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Simultaneous activated carbon adsorption within a membrane bioreactor for an enhanced micropollutant removal

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1 **Simultaneous activated carbon adsorption within a membrane bioreactor for**
2 **an enhanced micropollutant removal**

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10 **Abstract:** Significant adsorption of sulfamethoxazole and carbamazepine to powdered activated
11 carbon (PAC) was confirmed by a series of adsorption tests. In contrast, adsorption of these
12 micropollutants to the sludge was negligible. The removal of these compounds in membrane
13 bioreactor (MBR) was dependent on their hydrophobicity and loading as well as the PAC
14 dosage. Sulfamethoxazole exhibited better removal rate during operation under no or low (0.1
15 g/L) PAC dosage. When the PAC concentration in MBR was raised to 1.0 g/L, a sustainable and
16 significantly improved performance in the removal of both compounds was observed—the
17 removal efficiencies of sulfamethoxazole and carbamazepine increased to 82 ± 11 and $92\pm 15\%$
18 from the levels of $64\pm 7\%$, and negligible removal, respectively. The higher removal efficiency of
19 carbamazepine at high (1.0 g/L) PAC dosage could be attributed to the fact that carbamazepine is
20 relatively more hydrophobic than sulfmethoxazole, which subsequently resulted in its higher
21 adsorption affinity toward PAC.

22 **Keywords:** adsorption, biodegradation, membrane bioreactor, micropollutant, powdered
23 activated carbon.

26 **1. Introduction**

27 The widespread occurrence of micropollutants in raw sewage, secondary treated effluent and
28 sewage impacted water bodies as well as the associated environmental health concerns present
29 an underlying challenge for the implementation of water recycling. Owing to several advantages
30 including excellent effluent quality, low sludge production, small foot print, and flexibility in
31 future expansion, membrane bioreactor (MBR) has been widely recognized as the next
32 generation of wastewater treatment processes (Judd, 2008). Consequently, considerable
33 dedicated research efforts have been devoted to the assessment of micropollutant removal using
34 MBR (Clara et al., 2005; Kimura et al., 2005; Nghiem et al., 2009; Radjenovic et al., 2009;
35 Visvanathan et al., 2005). Adsorption and subsequent biodegradation of the micropollutants are
36 the dominant removal processes, and are influenced by operational conditions such as hydraulic
37 retention time (HRT), sludge retention time (SRT), biomass concentration, temperature and pH
38 (Cirja et al., 2008). This results in a rather variable and uncertain removal performance. Previous
39 studies have indicated significant variation in the removal of micropollutants by MBRs, ranging
40 from near complete removal for some compounds (e.g. ibuprofen and bezafibrate) to almost no
41 removal for several others (e.g. carbamazepine and diclofenac) (Clara et al., 2005; Kim et al.,
42 2007; Kimura et al., 2005; Nghiem et al., 2009).

43 Hydrophobic compounds can be removed from the influent via adsorption to the sludge particles
44 present in the system. Therefore, when the SRT in the wastewater treatment system is
45 sufficiently high (at least 8 d) the removal of organic compounds through adsorption and
46 subsequent biodegradation can be enhanced (Cirja et al., 2008). Compounds containing complex
47 structure and toxic groups (such as halogens and nitro group), however, can show higher
48 resistance to biodegradation and tend to have very low removal (Kimura et al., 2005). Because
49 the adsorption of micropollutants onto sludge facilitates their removal in the biological
50 processes, it is envisaged that addition of adsorbents such as powdered activated carbon (PAC)
51 directly into the MBR can lead to significant retention of soluble micropollutants. Due to the
52 complete retention of sludge by the membrane and application of longer SRT, the retained
53 micropollutants may be efficiently removed in an MBR to which PAC has been added.

54 The PAC-amended MBR to date has been mainly studied in relation to membrane fouling
55 mitigation (Guo et al., 2008) and rarely to assess recalcitrant pollutant removal enhancement
56 (Hai et al., 2008). Only one study (Zhang et al., 2008) to date have explored PAC-amended
57 MBR specifically for the removal of micropollutants. Although Zhang et al., (2008) confirmed
58 improved removal efficiency, a comprehensive understanding of the involved phenomena is yet
59 to be developed.

