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Effects of sulphur on the performance of an anaerobic membrane bioreactor: Biological stability, trace organic contaminant removal, and membrane fouling

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Effects of sulphur on the performance of an anaerobic membrane bioreactor: Biological stability, trace organic contaminant removal, and membrane fouling

Abstract

This study investigated the impact of sulphur content on the performance of an anaerobic membrane bioreactor (AnMBR) with an emphasis on the biological stability, contaminant removal, and membrane fouling. Removal of 38 trace organic contaminants (TrOCs) that are ubiquitously present in municipal wastewater by AnMBR was evaluated. Results show that basic biological performance of AnMBR regarding biomass growth and the removal of chemical oxygen demand (COD) was not affected by sulphur addition when the influent $\text{COD}/\text{SO}_4^{2-}$ ratio was maintained higher than 10. Nevertheless, the content of hydrogen sulphate in the produced biogas increased significantly and membrane fouling was exacerbated with sulphur addition. Moreover, the increase in sulphur content considerably affected the removal of some hydrophilic TrOCs and their residuals in the sludge phase during AnMBR operation. By contrast, no significant impact on the removal of hydrophobic TrOCs was noted with sulphur addition to AnMBR.

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1 **Effects of sulphur on the performance of an anaerobic membrane**
2 **bioreactor: Biological stability, trace organic contaminant removal,**
3 **and membrane fouling**

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19 **ABSTRACT**

20 This study investigated the impact of sulphur content on the performance of an
21 anaerobic membrane bioreactor (AnMBR) with an emphasis on the biological
22 stability, contaminant removal, and membrane fouling. Removal of 38 trace organic
23 contaminants (TrOCs) that are ubiquitously present in municipal wastewater by
24 AnMBR was evaluated. Results show that basic biological performance of AnMBR
25 regarding biomass growth and the removal of chemical oxygen demand (COD) was
26 not affected by sulphur addition when the influent COD/SO₄²⁻ ratio was maintained
27 higher than 10. Nevertheless, the content of hydrogen sulphate in the produced biogas
28 increased significantly and membrane fouling was exacerbated with sulphur addition.
29 Moreover, sulphur increase considerably affected the removal of some hydrophilic
30 TrOCs and their residuals in the sludge phase during AnMBR operation. By contrast,
31 no significant impact on the removal of hydrophobic TrOCs was noted with sulphur
32 addition to AnMBR.

33

34 **Key words:** Anaerobic membrane bioreactor (AnMBR), sulphur increase, trace
35 organic contaminants (TrOCs), biogas production, bioenergy.

36 **1 Introduction**

37 Wastewater treatment and reuse is essential to protect public health and secure a
38 sustainable water supply (Shannon et al., 2008). Nevertheless, wastewater treatment
39 and reuse is energy-intensive. It has been estimated that municipal wastewater
40 treatment accounts for approximately 3% electricity consumption and 5% greenhouse
41 gas emission on a global basis (Li et al., 2015b). In particular, most current
42 wastewater treatment plants (WWTPs) are based on aerobic biological processes,
43 which require intensive energy for aeration (Li et al., 2015b). It is noteworthy that
44 aerobic treatment is not a suitable platform for resource recovery, because organic
45 carbon (a source of energy) and nitrogen (a valuable nutrient) in wastewater are
46 converted into carbon dioxide and nitrogen gas, respectively (Ansari et al., 2017).

47 Given global efforts to curb greenhouse gas emission, many water utilities have
48 actively explored new treatment alternatives to reduce their energy footprint and even
49 achieve energy self-sufficiency (Shen et al., 2015; Nghiem et al., 2017). Amongst
50 these potential alternatives, anaerobic treatment is particularly promising. Compared
51 to aerobic processes, anaerobic treatment does not only consume significantly less
52 energy, but also produce methane, which is a renewable fuel. In particular, anaerobic
53 membrane bioreactor (AnMBR) has emerged as a promising technology to achieve
54 energy neutrality in future WWTPs. AnMBR integrates the membrane separation
55 process with anaerobic treatment to simultaneously achieve the recovery of water and
56 energy from waste streams. It has been well established that AnMBR has much less
57 energy consumption and lower sludge production in comparison with its aerobic
58 counterpart (Liao et al., 2006; Lew et al., 2009; Skouteris et al., 2012).

59 Currently, AnMBR has been applied mostly for the treatment of industrial waste
60 streams. Municipal wastewater often has a low content of organic carbon, thus, is not
61 ideal for anaerobic treatment (Visvanathan and Abeynayaka, 2012; Judd, 2016). To
62 overcome this issue, several techniques to fortify municipal wastewater have been
63 explored and developed. They include co-digesting municipal wastewater with other
64 high strength waste streams, such as liquid food waste (Tuyet et al., 2016; Becker et
65 al., 2017), and pre-concentrating municipal wastewater by membrane processes, such
66 as forward osmosis (FO) (Zhang et al., 2014; Ansari et al., 2016). Nevertheless, the
67 co-digestion of food waste and municipal wastewater can undesirably increase the

68 sulphate load to AnMBR due to the high sulphate content of food waste (Drews et al.,
69 2005; Meng et al., 2009; Zhang et al., 2014). On the other hand, the pre-concentration
70 of municipal wastewater by FO can also result in the enrichment of sulphate in the
71 concentrated stream (Ansari et al., 2017). In addition, industrial wastewater from
72 pharmaceutical and chemical manufacturing industry, pulp and paper production, and
73 food processing may also contain high sulphur content (Siles et al., 2010).

74 Effects of sulphate on anaerobic treatment have been demonstrated in previous studies.
75 High sulphate concentration can strengthen the competition of sulphate reducing
76 bacteria over methanogenic microbes for available organic substrates, thereby
77 reducing biogas production during anaerobic treatment. Moreover, sulphate can
78 induce the precipitation of non-alkaline metals in anaerobic reactors, limiting their
79 availability as micro-nutrients for methane producing microbes (Oude Elferink et al.,
80 1994; Siles et al., 2010). In addition, sulphate reduction produces hydrogen sulphate
81 (H_2S), which is a corrosive, malodourous, and toxic gas (Muyzer and Stams, 2008;
82 Sarti and Zaiat, 2011; Park et al., 2014). H_2S can readily penetrate bacterial cell
83 membrane and denature native proteins inside the cytoplasm producing sulphide and
84 disulphide cross-links between polypeptide chains (Siles et al., 2010). It is noteworthy
85 that the negative impact of sulphate on anaerobic treatment may be alleviated by
86 maintaining an adequate $\text{COD}/\text{SO}_4^{2-}$ ratio (> 10) to provide sufficient organic
87 substances for both methane producing and sulphate reducing microbes (Rinzema and
88 Lettinga, 1988). In some cases, with adequate organic matter, sulphate addition is
89 beneficial to methane production by promoting the degradation of propionic acid (Li
90 et al., 2015a). Thus, in practice, the undesirable effects of sulphur shocks on anaerobic
91 treatment can be potentially alleviated by adjusting the ratio between carbon- and
92 sulphate-rich substrates.

93 An emerging issue in wastewater treatment and reuse is the ubiquitous occurrence of
94 trace organic contaminants (TrOCs) (Luo et al., 2014). TrOCs are emerging chemicals
95 of significant concern that typically include but are not limit to steroid hormones,
96 pharmaceuticals, personal care products, surfactants, pesticides, and disinfection by
97 products (Ternes et al., 2004; Kummerer, 2009). They present in wastewater and other
98 water bodies at trace concentrations (i.e., up to several micrograms per litre) (Luo et
99 al., 2014). Although there remains uncertainty, these TrOCs can adversely impact the

100 health of living organisms by inducing estrogenic, mutagenic, endocrine disrupting
101 and genotoxic effects (Schwarzenbach et al., 2006).

