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Abstract

In this study, a direct contact membrane distillation (MD) unit was integrated with an anaerobic membrane bioreactor (AnMBR) to simultaneously recover energy and produce high quality water for reuse from wastewater. Results show that AnMBR could produce 0.3-0.5 L/g COD_{added} biogas with a stable methane content of approximately 65%. By integrating MD with AnMBR, bulk organic matter and phosphate were almost completely removed. The removal of the 26 selected trace organic contaminants by AnMBR was compound specific, but the MD process could complement AnMBR removal, leading to an overall efficiency from 76% to complete removal by the integrated system. The results also show that, due to complete retention, organic matter (such as humic-like and protein-like substances) and inorganic salts accumulated in the MD feed solution and therefore resulted in significant fouling of the MD unit. As a result, the water flux of the MD process decreased continuously. Nevertheless, membrane pore wetting was not observed throughout the operation.

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2 **system for energy recovery and water reuse: Removal performance of**
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1 ABSTRACT

2 In this study, a direct contact membrane distillation (MD) unit was integrated with an
3 anaerobic membrane bioreactor (AnMBR) to simultaneously recover energy and
4 produce high quality water for reuse from wastewater. Results show that AnMBR could
5 produce 0.3 – 0.5 L/g COD_{added} biogas with a stable methane content of approximately
6 65%. By integrating MD with AnMBR, bulk organic matter and phosphate were almost
7 completely removed. The removal of the 26 selected trace organic contaminants by
8 AnMBR was compound specific, but the MD process could complement AnMBR
9 removal, leading to an overall efficiency from 76% to complete removal by the
10 integrated system. The results also show that, due to complete retention, organic matter
11 (such as humic-like and protein-like substances) and inorganic salts accumulated in the
12 MD feed solution and therefore resulted in significant fouling of the MD unit. As a
13 result, the water flux of the MD process decreased continuously. Nevertheless,
14 membrane pore wetting was not observed throughout the operation.

15 **Key words:** anaerobic membrane bioreactor (AnMBR); membrane distillation (MD);
16 trace organic contaminants (TrOCs); energy recovery; wastewater treatment and reuse.

17 1 Introduction

18 Water scarcity driven by population growth, climate change, and environmental
19 pollution has prompted the development of new technologies, such as membrane
20 distillation (MD), and the improvement of existing ones, such as membrane bioreactor
21 (MBR) for wastewater treatment and reuse (Shannon et al., 2008). MBR integrates the
22 membrane separation process with biological treatment to produce high standard water
23 for recycling applications (Nguyen et al., 2012; Huang and Lee, 2015; Jegatheesan et
24 al., 2016; Judd, 2016). Previous studies have demonstrated the capacity of MBR for
25 wastewater treatment and reuse regarding both basic water quality parameters and high
26 removal efficiency of a broad range of trace organic contaminants (TrOCs) (Tadkaew et
27 al., 2011; Boonyaroj et al., 2012; Navaratna et al., 2012; Wijekoon et al., 2013; Di Bella
28 et al., 2015; Prasertkulsak et al., 2016).

29 The widespread occurrence of TrOCs in municipal and industrial wastewater is of
30 significant concern to water reuse (Acuña et al., 2015; Huerta et al., 2016). TrOCs

31 include a diverse range of emerging chemicals that are widely used in our modern
32 society for health care, agriculture, aquaculture, live stocking, and industrial production.
33 They are continuously released into the environment either accidentally through
34 agricultural and industrial activities or inevitably through human and livestock excretion.
35 TrOCs are ubiquitously detected in wastewater and sewage-impacted water bodies at
36 trace levels up to a few micrograms per litre ($\mu\text{g/L}$) (Osorio et al., 2012). Although the
37 impact of long-term exposure to low concentrations of TrOCs on human health is still
38 largely unknown, ecological data to date have evidenced their chronic effects on a range
39 of sensitive aquatic organisms, such as fish and reptiles (Schwarzenbach et al., 2006;
40 Guillén et al., 2012). Thus, adequate removal of TrOCs is essential for water reuse
41 applications and environmental protection (Luo et al., 2014).

42 MBR can be operated in aerobic or anaerobic conditions according to the presence or
43 absence of oxygen in the biological reactor (Huang et al., 2015). Recent studies have
44 focused mostly on aerobic MBR systems as they can be readily deployed for wastewater
45 treatment and reuse. There is also a growing interest in the development of anaerobic
46 MBR (AnMBR) for energy efficient wastewater treatment and reuse (Stuckey, 2012).
47 Compared to aerobic MBR, which requires significant energy input for aeration,
48 AnMBR is more energy-efficient and can even be an energy positive system by
49 producing biogas for beneficial usage. However, AnMBR often has a lower treatment
50 capacity to remove nutrients and TrOCs in comparison with aerobic MBR. Recent
51 studies have demonstrated that some TrOCs (such as carbamazepine, atrazine, and
52 diclofenac) are poorly removed by AnMBR due to their resistance to biodegradation
53 (Monsalvo et al., 2014; Wijekoon et al., 2015). As a result, it is necessary to
54 complement AnMBR with an additional treatment process to achieve a suitable product
55 water quality for reuse.

56 MD is a thermally driven membrane separation process and has been recognized as an
57 emerging technology in wastewater treatment and reuse (Wijekoon et al., 2014a;
58 Wijekoon et al., 2014b; Nguyen et al., 2016). During MD operation, water in the vapour
59 form transports under a partial vapour pressure gradient across a microporous and
60 hydrophobic membrane from a high temperature solution to a low temperature solution.
61 MD can utilize low-grade waste heat and solar thermal that is otherwise unusable by

62 other means. Thus, MD can potentially be used for the further purification of wastewater
63 effluents, particularly after anaerobic treatment where thermal heat from the combustion
64 of produced biogas can be utilised as energy input to the MD process. Kim et al. (2015)
65 has demonstrated that MD could further treat effluent from an anaerobic moving bed
66 biofilm reactor by achieving complete rejection of phosphorus and more than 98%
67 rejection of dissolved organic carbon. Similarly, Jacob et al. (2015) reported 90%
68 rejection of chemical oxygen demand (COD) and ammonia from AnMBR effluent by
69 MD. Nevertheless, data from these previous studies were from batch test experiments
70 and little is known about the MD performance when simultaneously operated with
71 AnMBR.

72 This study aimed to investigate the performance of an integrated AnMBR-MD system
73 for water reuse and energy recovery from wastewater. The hybrid system performance
74 was examined in terms of biogas production, biomass characteristics, contaminant
75 removal, and membrane fouling. Removal of organic matter, nutrients, and TrOCs by
76 both the AnMBR and MD processes were evaluated. Fouling behavior of the MD
77 membrane was delineated.