60 This study aimed to investigate the long-term removal performance of two chemically different
61 pharmaceutically active compounds namely sulfamethoxazole and carbamazepine in a PAC-
62 amended MBR system. In order to explain the performance of the MBR, the adsorption
63 capacities of PAC and MBR sludge were compared in batch tests. The effects of compound
64 structure and its capacity to adsorb onto PAC on their removal efficiencies were discussed.
65 Special focus was given to the effects of micropollutant loading rate, PAC concentration in MBR
66 and the role of membrane filtration on the overall removal of the two selected micropollutants.
67 This study provides unique insights into the strategies to enhance micropollutant removal.

68 **2. Materials and methods**

69 **2.1 Model micropollutants and synthetic wastewater**

70 Two micropollutants, namely sulfamethoxazole (SMX) and carbamazepine (CBZ), were selected
71 in this study on the basis of their widespread occurrence in domestic sewage. These compounds
72 have similar molecular weights; however, their dissociation constants and effective
73 hydrophobicity (log D) differ markedly (Table 1). SMX is a sulfonamide antibiotic with very
74 low hydrophobicity. CBZ, which is an anti-epileptic drug, is composed of two benzene rings
75 fused to an azepine group, which in turn is connected to an amide group. The selected
76 micropollutants were of analytical grade and were purchased from Sigma-Aldrich (Saint Louis,
77 MO, USA). Stock solution was prepared at a concentration of 1 g/L in pure methanol, stored in
78 refrigerator and was used within less than a month.

79 A previously reported (Zhang et al., 2006) synthetic wastewater was used in this study to
80 simulate high strength municipal wastewater and to accelerate sludge build-up in the reactor. The
81 concentrated synthetic wastewater was prepared and stored in a refrigerator at 4°C. It was then
82 diluted with distilled water on a daily basis to make up a feed solution containing glucose (800

83 mg/L), peptone (150 mg/L), KH_2PO_4 (35 mg/L), MgSO_4 (35 mg/L), FeSO_4 (20 mg/L), and
84 sodium acetate (450 mg/L). All the chemicals were of analytical grade and were obtained from
85 Chemsupply, SA, Australia. Although the studied micropollutants can be found in municipal
86 wastewater in the range from a few ng/L to tens of $\mu\text{g/L}$, a rather high micropollutant loading
87 was applied in this study in order to confirm the capacity of the proposed PAC amended MBR.
88 Each of the micropollutants was continuously introduced to the feed solution at a concentration
89 of 750 $\mu\text{g/L}$. The feed solution was kept in a stainless steel reservoir at room temperature
90 ($22\pm 2^\circ\text{C}$).

91 **2. 2 Design and operating conditions of the MBR**

92 A laboratory scale MBR set-up consisting of a glass reactor with active volume of 14 L, two air
93 pumps, a pressure sensor, and influent and effluent pumps was used in this study. One Sterapore
94 SADFTM (SADF0790M mini module) submerged PVDF hollow fiber membrane module
95 supplied by Mitsubishi Rayon Engineering, Japan was used in this set-up. The membrane has a
96 nominal pore size of 0.4 μm , with a total effective membrane surface area of 0.074 m^2 .
97 Transmembrane pressure was continuously monitored using a high resolution (± 0.1 kPa)
98 pressure sensor (Vacuum meter 840064, Cole-Parmer Instrument Co., Australia) which was
99 connected to a personal computer for data recording. The personal computer was also used to
100 control the permeate peristaltic pump to operate the membrane under a selected average flux of
101 0.19 $\text{m}^3/(\text{m}^2\cdot\text{d})$ on a 5 minutes on/off cycle. Flow rate of the influent pump was matched with
102 that of the permeate pump to maintain a constant reactor volume. The reactor was seeded with
103 activated sludge from a laboratory scale MBR operated long term for treatment of a broad
104 spectrum of micropollutants (Tadkaew et al., 2010). The hydraulic retention time was set at 24
105 hours. Performance of the MBR setup with regard to basic water quality parameters was first
106 monitored for about 2 months and then the specific investigations of the current study were
107 initiated under a mixed liquor suspended solids (MLSS) concentration of approximately 11 g/L.
108 Except for MLSS sampling, no sludge was extracted from the reactor. PAC (PS1000, Activated
109 carbon technologies Pty Ltd, Victoria, Australia) was added into the MBR on day 32 and day 64
110 of continuous operation to obtain a PAC concentration of 0.1 and 1.0 g/L, respectively in the
111 MBR. According to the manufacturer, the iodine number and D50 value of the PS1000 were
112 1160 and 22.3 μm , respectively. The specific surface area of this PAC was at least 1000 m^2/g .