102 Recent studies have demonstrated the removal of TrOCs by AnMBR. Monsalvo et al.
103 (2014) investigated the removal of 38 TrOCs by AnMBR and reported over 90%
104 removal for nine compounds; while others were removed by less than 50%. They
105 further postulated that the main mechanisms of TrOC removal in AnMBR included
106 biodegradation, adsorption onto biosolids, and deposition onto the membrane surface.
107 Wijekoon et al. (2015) subsequently related the removal of TrOCs by AnMBR their
108 physicochemical properties, particularly hydrophobicity and molecular structure. Their
109 results showed that all hydrophobic compounds out of 27 TrOCs were removed by
110 more than 70%; while the removal of hydrophilic TrOCs varied significantly, relying
111 on their intrinsic biodegradability, which was further governed by their molecular
112 structures. However, until now, little is known about the impact of sulphate on the
113 performance of AnMBR, particularly the removal of TrOCs.

114 This study aims to investigate the effects of sulphur on the performance of AnMBR
115 with an emphasis on biological stability, TrOC removal, and membrane fouling.
116 Sulphur content of AnMBR influent was gradually increased by adding sodium
117 sulphate (Na_2SO_4). Biological stability was evaluated in terms of biomass
118 concentration and biogas production. The removal of bulk organic matter and TrOCs
119 by AnMBR was assessed. In addition, membrane fouling profile during AnMBR
120 operation with sulphur increase was also elucidated. Results from this study provide
121 unique insights to AnMBR applications for the treatment of sulphur-rich wastewater
122 and the co-management of wastewater and sulphur-rich food waste.

123 **2 Materials and methods**

124 *2.1 Synthetic wastewater and trace organic contaminants*

125 A synthetic solution was used in this study to simulate high strength domestic
126 wastewater (Wijekoon et al., 2015). The synthetic wastewater was consisted of 4000
127 mg/L glucose, 750 mg/L peptone, 175 mg/L potassium dihydrogen phosphate, 175
128 mg/L magnesium chloride, 2250 mg/L sodium acetate, 175 mg/L urea, 45 mg/L
129 ferrous chloride, 10 nickel chloride, 6 mg/L cobalt chloride, and 4 mg/L ammonium
130 molybdate. Key physicochemical properties of the synthetic wastewater were
131 determined every four days. The synthetic wastewater contained 1176 ± 30 mg/L

132 chemical oxygen demand (COD) and 6.3 ± 0.4 mg/L total nitrogen (TN). The
133 electrical conductivity and pH of this synthetic wastewater were 5.9 ± 2.5 mS/cm and
134 6.9 ± 0.2 , respectively.

135 A set of 38 TrOCs with diverse physiochemical properties was selected in this study.
136 These compounds represent major TrOC groups, namely pharmaceuticals, personal
137 care products, industrial chemicals, and pesticides, which are ubiquitous in municipal
138 wastewater (Luo et al., 2014). A combined stock solution of all 38 TrOCs was
139 prepared in pure methanol and stored at -18 °C in the dark. These TrOCs were
140 introduced daily into the synthetic wastewater at a concentration of approximately 2
141 $\mu\text{g/L}$ of each compound.

142 2.2 *AnMBR system*

143 A lab-scale AnMBR system was used in this study. Detailed description of the
144 AnMBR system has been provided elsewhere (Song et al., 2016). Briefly, the
145 AnMBR system was mainly consisted of a bioreactor, an external microfiltration (MF)
146 membrane unit, and several peristaltic pumps. The bioreactor was made of stainless
147 steel with an effective working volume of 20 L and a head space of 8 L in case of
148 unexpected foaming in the reactor. A peristaltic pump (Masterflex L/s, USA)
149 controlled by a water level sensor (Omron, Japan) was used to feed the bioreactor. An
150 industrial grade hose pump (ProMinent, Australia) was used to circulate the mixed
151 liquor from the bottom to the top of the bioreactor to maintain a well-mixed condition.
152 A peristaltic pump (Masterflex L/s, USA) was used to circulate the mixed liquor
153 through a ceramic MF membrane (NGK, Japan), which was housed in an external
154 column module, and then back to the bioreactor. A ceramic membrane was used
155 because of its resistance to corrosive chemicals, such as cleaning reagents and harsh
156 environmental conditions, such as high temperature for chemical cleaning. The MF
157 membrane had a pore size of 0.1 μm and an effective area of 0.09 m^2 . Another
158 peristaltic pump (Masterflex L/s, USA) was used to extract water from the membrane
159 module in a suction and relaxation cycle of 14 min on and 1 min off, respectively.
160 This operational cycle was specifically employed to alleviate membrane fouling.

161 The bioreactor was wrapped with a rubber hose, which was connected to a
162 proportional-integral-derivative controlled heater (Neslab RTE7, Thermo Scientific,
163 USA), to maintain the mixed liquor temperature at 35 °C. The bioreactor and all

164 pipelines were insulated with polystyrene foam to minimize heat loss. A biogas
165 counter was used to measure the rate of biogas production. A Tedlar sampling bag
166 was also used to collect biogas for composition analysis. Trans-membrane pressure
167 (TMP) was continuously monitored by a high resolution (± 0.1 kPa) pressure sensor
168 (Extech Equipment, Australia) to indicate the profile of membrane fouling.

169 2.3 *Experimental protocol*

170 The AnMBR system was inoculated with anaerobic digesters from a local wastewater
171 treatment plant (Wollongong, NSW, Australia) and fed with the synthetic wastewater
172 under laboratory conditions as mentioned below. When AnMBR had achieved a
173 stable removal of bulk organic matter (indicated by COD) for more than two months,
174 sulphur content in the synthetic wastewater was increased gradually by adding
175 Na_2SO_4 . Stepwise increase of 100 mg/L sulphate every 10 days was adapted to avoid
176 mortal effects of sulphur shock on anaerobic digesters. In this study, the influent
177 sulphate concentration was increased up to 600 mg/L, corresponding to a decreased of
178 the $\text{COD}/\text{SO}_4^{2-}$ ratio to approximately 10, which is commonly considered as a
179 threshold for effective anaerobic treatment of sulphur-containing wastewater (Hu et
180 al., 2015; Yurtsever et al., 2016). The permeate flux was maintained at approximately
181 $2 \text{ L}/\text{m}^2\text{h}$, resulting in a hydraulic retention time (HRT) of 5 days. This relatively long
182 HRT was applied to allow for the adequate biodegradation of organic substances and
183 mitigation of membrane fouling. Sludge samples (approximately 100 mL) were
184 collected daily, leading to an operating sludge retention time (SRT) of 180 days. The
185 mixed liquor pH was maintained at approximately 7 throughout AnMBR operation by
186 periodically adding sodium bicarbonate into the bioreactor. Membrane backwashing
187 was conducted ex-situ when the TMP reached approximately 0.9 bar.

188 2.4 *Basic analytical methods*

189 Mixed liquor pH and electrical conductivity were monitored using an Orion 4 Star
190 Plus portable pH/conductivity meter (Thermo Scientific, USA). COD of the feed,
191 mixed liquor supernatant, and effluent, was measured based on the standard
192 dichromate method using high range plus digestion vials (Hatch, USA). Oxidation
193 reduction potential (ORP) was monitored by a WP-80D dual pH-mV meter (TPS,
194 Australia). Biogas composition was analysed using a biogas meter (Biogas 5000,
195 Geotech, UK) (Nghiem et al., 2014). Alkalinity, mixed liquor suspended solids

196 (MLSS) and mixed liquor volatile suspended solids (MLVSS) concentrations were
197 measured based on the Standard Methods for Examination of Water and Wastewater.

198 2.5 *TrOC analysis*

199 TrOC concentrations in the aqueous phase were determined by an analytical method
200 previously reported by Wijekoon et al. (2015). Briefly, this method included solid
201 phase extraction (SPE) and liquid chromatography followed by quantitative
202 determination by tandem mass spectrometry with electrospray ionisation. Duplicate
203 samples (250 mL for each) were analysed each time. Samples were spiked with a
204 surrogate solution containing 50 ng of an isotopically labelled version of each target
205 TrOC. Hydrophilic/lipophilic balance cartridges (Waters, Millford, MA, USA) were
206 preconditioned with 5 mL methyl tert-butyl ether, 5 mL methanol and 10 mL reagent
207 water, and then used for TrOC extraction. After SPE, cartridges used for TrOC
208 extraction were rinsed twice with 5 mL reagent and dried completely using a stream
209 of nitrogen for 50 min. All cartridges loaded with TrOCs were stored at 4 °C in sealed
210 bags until elution and analysis. Analytes were eluted from the loaded cartridges with 5
211 mL methanol and then 5 mL methanol/methyl tertiary butyl ether (1/9, v/v) into
212 centrifuge tubes. The resultant extract was concentrated under a stream of nitrogen to
213 approximately 100 µL and then diluted to a final volume of 1 mL with methanol.