78 **2 Materials and methods**

79 *2.1 Synthetic wastewater and trace organic contaminants*

80 A synthetic solution, simulating high strength domestic wastewater, was used and was
81 prepared daily to consist of 4000 mg/L glucose, 750 mg/L peptone, 2250 mg/L sodium
82 acetate, 175 mg/L potassium dihydrogen phosphate, 175 mg/L magnesium chloride, and
83 175 mg/L urea. Key physicochemical properties of the synthetic wastewater were
84 determined every four days throughout the experiment. In particular, the synthetic
85 wastewater contained 6252.3 mg/L COD, 166.8 mg/L total nitrogen (TN), 195.4
86 orthophosphate (PO_4^{3-}), and 34.7 mg/L ammonium (NH_4^+). The electrical conductivity
87 and pH of the synthetic wastewater were 4.01 ± 0.9 mS/cm and 7.0 ± 0.2 , respectively.
88 It is noteworthy that anaerobic treatment is not viable for biogas production from low
89 strength wastewater due to the low methane production over heating requirement ratio.
90 As a result, it is necessary to pre-concentrate municipal wastewater to increase the COD
91 content by processes such as forward osmosis prior to anaerobic treatment (Ansari et al.,

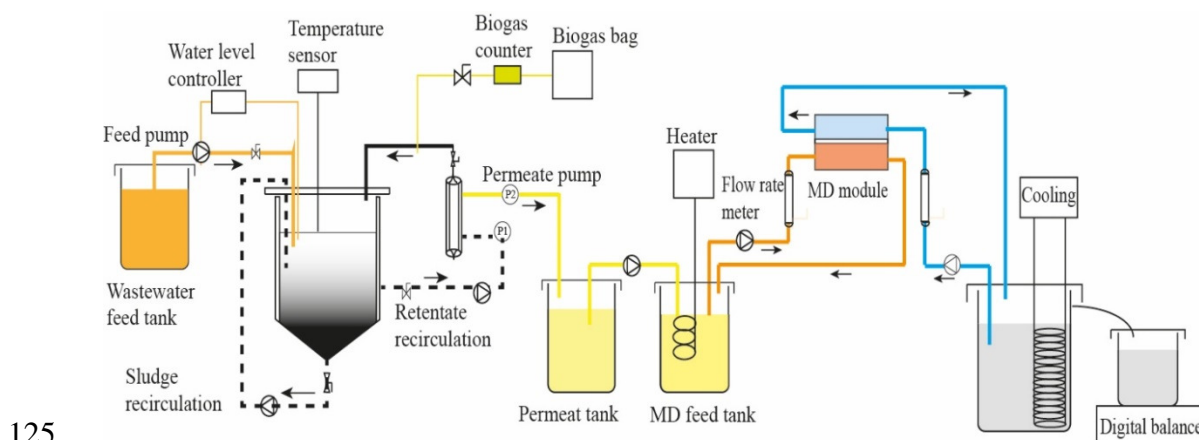
92 2016). Thus, the synthetic wastewater with higher strength than typical municipal
93 wastewater was used in this study.

94 A set of 26 TrOCs was selected for study. These TrOCs represent four major groups of
95 chemicals of emerging concern that are ubiquitously present in domestic wastewater,
96 including pharmaceuticals and personal care products, endocrine disruptors, industrial
97 chemicals, and pesticides. Key physicochemical properties of these TrOCs are
98 summarized in Table S1, Supplementary Data. Based on their effective octanol – water
99 partition coefficient (i.e. Log D) at solution pH 7, the 26 TrOCs could be categorized as
100 hydrophobic (i.e. Log D > 3.2) and hydrophilic (i.e. Log D < 3.2) (Tadkaew et al.,
101 2011). A stock solution containing 10 mg/L of each TrOC compound was prepared in
102 pure methanol and then stored at -18 °C in the dark. The TrOC stock solution was added
103 daily to the synthetic wastewater described above to obtain a concentration of 2 µg/L of
104 each compound.

105 2.2 *Anaerobic membrane bioreactor – membrane distillation*

106 A lab-scale AnMBR-MD system was used in this study (Figure 1). This system
107 consisted of a feed reservoir, an anaerobic bioreactor with a working volume of 20 L, a
108 biogas collector, an external membrane module, and an effluent reservoir. A peristaltic
109 pump (Masterflex L/s, USA) controlled by a water level controller was employed to
110 feed the synthetic wastewater into the bioreactor. A proportional-integral-derivative
111 temperature controller (Neslab RTE7, ThermoScientific, USA) equipped with a plastic
112 coil was used to maintain the bioreactor temperature at 35 ± 1 °C. A Tedlar sampling
113 bag was connected to the bioreactor for biogas collection and subsequent biogas
114 composition analysis using a biogas meter (Biogas 5000, Geotech, UK) as described in
115 a previous study (Nghiem et al., 2014). A ceramic microfiltration (MF) membrane
116 module (NGK, Japan) in stainless steel housing was externally integrated with the
117 bioreactor. The normalized pore size and effective area of the MF membrane was 1 µm
118 and 0.09 m², respectively. A peristaltic pump (Masterflex L/s, USA) was applied to
119 circulate digested sludge from the bioreactor to the external MF membrane module and
120 then back to the bioreactor. At the same time, an industrial grade peristaltic pump
121 (ProMinent, Australia) was employed to circulate digested sludge from the bottom to
122 the top of the bioreactor for sludge mixture. The bioreactor and all pipelines involved in

123 this system were wrapped with insulation foam to minimise heat loss. Detailed
124 description of the AnMBR system is also available elsewhere (Song et al., 2016).



126 **Figure 1:** Schematic diagram of the laboratory scale AnMBR-MD hybrid system.

127 A direct contact MD system was integrated with AnMBR as a post-treatment step
128 (Figure 1). The MD system comprised of a feed reservoir, a plate-and-frame membrane
129 module, a distillate reservoir, and two identical gear pumps (Micropump, Vancouver,
130 WA). A separate MD feed reservoir with a working volume constant at 10 L was set to
131 ensure a continuous feed supply. A peristaltic pump controlled by a water level
132 controller was used to transfer the AnMBR effluent to the MD feed reservoir. The
133 membrane module was made of acrylic plastic and consisted of two identical semi-cells.
134 Each cell was engraved with a flow channel of 142 mm long, 91 mm wide and 3 mm
135 deep. A hydrophobic microporous membrane from Porous Membrane Technology
136 (Ningbo, China) was used. The membrane was composed of a thin
137 polytetrafluorethylene (PTFE) layer on the top of a polypropylene (PP) support layer
138 and had a thickness, nominal pore size, and porosity of 60 μm , 0.2 μm , and 80%,
139 respectively. The feed and distillate temperatures were maintained at 45 ± 1 $^{\circ}\text{C}$ and $20 \pm$
140 1 $^{\circ}\text{C}$, respectively, using two temperature controllers (Neslab RTE7, Thermo Scientific,
141 USA). The overflowing distillate was weighed by a digital balance connected to a
142 computer for determining the MD water flux.