113 The set-up was housed in an air-conditioned room to maintain the temperature within a range of
114 22 ± 2 °C. The mixed liquor pH could be maintained at 7.8 ± 0.1 .

115 **2.3 Batch adsorption test**

116 PAC was added in amounts ranging from 10 to 30 mg in glass beakers containing 150 mL
117 solutions of each micropollutant separately. The test solutions were then incubated for 24 hours
118 under 25°C and 150 rpm in a temperature controlled rotary shaker (BL 4500, Bioline, Edward
119 Instrument Company, NSW, Australia). Because of the high adsorption capacity of PAC, a
120 rather high initial concentration of 30 mg/L of the micropollutants in the test solutions was
121 applied. This confirmed the inclusion of the MBR influent micropollutant concentration (750
122 µg/L) within the range of equilibrium concentrations obtained during the batch adsorption test.
123 Batch adsorption test with sludge was performed with sludge collected from MBR on day 25. In
124 order to exclude biodegradation, the sludge was first autoclaved (SA-252, Bio-Clean, Medical
125 Industries, Pty, NSW, Australia) at 121°C and 1.2 kg/cm². The autoclaved mixed liquor was then
126 repeatedly centrifuged (Allegra X-12R, Beckman Coulter, USA) at 3270 G and washed with
127 Milli-Q water to minimize the amount of residual micropollutant. Then 80-480 mg sludge (dry
128 weight) samples were incubated with micropollutant solutions in the same manner as described
129 above.

130 **2.4 Analytical methods**

131 A Shimadzu HPLC system (Shimadzu, Kyoto, Japan) equipped with a Supelco Drug Discovery
132 C-18 column (with diameter, length and pore size of 4.6 mm, 150 mm, and 5µm, respectively)
133 and a UV-Vis detector was used to measure the concentrations of the trace organic contaminants
134 in the feed and permeate. The detection wavelength was set at 280 nm. The mobile phase used
135 for gradient elution was MilliQ grade deionized water buffered with 25 mM KH₂PO₄ and
136 acetonitrile, which was delivered at 1 mL/min through the column. A sample injection volume of
137 50 µL was used. Total organic carbon (TOC) and total nitrogen (TN) were analyzed using a
138 Shimadzu TOC/TN-V_{CSH} analyzer (Japan). TOC analysis was conducted in non-purgeable
139 organic carbon (NPOC) mode. Samples were kept at 4°C until analyzed and calibrations were
140 performed in the range between 0 and 1000 mg/L and 0 to 100 mg/L for TOC and TN,
141 respectively. MLSS concentration in the reactor was measured in accordance to the Standard
142 Methods for the Examination of Water and Wastewater (Clescerl *et al.*, 2005). Removal

143 efficiency was calculated as $R = 100 \times \left(1 - \frac{C_{Eff}}{C_{Inf}} \right)$, where C_{Eff} and C_{Inf} are effluent (or permeate)
144 and influent concentrations ($\mu\text{g/L}$), respectively. It is noteworthy that the term removal here does
145 not necessarily indicate complete mineralization of the trace organics to carbon dioxide and
146 water. A spectrophotometer (UV 1700, Shimadzu, Japan) was used to measure the diminution of
147 UV absorbance after MBR treatment.

148 **3. Results and discussion**

149 **3.1 Micropollutant adsorption capacity of MBR sludge and PAC**

150 The batch adsorption test data for PAC fitted both the Langmuir and Freundlich isotherms very
151 well (Table 2). The partitioning coefficients (K) estimated from the Freundlich isotherm
152 indicated slightly higher adsorption of CBZ onto PAC in comparison to SMX, while the
153 maximum adsorption capacities (q_m) estimated from the Langmuir isotherm were almost the
154 same (approximately 280 mg/gm) for the two compounds. The reported data is consistent with
155 the reported high adsorption capacity of different micropollutants onto PAC (Kyriakopoulos and
156 Doulia, 2006; Nowotny et al., 2007). The adsorption data is particularly in good agreement with
157 the CBZ adsorption capacity onto PAC reported by Zhang et al. (Zhang et al., 2008). No
158 information about SMX adsorption on PAC could be found in the literature for comparison.
159 Nevertheless, more relevant to our study was the fact that the batch test data confirmed our
160 expectation of enhanced adsorption of the micropollutants onto PAC.