214 Analytes were separated using an Agilent 1200 series high performance liquid
215 chromatography (HPLC) system (Palo Alto, CA, USA) on a Luna C18 (2) column
216 (Phenomenex, Torrance CA, USA). Peaks were identified and quantified by isotope
217 dilution method using an API 4000 triple quadrupole mass spectrometer (MS)
218 (Applied Biosystems, Foster City, CA, USA) that was equipped with a turbo-V ion
219 source and employed in both positive and negative electro-spray modes. The detection
220 limit of this analytical method was 5 ng/L for all analytes except for meprobamate and
221 bisphenol A (10 ng/L) and aspartame, propylparaben (20 ng/L). Detailed description
222 of the HPLC–MS/MS settings is available elsewhere (Wijekoon et al., 2015)

223 Feed and permeate samples were collected weekly for the analysis of TrOCs to
224 determine their removal by AnMBR:

$$R = \frac{C_f - C_p}{C_f} \times 100\%$$

225

226 where C_f and C_p were TrOC concentrations in the feed and permeate, respectively.
227 TrOC concentrations in the sludge phase were determined based on a method reported
228 previously by Yang et al. (2016). Briefly, the mixed liquor was first centrifuged at
229 3750g for 20 mins to obtain sludge pellet, which was then freeze-dried completely
230 using an Alpha 1–2 LD plus Freeze Dryer (Christ GmbH, Germany). The dry sludge
231 was grounded to powder before weighing 0.5 g into a glass tube and being thoroughly
232 mixed with 5 mL methanol, followed by ultrasonication at 40 °C for 10 min. The
233 mixture was then centrifuged at 3270 g for 10 min to obtain supernatant, which was
234 collected into an amber bottle. The ultrasonication and centrifugation steps were
235 repeated after mixing 5 mL blend of dichloromethane and methanol (1:1 v:v) with the
236 remaining sludge in the test tube. Supernatants from these two centrifuge steps were
237 mixed completely; while residual methanol and dichloromethane were purged using
238 nitrogen gas. Milli-Q water was added to obtain a 250 mL aqueous sample for TrOC
239 extraction and analysis according to the method described above.

240 **3 Results and discussion**

241 *3.1 Biomass concentration*

242 An increase in the influent sulphur content up to 600 mg/L (as sulphate),
243 corresponding to a decrease in the COD/SO₄²⁻ ratio from 60 to 10, did not
244 significantly affect the biomass concentration as indicated by both the MLSS and
245 MLVSS concentrations during AnMBR operation (Fig. 1). In this study, the MLSS
246 and MLVSS concentrations were stable at approximately 15.0 ± 1.4 and 10.0 ± 1.5
247 g/L, respectively, with a MLVSS/MLSS ratio of around 0.6. The stable
248 MLVSS/MLSS ratio also confirms that sulphate addition to the influent did not cause
249 any increase in the MLSS inorganic fraction. Results shown in Fig. 1 are consistent
250 with reports from other anaerobic treatment systems, where no significant impacts on
251 biomass concentration were observed with sulphur increase provided the influent
252 COD/SO₄²⁻ ratio was at or above the threshold of 10 (Hu et al., 2015). Indeed, the
253 COD/SO₄²⁻ ratio of the influent significantly affects the performance of anaerobic
254 treatment systems by governing the competition between sulphate reducing bacteria
255 and other bacteria, particularly predominant species belonged to *proteobacteria* (Sarti
256 et al., 2010).

257

[Figure 1]

258 3.2 Removal of bulk organic matter

259 No significant impact on the removal of COD was observed with sulphur increase in
260 the AnMBR influent. As can be seen in Fig. 2, COD removal by AnMBR was stable
261 at approximately 98% when sulphate addition to the feed solution was increased to
262 600 mg/L. This result is consistent with the stable biomass concentration as discussed
263 above, corroborating that sulphur increase does not significantly affect the basic
264 performance of AnMBR regarding the biomass growth and biodegradation of bulk
265 organic matter, as long as the the influent COD/SO₄²⁻ ratio is above 10. Similar results
266 were also observed by Sarti et al. (2010) who reported that COD removal by an
267 anaerobic sequencing batch biofilm reactor was not impacted by an increase in the
268 influent sulphur content. Sarti et al. (2010) attributed their observation to the fact that
269 organic carbon was the dominating energy source for microbial metabolism. It is
270 noteworthy that sulphate reducing bacteria appeared to proliferate in AnMBR with
271 sulphur addition, as indicated by a significant increase in the H₂S production (Fig. 3).
272 Despite the competition between methane-producing and sulphate-reducing bacteria
273 in the anaerobic bioreactor, they both utilize organic carbon for assimilation (Hu et al.,
274 2015), thereby contributing a relatively stable COD removal by AnMBR.

275

[Figure 2]

276 3.3 Biogas production

277 Sulphur increase significantly affected biogas production during AnMBR operation
278 (Fig. 3A). Without sulphate addition to the influent (i.e., the first 10 days), biogas
279 production of AnMBR varied slightly between 0.4 and 0.6 L/g COD_{added}. When 100
280 mg/L SO₄²⁻ was added to the AnMBR influent between day 10 and 20, biogas
281 production gradually decreased to 0.2 L/g COD_{added} (Fig. 3A). A significant reduction
282 also occurred to the methane content in the produced biogas when 100 mg/L SO₄²⁻
283 was added to the influent. Such observed reductions in both biogas production and its
284 methane content could be attributed to the adverse effects of sulphur loading on
285 methanogens (Hu et al., 2015). Similar variations in biogas production were also
286 noted in the following AnMBR operation with a step-wise increase of the influent
287 SO₄²⁻ concentration up to 600 mg/L (i.e. increasing 100 mg/L every 10 days).
288 Although biogas production could be recovered to some extent when the influent

289 SO_4^{2-} concentration was maintained at a certain level for a few days, a downward
290 trend to approximately 0.2 L/g $\text{COD}_{\text{added}}$ was observed when SO_4^{2-} addition was
291 increased to 600 mg/L (Fig. 3A).

292 **[Figure 3]**

293 The reduced methane content in biogas with sulphur increase can be attributed to the
294 competition of sulphate reducing bacteria over methane producing microbes (Silva et
295 al., 2002; Hu et al., 2015). Hu et al. (2015) reported that sulphur increase could
296 enhance the utilization of electrons by sulphate reducing bacteria. Indeed, sulphate
297 addition increased considerably the H_2S production (Fig. 3B), suggesting the active
298 metabolism of sulphate reducing bacteria. Moreover, the produced H_2S inside the
299 anaerobic bioreactor could be toxic to methanogenic bacteria and archaea by diffusing
300 through their cell membranes and denature their functional proteins (Siles et al., 2010).
301 Nevertheless, despite a continuous increase in the influent SO_4^{2-} concentration up to
302 600 mg/L, the methane content in the produced biogas was recovered to its initial
303 level (approximately 62%) from day 25 onward. This observation confirms that at a
304 $\text{COD}/\text{SO}_4^{2-}$ ratio at or above 10, there was adequate organic carbon for both methane
305 producing and sulphate reducing bacteria, thereby maintaining the basic performance
306 of anaerobic systems after microbial acclimatization. It is noted that biogas
307 purification to remove H_2S , for example by adsorption using inert materials, is
308 necessary for effective and safe methane utilization when sulphate-rich wastewater is
309 treated by AnMBR in practice.

