported from National Key Research and Development Program
386 (2019YFC0408202), Shanghai Pujiang Program (19PJ1404000), National Natural Science
387 Foundation of China (21906027) and Suzhou Science and Technology Project (SS202015).

388 **Reference**

- 389 [1] S. Jiang, Y. Li, B.P. Ladewig, A review of reverse osmosis membrane fouling and control
390 strategies, *Sci. Total Environ.*, 595 (2017) 567-583.
- 391 [2] C.Y. Tang, Z. Yang, H. Guo, J.J. Wen, L.D. Nghiem, E. Cornelissen, Potable water reuse
392 through advanced membrane technology, *Environ. Sci. Technol.*, 52 (2018) 10215-10223.
- 393 [3] T. Fujioka, B.E. O'Rourke, K. Michishio, Y. Kobayashi, N. Oshima, H. Kodamatani, T.
394 Shintani, L.D. Nghiem, Transport of small and neutral solutes through reverse osmosis
395 membranes: Role of skin layer conformation of the polyamide film, *J. Membr. Sci.*, 554 (2018)
396 301-308.
- 397 [4] N.K. Khanzada, M.U. Farid, J.A. Kharraz, J. Choi, C.Y. Tang, L.D. Nghiem, A. Jang, A.K.
398 An, Removal of organic micropollutants using advanced membrane-based water and
399 wastewater treatment: A review, *J. Membr. Sci.*, 598 (2020).
- 400 [5] Y. Zhao, L. Song, S.L. Ong, Fouling of RO membranes by effluent organic matter (EfOM):
401 Relating major components of EfOM to their characteristic fouling behaviors, *J. Membr. Sci.*,
402 349 (2010) 75-82.
- 403 [6] C. Jarusutthirak, G. Amy, Role of soluble microbial products (SMP) in membrane fouling
404 and flux decline, *Environ. Sci. Technol.*, 40 (2006) 969-974.
- 405 [7] S. Lee, W.S. Ang, M. Elimelech, Fouling of reverse osmosis membranes by hydrophilic
406 organic matter: implications for water reuse, *Desalination*, 187 (2006) 313-321.
- 407 [8] X. Zhang, L. Fan, F.A. Roddick, Understanding the fouling of a ceramic microfiltration
408 membrane caused by algal organic matter released from *Microcystis aeruginosa*, *J. Membr. Sci.*,
409 447 (2013) 362-368.

- 410 [9] S. Daly, A. Allen, V. Koutsos, A.J.C. Semião, Influence of organic fouling layer
411 characteristics and osmotic backwashing conditions on cleaning efficiency of RO membranes,
412 J. Membr. Sci., 616 (2020) 118604.
- 413 [10] S. Wang, K. Xiao, X. Huang, Characterizing the roles of organic and inorganic foulants in
414 RO membrane fouling development: The case of coal chemical wastewater treatment, Sep.
415 Purif. Technol., 210 (2019) 1008-1016.
- 416 [11] K. Kimura, S. Okazaki, T. Ohashi, Y. Watanabe, Importance of the co-presence of silica
417 and organic matter in membrane fouling for RO filtering MBR effluent, J. Membr. Sci., 501
418 (2016) 60-67.
- 419 [12] I. Ćurić, D. Dolar, J. Bošnjak, Reuse of textile wastewater for dyeing cotton knitted fabric
420 with hybrid treatment: Coagulation/sand filtration/UF/NF-RO, J. Environ. Manage., 295 (2021)
421 113133.
- 422 [13] Z. Yin, T. Wen, Y. Li, A. Li, C. Long, Alleviating reverse osmosis membrane fouling
423 caused by biopolymers using pre-ozonation, J. Membr. Sci., 595 (2020) 117546.
- 424 [14] G.K. Pearce, The case for UF/MF pretreatment to RO in seawater applications,
425 Desalination, 203 (2007) 286-295.
- 426 [15] G.-Q. Chen, Y.-H. Wu, Y.-J. Tan, Z. Chen, X. Tong, Y. Bai, L.-W. Luo, H.-B. Wang,
427 Y.-Q. Xu, Z.-W. Zhang, N. Ikuno, H.-Y. Hu, Pretreatment for alleviation of RO membrane
428 fouling in dyeing wastewater reclamation, Chemosphere, 292 (2022) 133471.
- 429 [16] G.-Q. Chen, Y.-H. Wu, P.-S. Fang, Y. Bai, Z. Chen, Y.-Q. Xu, Y.-H. Wang, X. Tong, L.-
430 W. Luo, H.-B. Wang, Z.-W. Zhang, N. Ikuno, H.-Y. Hu, Performance of different pretreatment
431 methods on alleviating reverse osmosis membrane fouling caused by soluble microbial