161 The test data regarding adsorption of SMX and CBZ onto MBR sludge fitted poorly to the
162 adsorption isotherms. Accordingly, instead of the isotherm parameters, the maximum unit
163 adsorption values (approximately 0.017 and 0.020 mg/g for SMX and CBZ, respectively)
164 observed during the experiment are reported for comparison purposes (Table 2). The observed
165 negligible adsorption of SMX and CBZ onto sludge is in line with the literature reports
166 (Abegglen et al., 2009; Tadkaew et al., 2010).

167 **3.2 Basic performance of the MBR**

168 In order to confirm that the micropollutants removal efficiencies used in analyses were obtained
169 under stable biological activity in the MBR the basic water quality parameters and the key
170 operational parameters were periodically monitored. The average values of the different basic

171 parameters during the MBR operation are shown in Table 3. For the most part of the operation
172 the TOC removal remained around 97%. However, two periods, when the TOC removal
173 deviated from the original level, can be noticed in Figure 1a. Relatively lower TOC removal
174 during day 21-30 and 46-53 can be attributed to the malfunctioning of the air conditioning
175 system around at the same time which caused the temperature of the reactor during that period to
176 frequently fall below 15°C. Previous studies have demonstrated the effect of low temperature on
177 TOC and especially on TN removal in MBR (Chiemchaisri and Yamamoto, 1994; Chu et al.,
178 2005). Although a significant drop in TOC removal may not be encountered up to a temperature
179 of 10°C, the level of TOC variation observed in our experiment can be explained by the low
180 temperature effect.

181 The TN removal rate, on the other hand, remained stable over the whole period with an average
182 value of 96±5%. In the absence of an anoxic compartment, the denitrification capacity of the
183 MBR system used in this study was limited. However, the synthetic wastewater in use had a
184 significantly high carbon to nitrogen ratio (~20), therefore, the high TN removal observed here
185 could possibly be attributed to the conversion of dissolved organic nitrogen to biomass, which
186 would then be retained by the membrane. This appears to be also the reason why TN removal
187 was less influenced by the accidental temperature drop in the reactor.

188 Only slightly improved removal rates of both TOC and TN were observed following the higher
189 dose PAC addition on day 64 (Figure 1a). The micropollutants contributed a negligible portion
190 of the TOC and TN (few µg/L in contrast to combined TOC and TN of 500 and 25 mg/L,
191 respectively) and, hence, the variations of SMX and CBZ removal were not reflected in the TOC
192 and TN profiles.

193 It is noteworthy that the continuous high dosing of micropollutants to the feed water for extended
194 period did not result in any abnormal variation in TOC/TN removal, MLSS concentration,
195 turbidity (Table 3) or hydraulic performance of the membrane (data not shown). The UV
196 absorbance of permeate in fact decreased many folds after PAC addition in the MBR. Delgado et
197 al. (2010) suggested that the inhibitory effect of pharmaceutical compounds can be off-set by a
198 high biomass over substrate ratio typical of MBR, and hence no discernible effect on basic water
199 quality parameters would be observed.

200 **3.3 Micropollutant removal before PAC addition**

201 The removal rate of CBZ remained very low for the entire period of operation without PAC
202 (Figure 1). No significant removal of CBZ was observed during the first week of the experiment.
203 The poor biodegradation rate of CBZ during MBR treatment has also been widely reported in the
204 literature. To date both laboratory and pilot scale MBR plant studies have reported negligible
205 (Abegglen et al., 2009; Kim et al., 2007; Radjenovic et al., 2009) to moderate (Bernhard et al.,
206 2006; Kreuzinger et al., 2004; Tadkaew et al., 2010) removal of CBZ, usually less than 10%.
207 The highest removal (around 30%) in conventional MBR to date has been reported by Urase et
208 al. (2005) under acidic pH. The very low removal rate of CBZ observed in this study without
209 PAC addition is, hence, not surprising. The removal rate occasionally rose up to 10% in the
210 following days, presumably due to the progressive conditioning of the sludge. However, towards
211 the end of the first period of accidental low temperature in the MBR (day 21-30), as mentioned
212 before, the removal rate plummeted to almost zero again. Although it is difficult to pinpoint an
213 appropriate temperature range, it is generally accepted in the literature that lower temperature
214 operation (especially under 15°C) can cause deteriorated micropollutant removal rate. For
215 instance, Carballa et al. (2005) previously reported better removal of certain pharmaceuticals
216 under 25°C than in 12°C. It is interesting, however, to note that in this study the deterioration of
217 micropollutant removal started one week or so later than the onset of the TOC removal
218 deterioration.