310 *3.4 Membrane fouling*

311 High sulphate addition to the influent exacerbated membrane fouling during AnMBR
312 operation (Fig. 4). The TMP value was stable at approximately 0.5 bar when the
313 influent SO_4^{2-} concentration was lower than 200 mg/L, indicating no notable
314 membrane fouling at a low sulphur content. A sharp TMP increase was observed
315 when the SO_4^{2-} concentration was increased to 300 mg/L, possibly due to an
316 enhancement in the concentration of soluble microbial products (SMP) and
317 extracellular polymeric substances (EPS) in the mixed liquor at a high SO_4^{2-}
318 concentration. Indeed, Kobayashi et al. (2015) reported that the high sulphate
319 concentration (> 200 mg/L) could considerably increase the release of carbohydrate
320 and protein, which are major constituents of SMP and EPS, from anaerobic digesters,

321 during the operation of up-flow anaerobic sludge blanket reactors. Both SMP and EPS
322 play an important role in the formation of cake layer on the membrane surface and
323 pore blockage in either aerobic or anaerobic MBR systems (Lin et al., 2012). As a
324 result, to maintain a sustainable water production, membrane backwash using the
325 AnMBR effluent was conducted on day 35 when the TMP increased to 0.85 bar.
326 Nevertheless, similar increase in the TMP profile was observed when the influent
327 SO_4^{2-} concentration was further increased, thereby requiring another membrane
328 backwash on day 65.

329 **[Figure 4]**

330 *3.5 Removal of trace organic contaminants*

331 *3.5.1 General removal performance*

332 TrOC removal by AnMBR is governed by their physiochemical properties, including
333 hydrophobicity and molecular features. Based on the predictive framework developed
334 by Wijekoon et al. (2015), TrOC removal in AnMBR could be categorized by their
335 effective octanol – water partition coefficient (i.e. $\text{Log } D$) at a certain mixed liquor pH.
336 Thus, in this study, the selected 38 TrOCs were classified as hydrophilic ($\text{Log } D < 3.2$)
337 and hydrophobic ($\text{Log } D > 3.2$) as the mixed liquor pH was stable at 7.

338 All hydrophobic TrOCs with $\text{Log } D > 3.2$ were well removed by over 50% in
339 AnMBR with bisphenol A as the only exception (Fig. 5A). No discernible effects on
340 the removal of these hydrophobic compounds were observed with sulphur increase.
341 The effective removal of these hydrophobic TrOCs by AnMBR has also been
342 demonstrated by Wijekoon et al. (2015) under comparable experimental conditions
343 and can be attributed to their adsorption onto sludge due to hydrophobic interactions.
344 Bisphenol A is a precursor monomer for the production of many plastics and can
345 leach out from plastic materials. Thus, the low removal of bisphenol A (less than 20%)
346 could be an experimental artefact associated with its release from plastic components
347 (e.g. tubing) of the experimental system. Indeed, low bisphenol A removal by
348 anaerobic treatment has also been reported in several previous lab-scale studies
349 (Monsalvo et al., 2014; Wijekoon et al., 2015).

350 **[Figure 5]**

351 The removal of hydrophilic TrOCs ($\text{Log } D < 3.2$) by AnMBR was highly variable
352 (Fig. 5B). It has been established that the removal of hydrophilic TrOCs by either
353 aerobic or anaerobic MBR was dependent primarily on their intrinsic biodegradability
354 given their relatively weak adsorption onto sludge (Wijekoon et al., 2015). In this
355 study, some hydrophilic compounds could be effectively removed by AnMBR
356 regardless of the sulphur content in the influent. The removal of these compounds was
357 over 60% and they included aspartame, caffeine, sulfamethoxazole, trimethoprim,
358 PFOS, carazolol, verapamil, hydroxyzine, simazine, amitriptyline, omeprazole, and
359 linuron. Indeed, the effective removal of these hydrophilic TrOCs by AnMBR has
360 also been reported by Wijekoon et al. (2015) who attributed their high
361 biodegradability to the presence of electron donating functional groups, such as
362 hydroxyl and amine, in their structures. In addition, most of these hydrophilic
363 compounds had nitrogen in the molecular structure, which probably made them
364 amenable to anaerobic treatment (Wijekoon et al., 2015).

365 Several hydrophilic TrOCs were poorly removed by AnMBR (Fig. 5B). These
366 compounds were ketoprofen, paracetamol, meprobamate, ibuprofen, diltiazem, TCEP,
367 diclofenac, carbamazepine, germfibrozil, DEET, atrazine, diuron, and diazepam. The
368 low removal of these hydrophilic compounds could be ascribed to their poor
369 biodegradability due to the presence of electron withdrawing functional groups, such
370 as chloro and amide, irrespective of the presence of any electron donating functional
371 groups in their molecular structure (Monsalvo et al., 2014; Wijekoon et al., 2015).

372 Unlike hydrophobic TrOCs, sulphur addition to influent could significantly affect the
373 removal of hydrophilic TrOCs in AnMBR (Fig. 5B). These hydrophilic TrOCs could
374 be categorised into three groups based on their removal variations along with the
375 influent SO_4^{2-} addition from 0 to 600 mg/L. In the first group, the removal of two
376 hydrophilic compounds, namely caffeine and trimethoprim, continuously decreased as
377 the influent SO_4^{2-} concentration increased. The reason for the decreased removal of
378 these two compounds is not clear, but possibly due to the toxicity of H_2S to
379 microorganisms that were responsible for the removal of these two compounds. By
380 contrast, in the second group, SO_4^{2-} addition led to an increase in the removal of
381 propylparaben and linuron, which have relatively high hydrophobicity. At the mixed
382 liquor pH of 7, the $\text{Log } D$ values of propylparaben and linuron were 2.8 and 3.12,
383 respectively. Thus, the observed increase in their removal could be attributed to the

384 enhanced hydrophobic interaction between these two compounds and sludge with
385 SO_4^{2-} increase in the influent. Indeed, as discussed above, it has been reported that
386 high SO_4^{2-} concentration could increase the release of EPS and thus enhance the
387 hydrophobicity of anaerobic sludge (Kobayashi et al., 2015). Most hydrophilic TrOCs
388 belong to the third group, which showed an initial decrease and then increase in the
389 removal by AnMBR with continuous increase in the influent SO_4^{2-} concentration.
390 These TrOCs included ketoprofen, paracetamol, ibuprofen, carazolol, TCEP, dilantin,
391 simazine, diclofenac, carbamazepine, germfibrozil, DEET, atrazine, diuron, and
392 diazepam. The results could be attributed to microbial adaption to the SO_4^{2-} addition,
393 which therefore recovered the biodegradation of these hydrophilic compounds.

394 3.5.2 *TrOC adsorption on sludge*

395 A major factor governing TrOC adsorption onto biosolids during AnMBR operation
396 is their hydrophobicity. Although hydrophobic TrOCs with $\text{Log } D > 3.2$ could readily
397 absorb onto sludge particles, their residual in sludge phase was relatively low with a
398 few exceptions (Fig. 6A). The observed low residual concentrations of these
399 hydrophobic TrOCs in the sludge phase could be attributed to their high
400 biodegradation, which also determines TrOC residues in the biosolids (Wijekoon et al.,
401 2015). Of the 10 hydrophobic TrOCs, t-octylphenol exhibited the highest
402 accumulation in the sludge phase, followed by triclosan, triclocarban, and
403 nonylphenol, respectively. Triclosan and triclocarban are known to be persistent to
404 biodegradation due to the chloro functional group (which is a strong electron
405 withdrawing functional group) in their molecular structure. On the other hand, both t-
406 octylphenol and nonylphenol are degradation by-products of alkylphenols, which are
407 widely used in domestic detergents. It is noted that concentrations of all hydrophobic
408 TrOCs in the sludge phase were relatively stable regardless of sulphur addition to the
409 influent.

410 **[Figure 6]**

411 Of the 28 hydrophilic TrOCs, only four compounds accumulated considerably in
412 sludge phase with concentrations higher than 200 ng/g total solid (Fig. 6B). They
413 were carazolol, paracetamol, amitriptyline, and hydroxyzine. Of a particular note,
414 when the SO_4^{2-} concentration increased from 0 to 600 mg/L, the concentration of
415 paracetamol in sludge decreased significantly (Fig. 6B), probably due to the enhanced

416 biodegradation with the proliferation of sulphate reducing bacteria, thereby improving
417 its overall removal by AnMBR (Fig. 6B). On the other hand, the residual
418 concentrations of carazolol, amitriptyline, and hydroxyzine in the sludge phase
419 increased with SO_4^{2-} addition. This result could be attributed to the change of biomass
420 characteristics, for example, surface charge and hydrophobicity, caused by an
421 enhanced release of EPS with sulphur addition (Kobayashi et al., 2015).