143 2.3 Experimental protocol

144 Digested sludge from a full-scale wastewater treatment plant was used to inoculate the
145 bioreactor. AnMBR was acclimatized to the synthetic wastewater and laboratory

146 conditions for over three months. Once stable operation had been achieved as indicated
147 by the removal of organic matter (i.e. > 97% total organic carbon (TOC) and COD
148 removal), TrOCs were introduced to the synthetic wastewater. After obtaining 10 L
149 effluent, the MD system was integrated downstream with AnMBR to form an AnMBR-
150 MD hybrid system (Figure 1).

151 The AnMBR-MD hybrid system was continuously operated for 30 days. A peristaltic
152 pump was used to extract water from the bioreactor through the MF membrane with a
153 permeate flux of 2 L/m²h in a cycle of 14 min suction and 1 min relaxation. The
154 relaxation time was provided to reduce the MF membrane fouling. To maintain a
155 constant working volume of the bioreactor, the feed flowrate was set at 3.5 mL/min,
156 which resulted in the hydraulic retention time (HRT) of AnMBR at approximately 4
157 days. Hydraulic backwash was conducted every two days using AnMBR effluent to
158 maintain the water flux. Mixed liquor (650 mL) was taken weekly for biomass
159 characterization, resulting in an operating sludge retention time of approximately 215
160 days. Sodium bicarbonate was added to maintain the mixed liquor pH at 7. AnMBR
161 effluent was continuously pumped to the MD feed reservoir to maintain its working
162 volume at 10 L. Deionized water (2 L) was used as the MD distillate. Both MD feed and
163 distillate were circulated to the membrane cell with a cross-flow rate of 1 L/min
164 (corresponding to a cross-flow velocity of 6.1 cm/s). The MD membrane was replaced
165 every ten days to maintain a desirable water production and provide samples for
166 membrane fouling investigation.

167 2.4 Analytical methods

168 2.4.1 Analysis of basic water quality parameter

169 Aqueous samples from the AnMBR feed, bioreactor, AnMBR effluent, MD feed, and
170 MD distillate were collected every three days for water quality analysis. Specifically,
171 TOC and TN concentrations were measured using a TOC/TN-V_{CSH} analyser (Shimadzu,
172 Japan). COD was quantified by using high range digestion vials (Hatch, USA)
173 following the standard dichromate method. The removal rates of TOC, TN, and COD
174 by the AnMBR and MD processes were quantified based on the method described in the
175 following section for TrOCs. A Flow Injection Analysis system (QuikChem 8500,
176 Lachat, CO) was used to detect NH₄⁺ and PO₄³⁻ concentrations. Electrical conductivity

177 and pH were monitored by an Orion 4 Star Plus portable pH/conductivity meter
178 (Thermo Scientific, USA).

179 2.4.2 Analysis of trace organic contaminants

180 Aqueous samples were collected in duplicate every five days for TrOC analysis
181 according to a method reported by Tadkaew et al. (2011). Briefly, this method involved
182 solid phase extraction (SPE), liquid chromatography, and quantitative determination by
183 tandem mass spectrometry with electrospray ionisation. Before SPE, most samples were
184 spiked with a surrogate standard solution containing 50 ng of an isotopically labelled
185 version of each compound except for oxybenzone, chlorpyrifos, fenofibrate,
186 propylparaben, phenylphenol, sucralose and aspartame, which were quantified by
187 external dilution. Hydrophilic/lipophilic balance cartridges (Waters, Millford, MA,
188 USA) were used for TrOC extraction after being preconditioned with 5 mL methyl tert-
189 butyl ether (MTBE), 5 mL methanol, and 10 mL reagent water. Compounds were eluted
190 from cartridges into centrifuge tubes using 5 mL methanol and 5 mL methanol/MTBE
191 blend (v/v = 1/9). Resultant extracts were concentrated to approximately 100 μ L by
192 nitrogen stream and then diluted to 1 mL with methanol before being analysed using a
193 high performance liquid chromatography (Agilent, Palo Alto, CA) and a triple
194 quadrupole mass spectrometer (Applied Biosystems, Foster City, CA) equipped with a
195 turbo-V ion source and employed in both positive and negative electro-spray modes.
196 The limit of quantification of propylparaben and phenylphenol was 20 ng/L while that
197 of all other compounds was 5 ng/L (Table S2).

198 The removal of TrOC by AnMBR is defined as:

$$199 \quad R_{AnMBR} = \frac{C_{Wastewater} - C_{Effluent}}{C_{Wastewater}} \times 100\% \quad (1)$$

200 Where $C_{Wastewater}$ and $C_{Effluent}$ are the measured TrOC concentrations in the synthetic
201 wastewater and AnMBR effluent, respectively. To calculate the removal of TrOCs by
202 MD, it is necessary to take into account the dilution of the MD permeate by the initial
203 water in the distillate loop of the DCMD process. Thus, the following equation is used:

$$204 \quad R_{MD} = \frac{C_{MDF} - C^*_{MDE}}{C_{MDF}} \times 100\% \quad (2)$$

205 C_{MDf} is the measured TrOC concentration in the MD feed; C^*_{MDE} is the calculated
 206 TrOC concentration in the MD permeate before being diluted with the existing distillate.
 207 C^*_{MDE} is obtained via a mass balance calculation.

$$208 \quad C^*_{MD} = \frac{M_{MD}}{V_{MD}} \quad (3)$$

$$209 \quad M_{MD} = (C_{Distillate(t)} - C_{Distillate(t-\Delta t)})V_{Distillate} + \frac{(C_{Distillate(t)} + C_{Distillate(t-\Delta t)})}{2}V_{MD} \quad (4)$$

210 where M_{MD} is the mass of the TrOC passing through the MD membrane between time t
 211 $-\Delta t$ and t ; $C_{Distillate(t)}$ and $C_{Distillate(t-\Delta t)}$ are TrOC concentrations measured in MD
 212 distillate at time $t - \Delta t$ and t , respectively; $V_{Distillate}$ is the effective volume of the
 213 distillate (2 L); V_{MD} is the volume of excessive distillate between time $t - \Delta t$ and t ,
 214 which can be determined by the MD water flux.