432 products, *J. Membr.Sci.*, 641 (2022) 119850.

433 [17] Q.Q. Cai, M.Y. Wu, L.M. Hu, B.C.Y. Lee, S.L. Ong, P. Wang, J.Y. Hu, Organics removal
434 and in-situ granule activated carbon regeneration in FBR-Fenton/GAC process for reverse
435 osmosis concentrate treatment, *Water Res.*, 183 (2020) 116119.

436 [18] H.N.P. Dayarathne, M.J. Angove, S. Jeong, R. Aryal, S.R. Paudel, B. Mainali, Effect of
437 temperature on turbidity removal by coagulation: Sludge recirculation for rapid settling, *J.*
438 *Water Process Eng.*, 46 (2022) 102559.

439 [19] Z. Yin, T. Wen, Y. Li, A. Li, C. Long, Pre-ozonation for the mitigation of reverse osmosis
440 (RO) membrane fouling by biopolymer: The roles of Ca^{2+} and Mg^{2+} , *Water Res.*, 171 (2020)
441 115437.

442 [20] H. Park, K.-H. Choo, H.-S. Park, J. Choi, M.R. Hoffmann, Electrochemical oxidation and
443 microfiltration of municipal wastewater with simultaneous hydrogen production: Influence of
444 organic and particulate matter, *Chem. Eng. J.*, 215-216 (2013) 802-810.

445 [21] A.M. Zaky, B.P. Chaplin, Mechanism of p-Substituted phenol oxidation at a TiO_2
446 reactive electrochemical membrane, *Environ. Sci. Technol.*, 48 (2014) 5857-5867.

447 [22] J. Zheng, J. Ma, Z. Wang, S. Xu, T.D. Waite, Z. Wu, Contaminant removal from source
448 waters using cathodic electrochemical membrane filtration: mechanisms and implications,
449 *Environ. Sci. Technol.*, 51 (2017) 2757-2765.

450 [23] Y.-K. Wang, W.-W. Li, G.-P. Sheng, B.-J. Shi, H.-Q. Yu, In-situ utilization of generated
451 electricity in an electrochemical membrane bioreactor to mitigate membrane fouling, *Water*
452 *Res.*, 47 (2013) 5794-5800.

453 [24] J. Ma, Z. Wang, D. He, Y. Li, Z. Wu, Long-term investigation of a novel electrochemical

454 membrane bioreactor for low-strength municipal wastewater treatment, *Water Res.*, 78 (2015)
455 98-110.

456 [25] K. Bani-Melhem, M. Elektorowicz, Development of a novel submerged membrane
457 electro-bioreactor (SMEBR): Performance for fouling reduction, *Environ. Sci. Technol.*, 44
458 (2010) 3298-3304.

459 [26] N. Mameda, H.-J. Park, K.-H. Choo, Membrane electro-oxidizer: A new hybrid membrane
460 system with electrochemical oxidation for enhanced organics and fouling control, *Water Res.*,
461 126 (2017) 40-49.

462 [27] Y.-H. Wu, Z. Chen, X. Li, Y.-H. Wang, B. Liu, G.-Q. Chen, L.-W. Luo, H.-B. Wang, X.
463 Tong, Y. Bai, Y.-Q. Xu, N. Ikuno, C.-F. Li, H.-Y. Zhang, H.-Y. Hu, Effect of ultraviolet
464 disinfection on the fouling of reverse osmosis membranes for municipal wastewater
465 reclamation, *Water Res.*, 195 (2021) 116995.