422 **4 Conclusion**

423 There were no discernible effects on the biological activity and COD removal by
424 AnMBR despite an increase in the influent SO_4^{2-} concentration provided that
425 COD/ SO_4^{2-} ratio was above 10. However, increasing sulphur content resulted in some
426 variations in biogas production and a notable increase in the production of H_2S during
427 AnMBR operation. Sulphur addition did not significantly affect the removal of
428 hydrophobic TrOCs. By contrast, the removal of some hydrophilic TrOCs was
429 considerably affected by sulphur increase. In addition, the residual concentrations of
430 some hydrophilic TrOCs in biosolids were also impacted by sulphur addition.

431 **Supplementary data**

432 Supplementary data of this study can be found in the e-version of this paper online.

433 **Acknowledgement**

434 Xiaoye Song would like to thank the Chinese Scholarship Council and the University
435 of Wollongong for PhD scholarship support.

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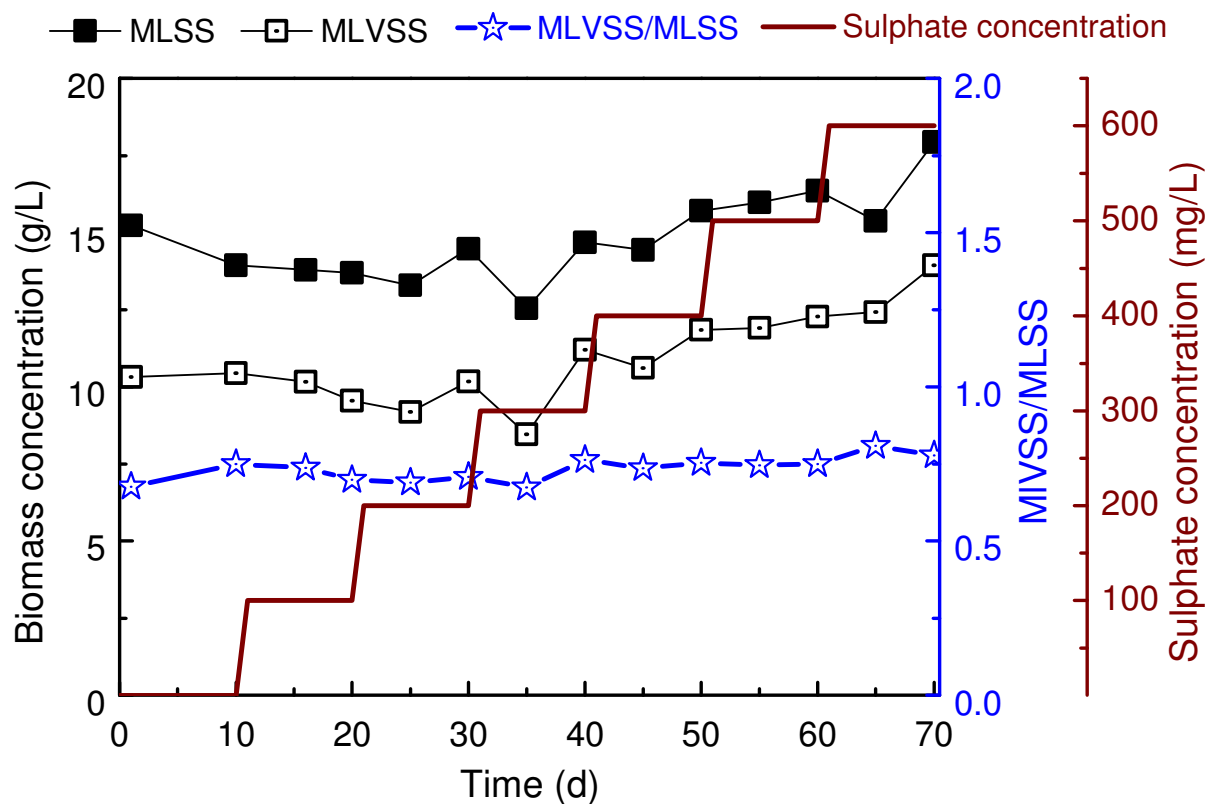
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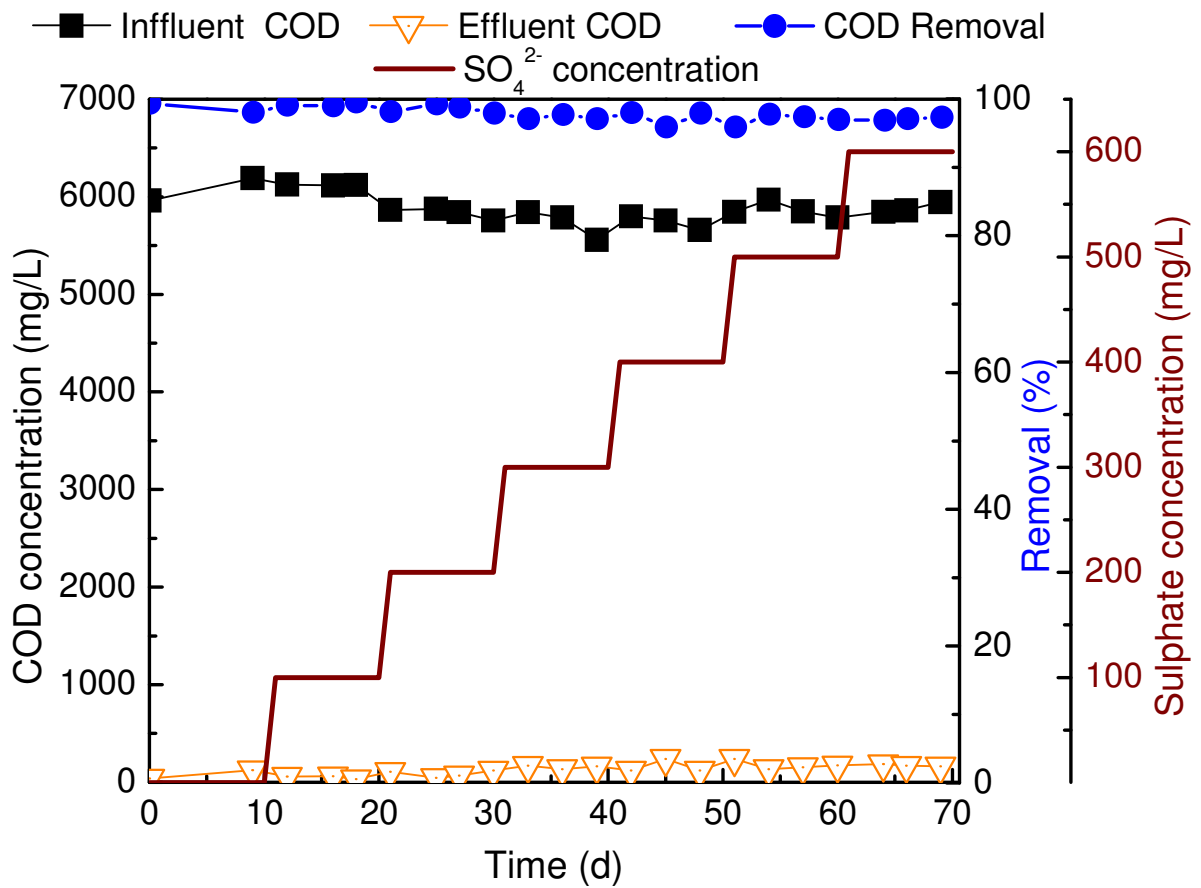
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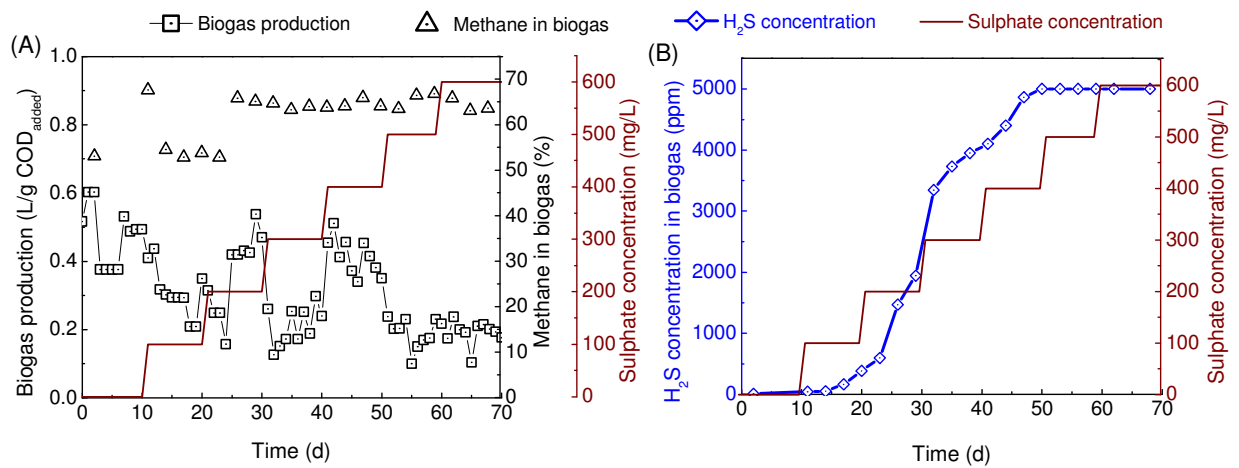
558