215 Finally, the removal of TrOCs by the AnMBR-MD hybrid system is calculated as:

$$216 \quad R_{AnMBR-MD} = \frac{C_{wastewater} - C^*_{MDE}}{C_{wastewater}} \times 100\% \quad (5)$$

217 The fate of TrOCs in the sludge (i.e. solid phase) was not investigated because sludge is
 218 completely retained by MF cannot reach the MD process.

219 2.4.3 Biomass characteristics

220 Oxidation reduction potential (ORP) was measured using WP-80D dual pH-mV meter
 221 (TPS, Australia). Mixed liquor suspended solid (MLSS), mixed liquor volatile
 222 suspended solids (MLVSS) concentrations and alkalinity were measured according to
 223 the Standard Methods for Examination of Water and Wastewater.

224 2.4.4 Fluorescence excitation – emission matrix spectroscopy

225 A two-dimensional fluorescence spectrophotometer (Perkin-Elmer LS-55) was used to
 226 measure the fluorescence intensity of aqueous samples with excitation wavelengths
 227 between 240 and 450 nm and emission wavelengths between 290 and 580 nm (in 5 nm
 228 increments). Fluorophores detected in the excitation-emission-intensity matrix (EEM)

229 were assigned to specific dissolved organic matter fractions (Luo et al., 2017). All
230 samples were diluted to the same TOC concentration of 5 mg/L for resolving and
231 comparing EEM spectra.

232 2.4.5 Membrane autopsy

233 A scanning electron microscopy (SEM) coupled with energy dispersion spectrometry
234 (EDS) (JCM-600, JEOL, Tokyo, Japan) was used to identify the morphology and
235 composition of the fouling layer on the MD membrane surface every ten days.
236 Membrane samples were air-dried in a desiccator before being coated with an ultra-thin
237 gold layer with a sputter coater (SPI Module, West Chester, PA) for SEM imaging.
238 Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectroscopy
239 (IRAffinity-1, Shimadzu, Kyoto, Japan) was also used to probe the chemical
240 composition of the fouling layer. The measured spectrum ranged between 600 and
241 4000 cm^{-1} with 2 cm^{-1} resolution. Each scan was performed 20 times. A background
242 correction was conducted before each measurement. Membrane hydrophobicity was
243 measured by contact angle measurements using a Rame-Hart Goniometer (Model 250,
244 Rame-Hart, Netcong, NJ) based on the standard sessile drop method. Ten water droplets
245 were applied to each membrane sample and contact angles on both sides of the droplet
246 were analysed.

247 3 Results and discussion

248 3.1 Biological stability of AnMBR

249 Stable biomass characteristics were achieved during AnMBR operation (Table 1). The
250 MLSS and MLVSS concentrations in the bioreactor were stabilized at approximately 10
251 and 5 g/L respectively, corresponding to a constant MLVSS/MLSS ratio of 0.5. This
252 result confirms the operational stability of the anaerobic bioreactor. It has been reported
253 that the effective biological treatment of AnMBR could be achieved with the
254 MLVSS/MLSS ratio of 0.4 – 0.9 under a wide range of operational conditions, such as
255 HRT and SRT (Baek et al., 2010; Huang et al., 2011; Zhang et al., 2015). The mixed
256 liquor alkalinity was stable at $2216 \pm 220\text{ mg CaCO}_3/\text{L}$. A relatively high ORP ($-190 \pm$
257 14 mV) was observed in this study compared to conventional anaerobic treatment
258 processes (Hafuka et al., 2016). The high ORP value observed here was possibly

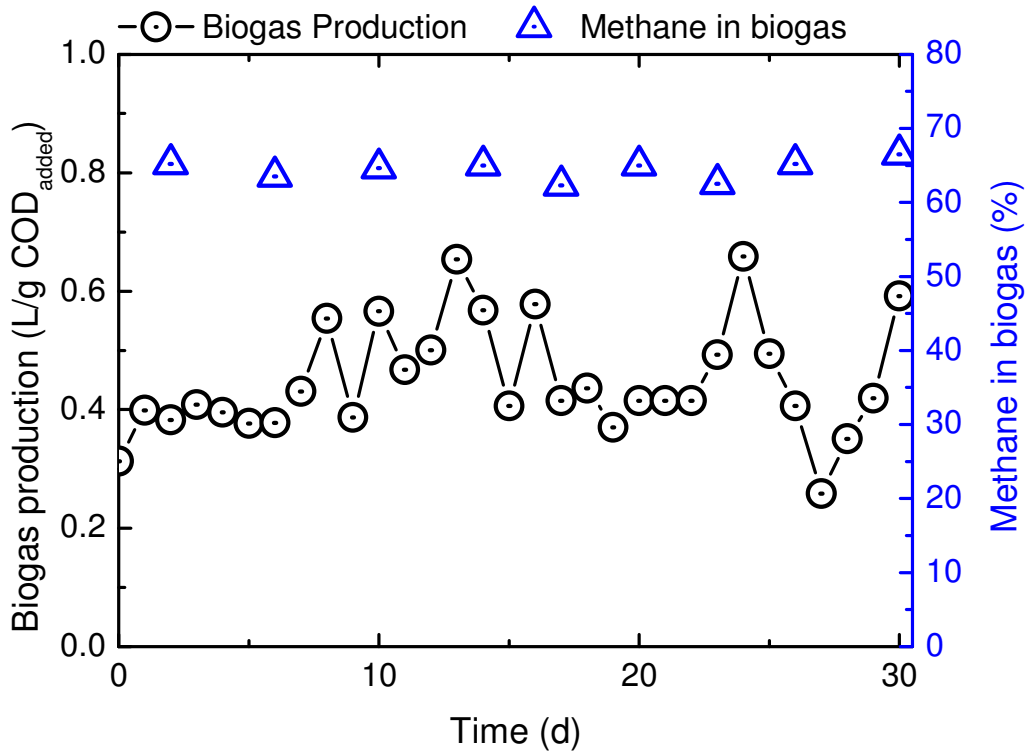
259 because of the circulation of biomass to the external membrane module and regular
260 mixed liquor sampling for ORP measurement.

261 **Table 1:** Key characteristics of the mixed liquor during AnMBR operation (mean value
262 \pm standard deviation from four measurements over 30 days)

Parameter	Value
MLSS (g/L)	10 ± 1
MLVSS (g/L)	4.9 ± 0.9
MLVSS/MLSS	0.5 ± 0.1
Alkalinity (mg CaCO ₃ /L)	2216 ± 220
Conductivity (mS/cm)	6.7 ± 0.2
ORP (mV)	-190 ± 14

263 A stable performance of AnMBR was also observed in terms of biogas production
264 (Figure 2) and organic removal (Table 2). During AnMBR operation, biogas production
265 was stabilized in the range from 0.3 to 0.5 L/g COD_{added} with the methane content at
266 approximately 65% (Figure 2). This observation is consistent with previous studies
267 (Wijekoon et al., 2015; Song et al., 2016), suggesting an effective biodegradation of
268 organic substances by anaerobic digesters. Indeed, near complete removal of both TOC
269 and COD could be achieved by AnMBR (Table 2).