219 In case of SMX, the MBR exhibited removal rates within the range of 64±7% for the first 28
220 days of operation without PAC (Figure 1). After that the removal rate dropped to approximately
221 half of the initial rate due to the adverse effect of accidental low temperature in the MBR. SMX
222 removal rates in the range between 50 – 92 % have been reported in the literature (Clara et al.,
223 2005; Radjenovic et al., 2009; Tadkaew et al., 2010). Results reported here indicate that SMX is
224 more readily biodegradable than CBZ. Accordingly it is particularly important to implement a
225 strategy to enhance the removal efficiency of CBZ during wastewater treatment.

226 **3.4 Effect of PAC addition on micropollutant removal**

227 **3.4.1 Removal under low PAC dosage**

228 The first dose of PAC (0.1 g/L) was added into the MBR on day 32 immediately after the return
229 of the reactor temperature to the expected value ($22\pm 2^\circ\text{C}$) following the first incidence of air
230 conditioning system malfunctioning. As noted from the TOC removal profile (Figure 1a) the
231 biological activity had not yet been reinstated to the original level when the PAC was added.
232 Nevertheless the CBZ removal rate instantaneously leaped up from the no removal stage to 87%
233 following the addition of PAC. A 25% jump in the removal of SMX also occurred. Higher
234 instantaneous jump in the CBZ removal rate suggests greater adsorption of CBZ onto PAC. PAC
235 can adsorb a wide spectrum of organics and inorganics (Hai et al., 2007; Kyriakopoulos and
236 Doulia, 2006). Although in our study the single solute adsorption isotherms derived using Milli-
237 Q water estimated somewhat similar adsorption of the two studied micropollutants onto PAC,
238 under the complex wastewater matrix preferential adsorption of CBZ can be explained by its
239 relatively higher hydrophobicity or log D value (Table 1).

240 The removal rates, however, gradually returned to the lower values that were maintained
241 immediately before the PAC addition. This indicated that the applied PAC dosage was not
242 adequate to provide long enough a retention of the micropollutants for the microbes to complete
243 their biodegradation. The theoretical adsorption capacity of the 0.1 g/L PAC based on the
244 adsorption isotherm (section 3.1) exceeds the micropollutant loading. However, Zhang et al.
245 (2008) estimated that under the competition with other organics in the synthetic wastewater only
246 30% of the added PAC into MBR was effectively utilized for CBZ adsorption. It was therefore
247 deemed imperative that a higher PAC dosage would be required to sustain the high
248 micropollutant loading as used in this study. Notably the SMX removal, but not the CBZ
249 removal, started to improve again on day 41, presumably due to the recovery of the biological
250 activity. The delay in CBZ removal rate recovery can be explained by the widely reported (Clara
251 et al., 2005; Kim et al., 2007; Radjenovic et al., 2009) relatively recalcitrant nature of CBZ.

252 As expected, compared to the level maintained up to day 31 (before addition of PAC) the CBZ
253 and SMX concentrations in permeate decreased significantly following lowering their respective
254 concentrations in the feed to 100 $\mu\text{g/L}$ on day 48. For the next two weeks or so the SMX
255 concentration in permeate remained in the range of $18\pm 10 \mu\text{g/L}$. However, the permeate CBZ
256 concentration very often exceeded the 100 $\mu\text{g/L}$ mark during this period and, hence, negative
257 removal rates of CBZ were calculated based on the feed concentration. This may be explained by

258 the fact that the second incidence of accidental temperature drop in the MBR unfortunately
259 coincided with this event of lowering the feed micropollutant concentrations; and CBZ, due to
260 the relative recalcitrance, was more affected by the reduced biological performance. Although
261 the unplanned incidence of temperature drop in MBR restricts accurate quantification of the
262 effect of lower feed concentration on removal rates, it does, on the other hand, manifest the
263 higher sensitivity of CBZ to change of key operating conditions under no or low dose of PAC.