559 **Fig. 1:** Effect of sulphate addition on biomass concentration (i.e. MLSS and MLVSS contents)
 560 during AnMBR operation. Sulphate concentration in the synthetic wastewater was increased
 561 to 600 mg/L with an increment of 100 mg/L every 10 days. Experimental conditions: HRT =
 562 5 d; mixed liquor pH = 7 ± 0.1 ; temperature = 35 ± 1 °C.

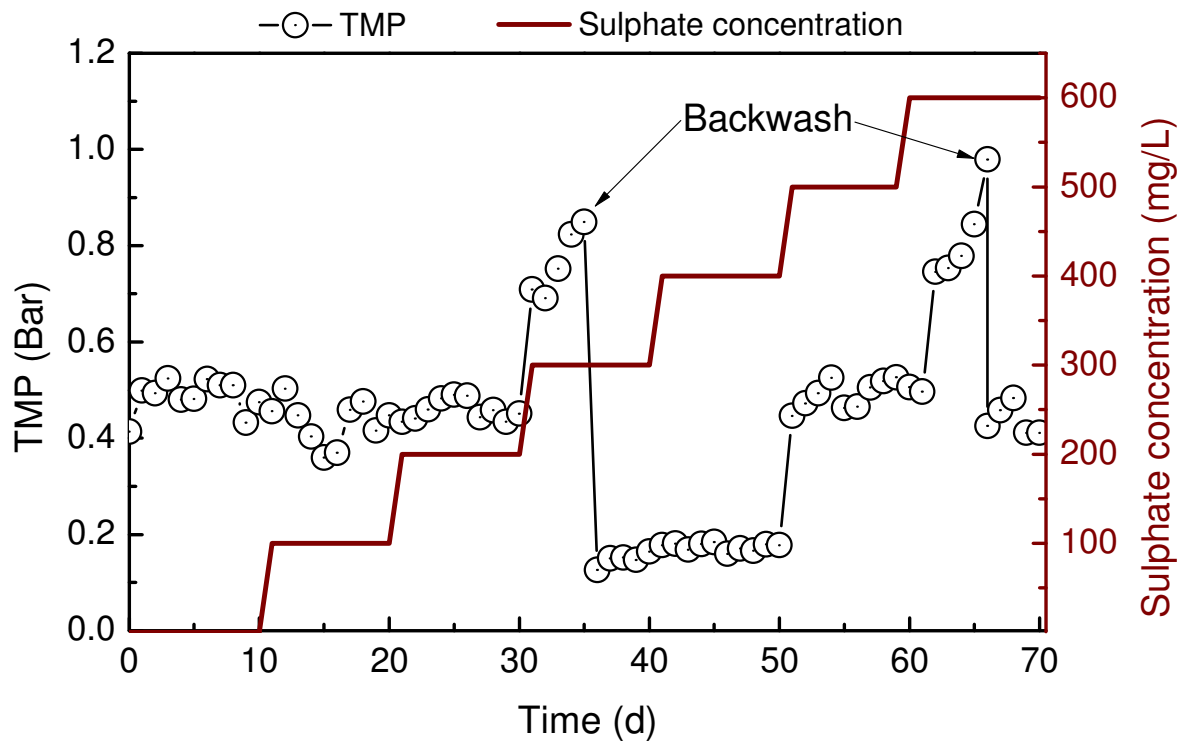


563

564 **Fig. 2:** Effect of sulphate concentration on COD removal by AnMBR. Sulphate concentration
 565 in the synthetic wastewater was increased to 600 mg/L with an increment of 100 mg/L every
 566 10 days. Experimental conditions are shown in Fig. 1.

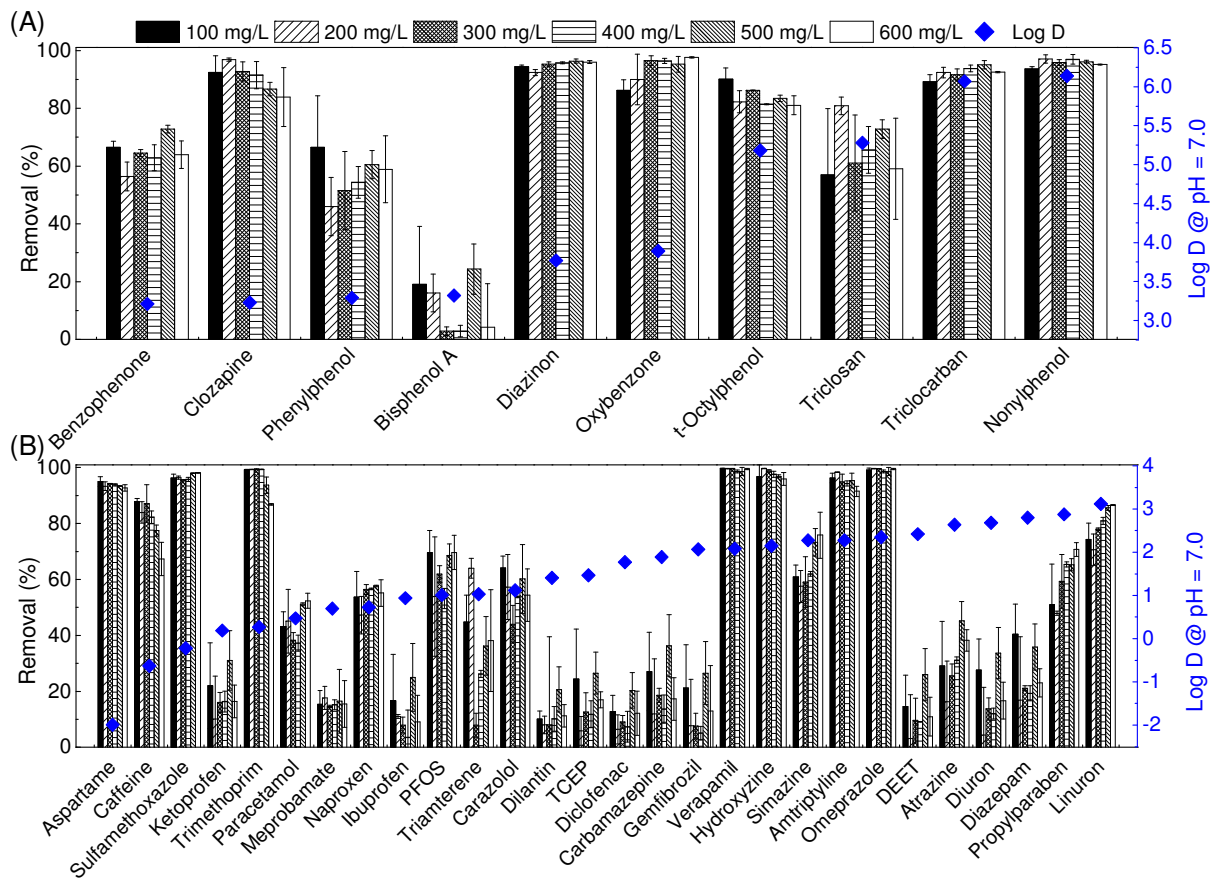


567
 568 **Fig. 3:** Effect of sulphate concentration on (A) biogas production and methane content, (B)
 569 H₂S concentration in biogas during AnMBR operation. Sulphate concentration in the
 570 synthetic wastewater was increased from 0 to 600 mg/L with an increment of 100 mg/L every
 571 10 days. Experimental conditions are as described in Fig. 1.