270 Despite the excellent capacity for the removal of organic matter, AnMBR exhibited a
271 low nutrient (i.e., nitrogen and phosphorus) removal (Table 2). Indeed, the low removal
272 of nutrients is a major concern in terms of the development and practical application of
273 AnMBR (Liu et al., 2016). Biological nutrient removal by microbial assimilation in
274 AnMBR is limited due to the slow biomass growth in anaerobic digesters (Smith et al.,
275 2012). On the other hand, NH₄⁺ is generated from N-bearing organic compounds during
276 anaerobic treatment (Chen et al., 2016). Thus, only small TN removal (10 – 30%) by
277 AnMBR was observed in this study while NH₄⁺ in the effluent was about ten times
278 higher than that in the influent. The anaerobic process also liberates phosphorus from P-
279 bearing organic in the form of PO₄³⁻. As a result, PO₄³⁻ concentration in the effluent was
280 also higher than that in the influent (Table 2).



281

282 **Figure 2:** Biogas production and its methane fraction during AnMBR operation.
 283 Experimental conditions: HRT = 4 d; bioreactor temperature = 35 ± 1 °C; mixed liquor
 284 pH = 6.8 ± 0.2 (controlled by adding NaHCO_3). No extra sludge was withdrawn except
 285 for mixed liquor sampling (650 mL per week).

286 **Table 2:** Removal of bulk organic matter and nutrients by AnMBR (mean value \pm
 287 standard deviation from ten measurements over 30 days)

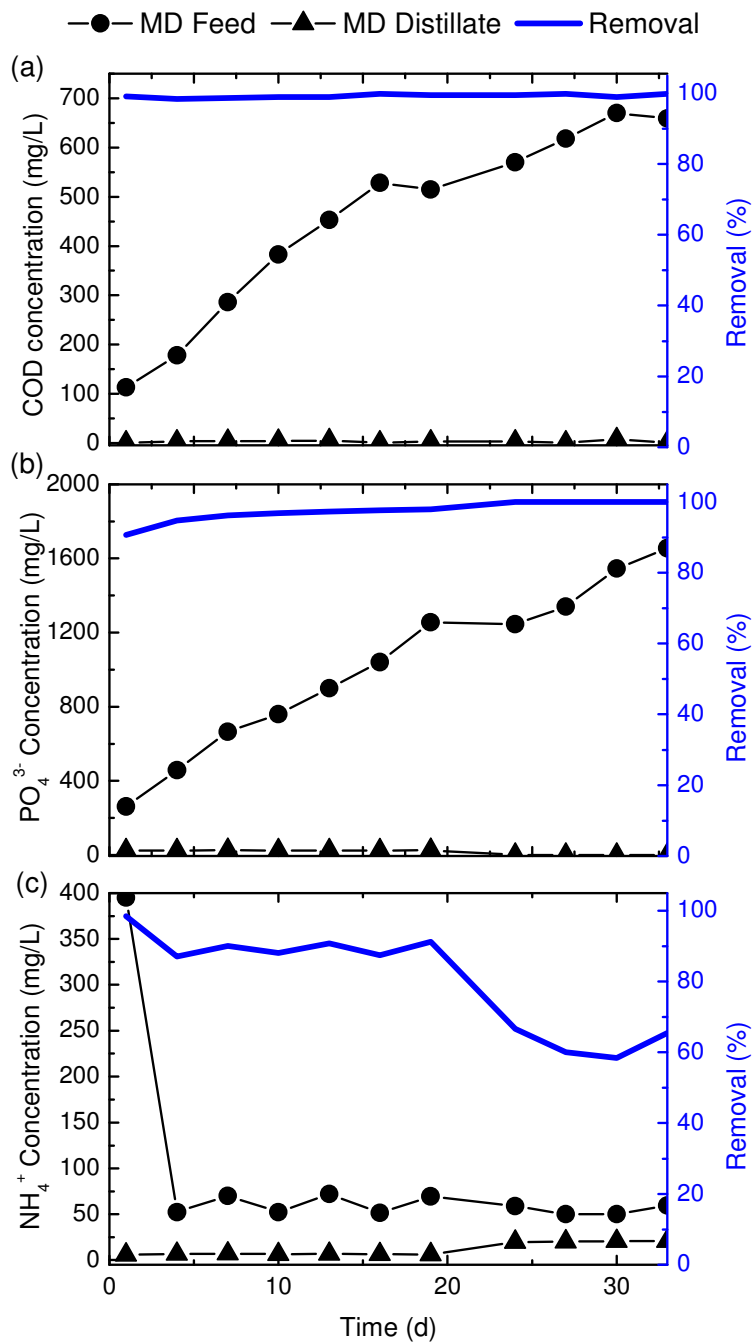
Parameters	Influent concentration (mg/L)	Effluent concentration (mg/L)	Removal (%)
TOC	2118.0 ± 66.5	26.5 ± 6.6	98.7 ± 0.3
COD	6252.3 ± 108.7	101.5 ± 22.9	98.4 ± 0.4
TN	166.8 ± 7.0	132.5 ± 16.9	20.4 ± 11.0
PO_4^{3-}	195.4 ± 11.4	213.7 ± 38.7	–
NH_4^+	34.7 ± 2.3	346.3 ± 37.0	–

288

289 3.2 *Performance of the MD process integrated with AnMBR*

290 3.2.1 *Removal of bulk organic matter and nutrients*

291 The MD process could complement AnMBR by further enhancing the removal of
292 organic substances and phosphate (Figure 3). By integrating MD with AnMBR,
293 complete and near complete removal of COD and phosphate was achieved, respectively
294 (Figure 3a and b). This is because the MD process can offer complete rejection of non-
295 volatile substances (Chen et al., 2016). As a result, a considerable accumulation of COD
296 and PO_4^{3-} in the MD feed solution was observed, which consequently resulted in
297 significant fouling to the MD membrane as discussed in the section 3.2.3.