466 [28] S.M. Elgengehi, S. El-Taher, K.E. El-Kelany, Adsorption of chlorine oxyanions, as water
467 disinfectant by-products, on graphene flakes: A quantum chemical investigation, *Surf.*
468 *Interfaces*, 28 (2022) 101601.

469 [29] X. Zhang, L. Fan, F.A. Roddick, Understanding the fouling of a ceramic microfiltration
470 membrane caused by algal organic matter released from *Microcystis aeruginosa*, *J. Membr. Sci.*,
471 447 (2013) 362-368.

472 [30] X. Zhang, M.C.E. Devanadera, F.A. Roddick, L. Fan, M.L.P. Dalida, Impact of algal
473 organic matter released from *Microcystis aeruginosa* and *Chlorella* sp. on the fouling of a
474 ceramic microfiltration membrane, *Water Res.*, 103 (2016) 391-400.

475 [31] K.R. Murphy, C.A. Stedmon, D. Graeber, R. Bro, Fluorescence spectroscopy and multi-

476 way techniques. PARAFAC, *Anal. Methods*, 5 (2013) 6557-6566.

477 [32] S.-J. Kim, B.S. Oh, H.-W. Yu, L.H. Kim, C.-M. Kim, E.-T. Yang, M.S. Shin, A. Jang,
478 M.H. Hwang, I.S. Kim, Foulant characterization and distribution in spiral wound reverse
479 osmosis membranes from different pressure vessels, *Desalination*, 370 (2015) 44-52.

480 [33] Y. Zhang, C. Hao, J. Zhang, J. Wu, Y. Yue, Y. Xu, G. Qian, Ratio of adsorptive abilities
481 for NH₃ and NO_x determined SCR activity of transition-metal catalyst, *Colloids Surf., A*, 635
482 (2022) 128080.

483 [34] T. Maqbool, J. Zhang, Y. Qin, L. Quang Viet, M.B. Asif, X. Zhang, Z. Zhang, Seasonal
484 occurrence of N-nitrosamines and their association with dissolved organic matter in full-scale
485 drinking water systems: Determination by LC-MS and EEM-PARAFAC, *Water Res.*, 183
486 (2020).

487 [35] S. Pradhan, L. Fan, F.A. Roddick, E. Shahsavari, A.S. Ball, X. Zhang, A comparative study
488 of biological activated carbon based treatments on two different types of municipal reverse
489 osmosis concentrates, *Chemosphere*, 240 (2020) 124925.

490 [36] J. Liu, Y. Zhao, Y. Fan, H. Yang, Z. Wang, Y. Chen, C.Y. Tang, Dissect the role of particle
491 size through collision-attachment simulations for colloidal fouling of RO/NF membranes, *J.*
492 *Membr. Sci.*, 638 (2021) 119679.

493 [37] F. Wei, D. Liao, Y. Lin, C. Hu, J. Ju, Y. Chen, D. Feng, Electrochemical degradation of
494 reverse osmosis concentrate (ROC) using the electrodeposited Ti/TiO₂-NTs/PbO₂ electrode,
495 *Sep. Purif. Technol.*, 258 (2021) 118056.

496 [38] M. Chen, X. Zhao, C. Wang, S. Pan, C. Zhang, Y. Wang, Electrochemical oxidation of
497 reverse osmosis concentrates using macroporous Ti-ENTA/SnO₂-Sb flow-through anode:

498 Degradation performance, energy efficiency and toxicity assessment, *J. Hazard. Mater.*, 401

499 (2021) 123295.

500 [39] A.Y. Bagastyo, D.J. Batstone, I. Kristiana, W. Gernjak, C. Joll, J. Radjenovic,

501 Electrochemical oxidation of reverse osmosis concentrate on boron-doped diamond anodes at

502 circumneutral and acidic pH, *Water Res.*, 46 (2012) 6104-6112.

503 [40] Y.-H. Wang, Y.-H. Wu, X. Tong, T. Yu, L. Peng, Y. Bai, X.-H. Zhao, Z.-Y. Huo, N. Ikuno,

504 H.-Y. Hu, Chlorine disinfection significantly aggravated the biofouling of reverse osmosis

505 membrane used for municipal wastewater reclamation, *Water Res.*, 154 (2019) 246-257.

506