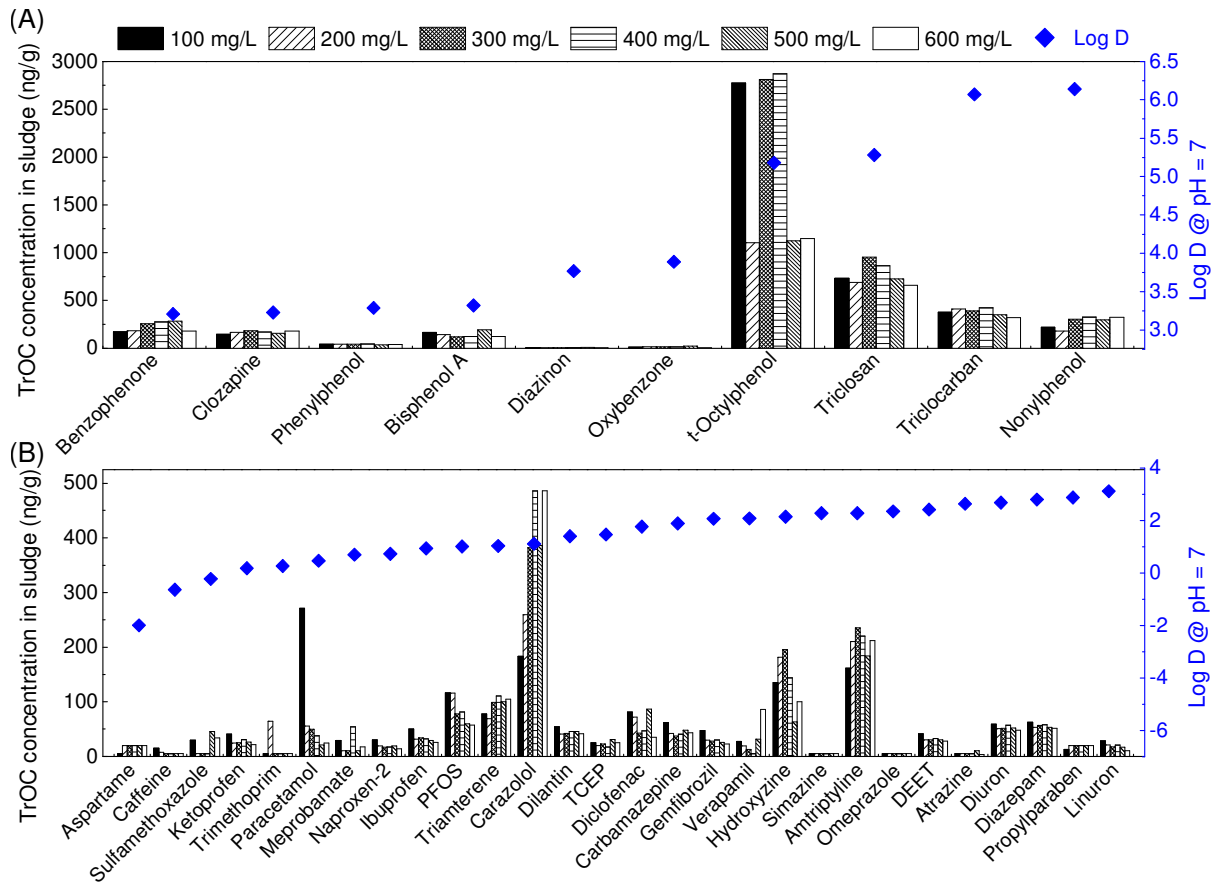
572

573 **Fig. 4:** Variation of the TMP profile during AnMBR operation. Membrane cleaning was
 574 conducted by backwashing using the AnMBR effluent. Experimental conditions are as
 575 described in Fig. 1.



576

577 **Fig. 5:** Effects of sulphate concentration on the removal of (A) hydrophobic (i.e. compounds
 578 with $\text{Log } D > 3.2$ at pH 7) and (B) hydrophilic (i.e. compounds with $\text{Log } D < 3.2$ at pH 7)
 579 TrOCs by AnMBR from the aqueous phase. Error bars represent the standard deviation from
 580 two measurements at each sulphate concentration (once every five days). Experimental
 581 conditions are given in Fig. 1.



582

583 **Fig. 6:** Effect of sulphate concentration on the residual of (A) hydrophobic and (B)
 584 hydrophilic TrOCs in the sludge phase during AnMBR operation. Experimental conditions
 585 are given in Fig. 1.

1 **Effects of sulphur on the performance of an anaerobic membrane**
2 **bioreactor: Biological stability, trace organic contaminant removal, and**
3 **membrane fouling**

4 Submitted to *Bioresource Technology*

5 November 2017

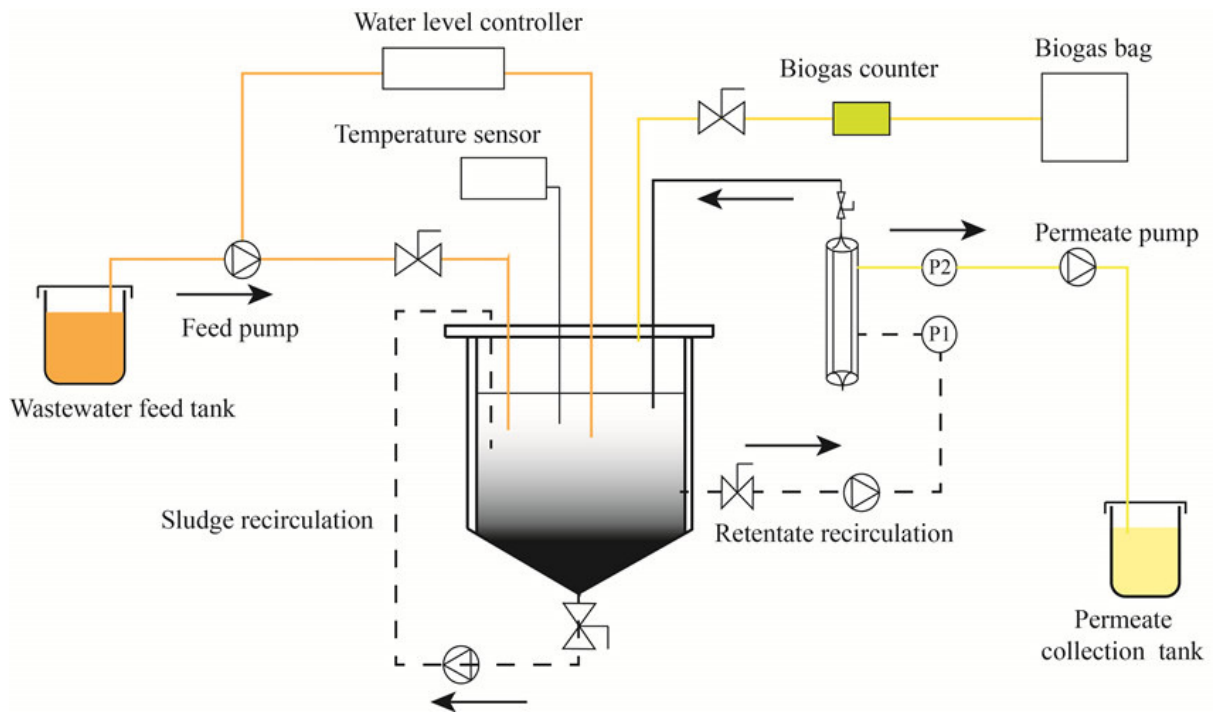
6 Xiaoye Song ^a, Wenhai Luo ^b, James McDonald ^c, Stuart J. Khan ^c, Faisal I. Hai ^a, Wenshan
7 Guo ^d, Hao H. Ngo ^d, Long D. Nghiem ^{a*}