298

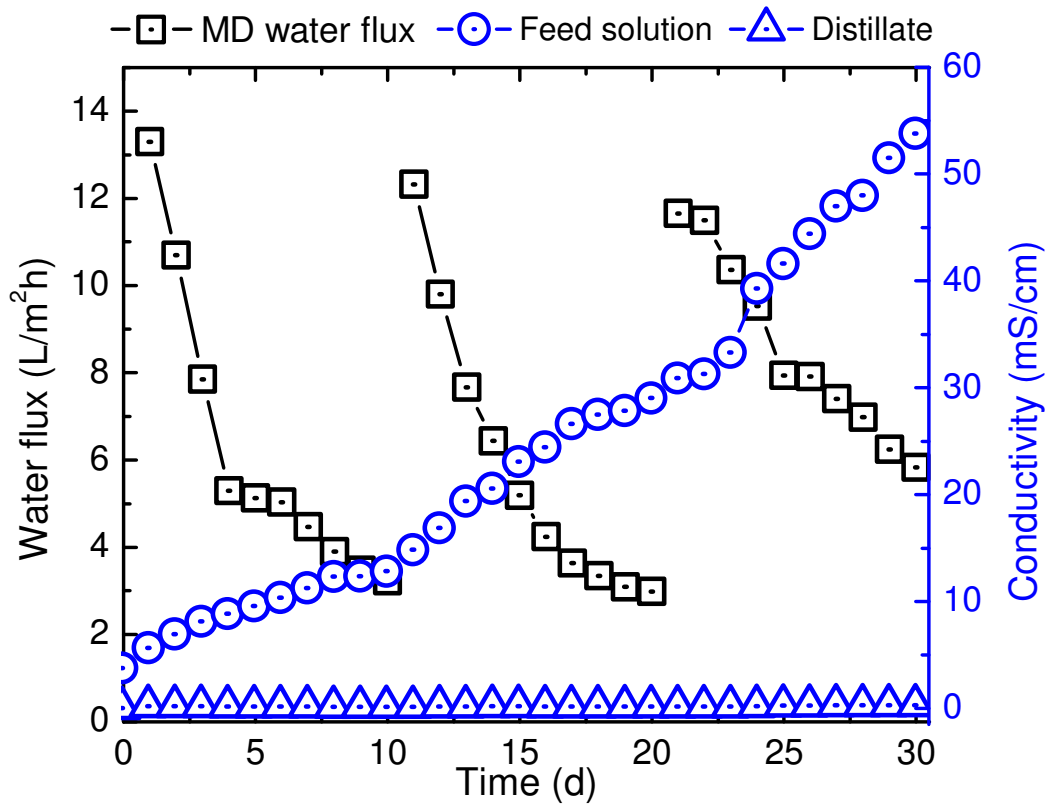
299 **Figure 3:** Distribution and removal of (a) COD, (b) PO_4^{3-} and (c) NH_4^+ by the MD
 300 process subsequently integrated with AnMBR. MD membrane was replaced every ten
 301 days. Operation condition of MD: feed temperature = 45 ± 1 ° C; distillate temperature
 302 = 20 ± 1 ° C; feed working volume = 2 L; feed and distillate flow rate = 1 mL/min (i.e.
 303 cross-flow velocity = 6.1 cm/s). AnMBR effluent was continuously replenished to

304 maintain the working volume of the MD feed at 10 L. Operation conditions of AnMBR
305 are summarized in the caption of Figure 2.

306 The removal of NH_4^+ by the MD process was nearly 90% within the first 20 days of
307 operation, but gradually decreased thereafter to approximately 60% on day 30 (Figure
308 3c). This decrease can be attributed to conversion to ammonia (NH_3) at a high feed
309 temperature of 45 °C. Ammonia is a highly volatile species and can be readily
310 transported through the MD membrane (Kim et al., 2015). As a result, a small but
311 clearly discernible increase in NH_4^+ concentration in the distillate was observed due to
312 ammonia transport through the MD membrane by volatilisation. In addition, NH_4^+
313 stripping (i.e. ammonia volatilisation) from the feed solution also occurred as evidenced
314 by its sharp decline and then constant feed concentration despite its moderate rejection
315 (60 – 90%) by the MD process. Results reported here indicate the need to control
316 ammonia volatilisation and to further remove it from the product water when MD is
317 utilized to purify the AnMBR effluent.

318 3.2.2 *Water flux*

319 Water flux of the MD process decreased continuously when used to purify the AnMBR
320 effluent (Figure 4). The observed flux decline can be attributed to salt accumulation in
321 the feed solution, and more importantly, membrane fouling. The feed conductivity
322 increased considerably from approximately 3 to 55 mS/cm over 30 days of continuous
323 operation (Figure 4). As a result, a small decrease in the initial water flux due to the
324 increase in feed salinity was observed after replacing a new MD membrane every 10
325 days. This observation also suggested a significant role for membrane fouling in the
326 water flux decline of the MD process. Membrane fouling could reduce the water flux by
327 restricting the active membrane area for water vapour transport. In addition, the fouling
328 layer may result in lowering the membrane surface hydrophobicity as indicated by a
329 decrease in the contact angle from $135 \pm 10^\circ$ for the pristine membrane to less than 60°
330 when the membrane was replaced. Nevertheless, pore wetting did not occur to the MD
331 membrane as evidenced by the consistently low distillate conductivity throughout the
332 experiment (Figure 4).