8 **Supplementary data**

9

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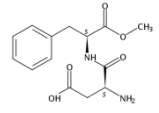
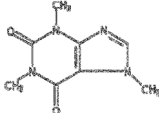
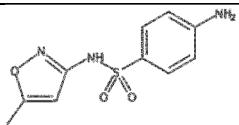
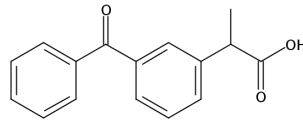
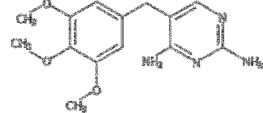
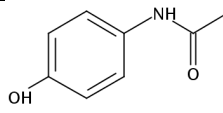
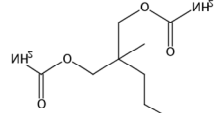
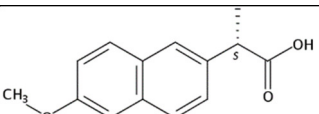
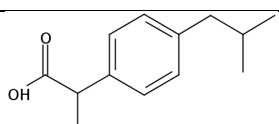
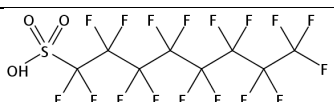
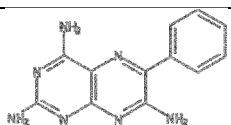
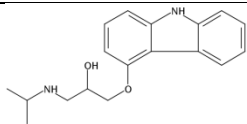
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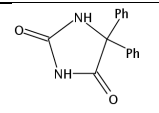
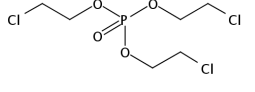
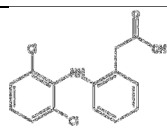
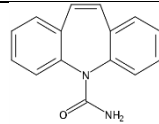
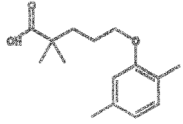
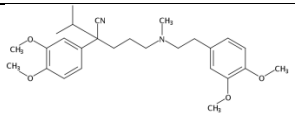
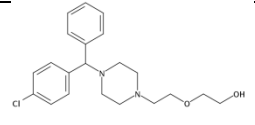
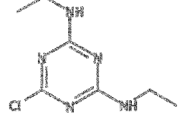
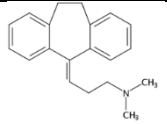
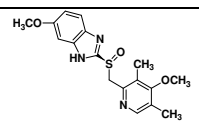
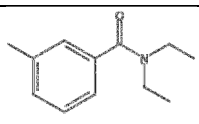
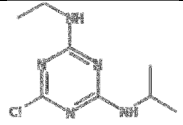
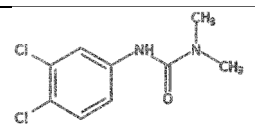
12 **Figure S1:** Schematic diagram of anaerobic membrane bioreactor (AnMBR)

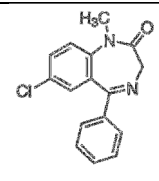
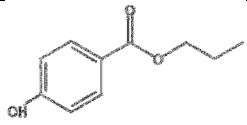
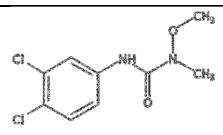
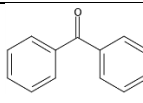
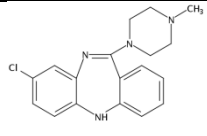
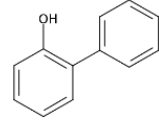
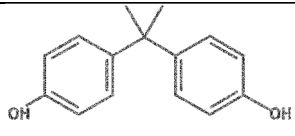
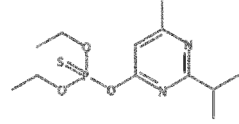
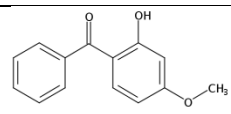
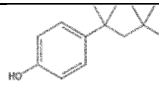
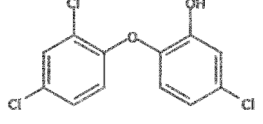
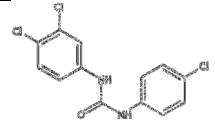
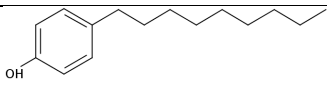
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15 **Table S1:** Physicochemical properties of the selected trace organic contaminants.

Compounds	Chemical formula	Log D at pH = 7	MW (g/mol)	Chemical structure
Aspartame	$C_{14} H_{18} N_2 O_5$	294.30	-1.99	
Caffeine	$C_8 H_{10} N_4 O_2$	194.19	-0.63	
Sulfamethoxazole	$C_{10} H_{11} N_3 O_3 S$	253.28	-0.22	
Ketoprofen	$C_{16} H_{14} O_3$	254.28	0.19	
Trimethoprim	$C_{14} H_{18} N_4 O_3$	290.32	0.27	
Paracetamol	$C_8 H_9 N O_2$	151.16	0.47	
Meprobamate	$C_9 H_{18} N_2 O_4$	218.25	0.70	
Naproxen	$C_{14} H_{14} O_3$	230.26	0.73	
Ibuprofen	$C_{13} H_{18} O_2$	206.28	0.94	
PFOS	$C_8 H F_{17} O_3 S$	500.13	1.01	
Triamterene	$C_{12} H_{11} N_7$	253.26	1.03	
Carazolol	$C_{18} H_{22} N_2 O_2$	298.38	1.12	

Dilantin	$C_{15} H_{12} N_2 O_2$	252.27	1.41	
TCEP	$C_6 H_{12} Cl_3 O_4 P$	285.49	1.47	
Diclofenac	$C_{14} H_{11} Cl_2 N O_2$	296.15	1.77	
Carbamazepine	$C_{15} H_{12} N_2 O$	236.27	1.89	
Gemfibrozil	$C_{15} H_{22} O_3$	250.33	2.07	
Verapamil	$C_{27} H_{38} N_2 O_4$	454.60	2.08	
Hydroxyzine	$C_{21} H_{27} Cl N_2 O_2$	374.90	2.15	
Simazine	$C_7 H_{12} Cl N_5$	201.66	2.28	
Amitriptyline	$C_{20} H_{23} N$	277.403	2.28	
Omeprazole	$C_{17} H_{19} N_3 O_3 S$	345.42	2.35	
DEET	$C_{12} H_{17} N O$	191.27	2.42	
Atrazine	$C_8 H_{14} Cl N_5$	215.68	2.64	
Diuron	$C_9 H_{10} Cl_2 N_2 O$	233.09	2.68	

Diazepam	$C_{16} H_{13} Cl N_2 O$	284.74	2.80	
Propylparaben	$C_{10} H_{12} O_3$	180.20	2.88	
Linuron	$C_9 H_{10} Cl_2 N_2 O_2$	249.09	3.12	
Benzophenone	$C_{13} H_{10} O$	182.22	3.21	
Clozapine	$C_{18} H_{19} Cl N_4$	326.82	3.23	
Phenylphenol	$C_{12} H_{10} O$	170.21	3.29	
Bisphenol A	$C_{15} H_{16} O_2$	228.29	3.64	
Diazinon	$C_{12} H_{21} N_2 O_3 P S$	304.35	3.77	
Oxybenzone	$C_{14} H_{12} O_3$	228.24	3.89	
t-Octylphenol	$C_{14} H_{22} O$	206.32	5.18	
Triclosan	$C_{12} H_7 Cl_3 O_2$	289.54	5.28	
Triclocarban	$C_{13} H_9 Cl_3 N_2 O$	315.58	6.07	
Nonylphenol	$C_{15} H_{24} O$	220.35	6.14	

16 Source: SciFinder Scholar (ACS) database.