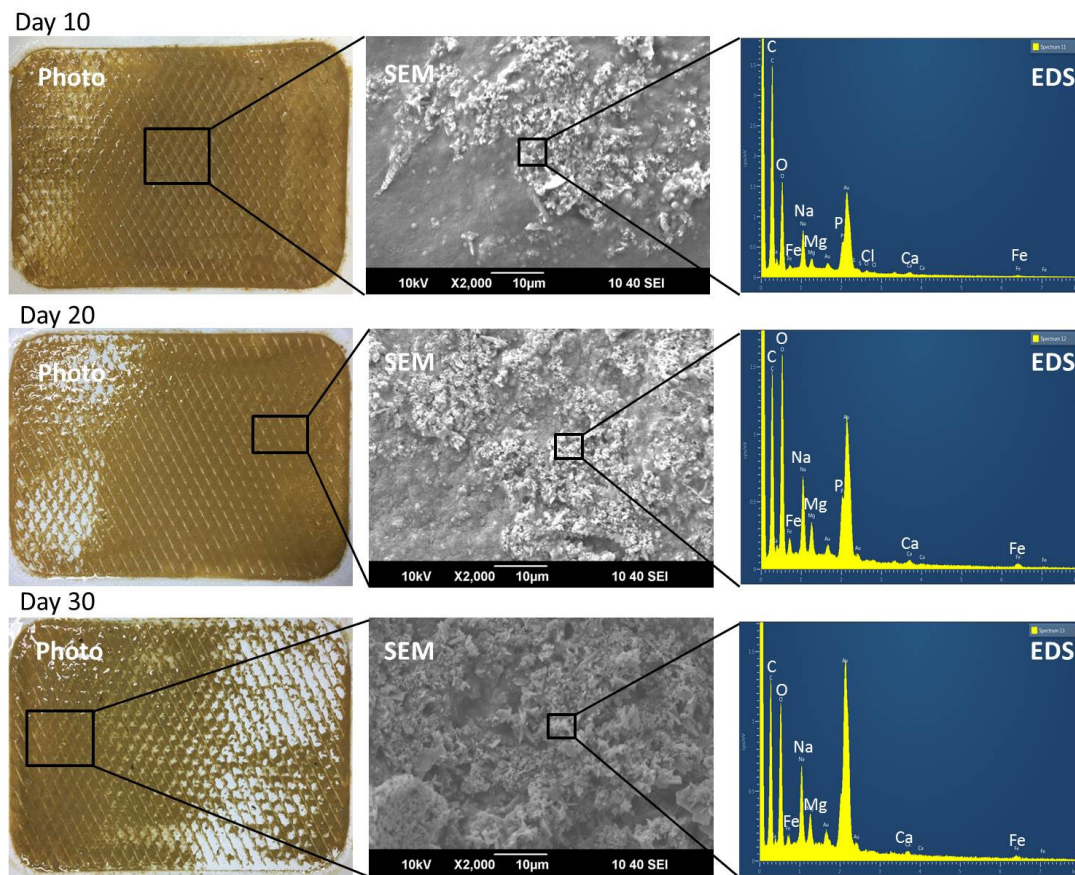


333

334 **Figure 4:** Water flux and the variation of the feed and distillate conductivity when the
 335 MD process was used to treat AnMBR effluent. Experimental conditions are
 336 summarized in the captions of Figures 2 and 3.

337 3.2.3 Membrane fouling characterisation

338 Membrane fouling layers were characterised to identify the fouling behaviour of the
 339 MD membrane for treating AnMBR effluent. A homogeneous cake layer was observed
 340 on each membrane surface after every 10 days of operation (Figure 5). The cake layer
 341 consisted of mainly carbon, oxygen, ferrous, sodium, chloride, magnesium, calcium,
 342 and phosphorus, suggesting the occurrence of both organic (biological) and inorganic
 343 fouling on the MD membrane surface. Indeed, inorganic crystals were visualized on the
 344 membrane surface through the SEM images and could be attributed to phosphate
 345 precipitates, such as calcium/magnesium phosphate and struvite given the accumulation
 346 of phosphate (Figure 3b) and inorganic salts in the feed solution (Figures 4).

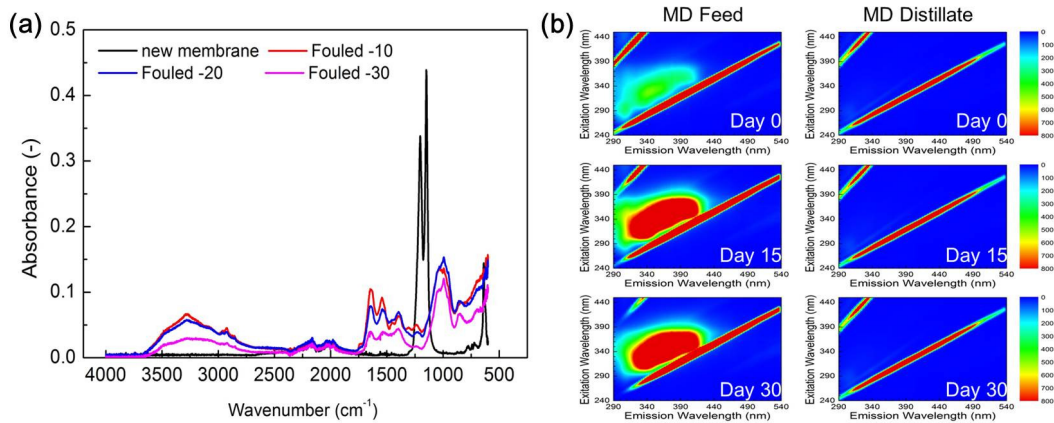


347

348 **Figure 5:** SEM images and EDS analyses of the fouled MD membranes. The MD
 349 membrane was replaced every ten days for fouling characterization. Operating
 350 conditions of MD were described in the caption of Figure 3.

351 Organic membrane fouling could also be evidenced by the ATR-FTIR measurement
 352 (Figure 6a). Compared to the pristine MD membrane, all fouled MD membranes
 353 exhibited distinctive adsorption peaks at 1653 cm^{-1} , which usually associates with
 354 alkene (C=C) in aliphatic structures and/or amide I (C=O) bonds, and at 1543 cm^{-1} ,
 355 representing amide II (C-N-H) bonds. The three fouled membranes also showed a sharp
 356 peak at 1032 cm^{-1} , indicating carbonyl (C=O) bonds of polysaccharides. These results
 357 indicated that protein and polysaccharides were major components contributing to the
 358 organic fouling of the MD membrane. EEM analysis identified a significant
 359 accumulation of humic-like ($\lambda_{\text{ex/em}}=300\text{-}370/400\text{-}500\text{ nm}$) and protein-like substances
 360 ($\lambda_{\text{ex/em}}=275\text{-}290/330\text{-}370\text{ nm}$) in the MD feed solution due to their high rejection by the
 361 MD membrane (Figure 6b).

362



363

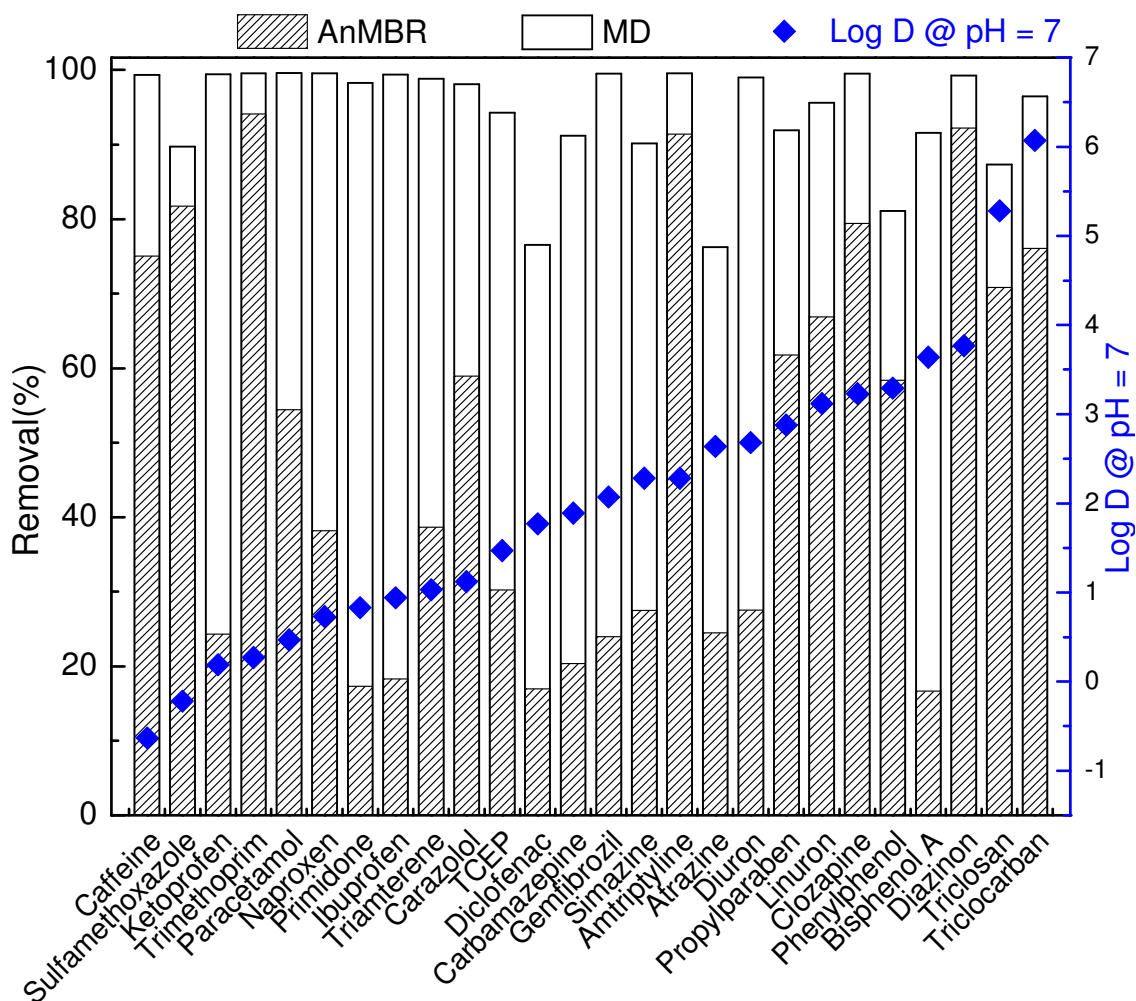
364 **Figure 6:** (a) ATR-FTIR adsorption spectra and (b) Fluorescence excitation and
 365 emission matrix (EEM) spectra for MD feed and MD distillate during AnMBR-MD
 366 operation. MD membrane was replaced every ten days for fouling characterization and
 367 named as fouled-10 d, fouled-20 d, and fouled-30 d, respectively.

368 3.3 TrOC removal by AnMBR integrated with MD

369 The role of the AnMBR and MD processes for TrOC removal in the integrated system
 370 was elucidated (Figure 7). In this study, the removal of TrOCs by AnMBR varied
 371 significantly from approximately 15.1% (i.e. primidone) to 94.2% (i.e. trimethoprim),
 372 depending on their molecular properties, such as hydrophobicity and molecular
 373 structures. Indeed, previous studies have demonstrated that TrOC removal by MBR is
 374 largely governed by their molecular properties, regardless of the presence or absence of
 375 oxygen in the bioreactor (Tadkaew et al., 2011; Wijekoon et al., 2015). In particular, the
 376 removal of ketoprofen, primidone, ibuprofen, diclofenac, carbamazepine, gemfibrozil,
 377 simazine, atrazine, and diuron by AnMBR alone was only in the range of 15 – 25%. The
 378 low biodegradability of these compounds under anaerobic conditions could be attributed
 379 to the presence of electron withdrawing groups, such as chloro, amide, and nitro in their
 380 molecular structures (Wijekoon et al., 2015). In addition, these compounds were
 381 relatively hydrophilic with Log D values lower than 3.2 (at solution pH = 7). As a result,
 382 they did not adsorb significantly to the sludge phase and biodegradation was their
 383 predominant removal mechanism from the aqueous phase.

384

385



386

387 **Figure 7:** TrOC removal by AnMBR integrated with MD. TrOCs are listed in the order
 388 of increasing hydrophobicity. Based on their effective octanol-water partition
 389 coefficient (Log D) at solution pH of 7, the 26 TrOCs investigated were classified as
 390 hydrophobic (Log D > 3.2) and hydrophilic (Log D < 3.2). Average removal rates from
 391 six measurements (once every five days) were shown with standard deviation in the
 392 range of 0.1 – 24%. Experimental conditions are summarized in the caption of Figure 2.

393 Several TrOCs were removed by AnMBR by over 70%. These TrOCs included caffeine,
 394 sulfamethoxazole, trimethoprim, amtriptyline, linuron, clozapine, diazinon, triclosan,
 395 and triclocarban (Figure 7). Given the relatively low hydrophobicity of caffeine,
 396 sulfamethoxazole, trimethoprim, and amitriptyline, their effective removal by AnMBR
 397 could be attributed to the high intrinsic biodegradability with the presence of electron
 398 donation groups, such as amine and hydroxyl, in their molecular structures (Tadkaew et
 399 al., 2011). By contrast, linuron, clozapine, diazinon, triclosan, and triclocarban were

400 highly hydrophobic with Log D values higher than 3.2 (at pH = 7). Thus, these
401 compounds could effectively be retained by anaerobic digesters and thus facilitate their
402 biodegradation and hinder their permeation through the MF membrane.

403 Although TrOC removal by AnMBR was highly variable and strongly dependent on the
404 specific molecular properties of each compound, the MD process could consistently
405 enhance the overall TrOC removal. Indeed, the MD process could effectively reject all
406 TrOCs selected in this study (Figure S1, Supplementary Data). As a result, over 76%
407 removal of all TrOCs could be achieved by the integrated AnMBR-MD system (Figure
408 7). The role of MD in this hybrid system for TrOC removal was most significant for
409 these compounds (such as, primidone, ibuprofen, diclofenac, and bisphenol A) that were
410 poorly removed by AnMBR.

411 **4 Conclusion**

412 Results reported here suggest that the MD process could complement very well with
413 AnMBR for energy and water recovery. AnMBR could produce 0.3 – 0.5 L/g COD_{added}
414 biogas (approximately 65% methane). By integrating MD with AnMBR, high removal
415 of organic matter and nutrients could be achieved. The high retention capacity of the
416 MD membrane resulted in significant phosphate accumulation in the feed solution,
417 thereby producing an opportunity for phosphorus recovery from AnMBR effluent. The
418 synergy between the biological treatment and the MD membrane rejection contributed
419 to 76% to complete removal of all 26 selected TrOCs by the integrated AnMBR-MD
420 system. Further research is necessary to address the issue of MD membrane fouling
421 when it is coupled with AnMBR for phosphorus recovery and water reuse applications.

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