264 **3.4.2 Removal under higher PAC dosage**

265 The beneficial effect of PAC addition, especially in case of CBZ, could be assessed fully after
266 raising the PAC concentration in the MBR to 1.0 g/L on day 64. After increasing the PAC
267 dosage, the CBZ concentrations in permeate dropped to below 20 µg/L in the following 10 days.
268 Slightly lower permeate concentrations of SMX were also observed during this time.

269 The permeate quality deteriorated to some extent when the feed micropollutant concentrations
270 were returned to 750 µg/L on day 72. For the rest of the observation period (3 weeks) the SMX
271 concentration in permeate was in the range of 127±80 µg/L (83±11% removal), which, when
272 compared to the level before PAC addition (280±55 µg/L, 64±7% removal), suggests moderate
273 improvement in removal performance. The CBZ concentration in permeate, on the other hand,
274 remained within the 80±55 µg/L (92±15% removal) range for the same period. This suggests a
275 significant improvement of the permeate quality in terms of CBZ concentration when compared
276 to the concentration observed before PAC addition (660±87 µg/L). Taking into account the
277 micropollutant loading rate of 0.75 mg/(L.d) the level of removal achieved in our study by far
278 exceeds that reported before.

279 **3.5 Additional removal by the MF membrane**

280 Microfiltration membranes as used in this study cannot retain the two selected micropollutants
281 because of their very large pore size in comparison to the dimensions of these compounds.
282 However, in the filtration of mixed liquor of activated sludge, additional removal by membranes
283 may be expected due to the additional barrier provided by the particle deposition on the
284 membrane surface (Urase et al., 2005). This additional effect is uncertain for hydrophilic
285 compounds in conventional MBR (Reemtsma et al., 2002). Hai et al. (2008) reported significant
286 additional removal of a polar dye by membrane in a PAC-amended MBR. Figure 2 shows the

287 average concentrations of CBZ and SMX in the reactor supernatant and also the ratios of
288 permeate to supernatant concentrations for the two compounds during operation with and
289 without PAC. It is evident that after the PAC addition the membrane achieved significant
290 additional removal of both the micropollutants, especially of CBZ. Nevertheless it should be
291 noted that although sorption on to membrane cake layer may have increased the retention time of
292 the micropollutants to some extent, without subsequent biodegradation long term and stable
293 removal as seen in our study would not be possible.

294 **3.6 Effects of feed micropollutant concentration and PAC dosage**

295 Table 4 shows the CBZ and SMX concentrations in permeate under different combinations of
296 feed micropollutant concentration and PAC dose. In order to have stable removal the
297 biodegradation rate needs to at least match the influent micropollutant loading which is in excess
298 of the adsorption capacity of the PAC. The overall removal then would depend, among others, on
299 the biodegradation rate and the amount of PAC dosing. For a certain feed concentration (750
300 $\mu\text{g/L}$) marked improvement in CBZ removal under a higher PAC dosage (1.0 g/L) is in line with
301 the observation reported by Zhang et al. (2008).

302 It is interesting to note from Table 4 that the concentration of SMX in the permeate was
303 relatively lower than that of CBZ during all the runs except the last one with higher dosage of
304 PAC (1.0 g/L) and higher feed concentration (750 $\mu\text{g/L}$). The much better removal of SMX over
305 CBZ before PAC addition is, as explained earlier, due to the higher biodegradability of SMX.
306 Under lower PAC dosage the SMX removal was better as due to insufficient adsorption sites the
307 biodegradation rate still predominantly governed the total removal. However, the mode of
308 degradation changes when sufficient PAC is present. In that case, co-adsorption of degrading
309 enzyme and pollutant onto PAC, and subsequent degradation of pollutant occurs on PAC surface
310 (Hai et al., 2008). Our results suggest that in such a case, compounds adsorbing more onto PAC
311 are more likely to have better removal. Under the higher PAC dosage when the influent
312 micropollutant concentrations were 100 $\mu\text{g/L}$ each, SMX was still better removed, presumably as
313 there were still enough adsorption sites for SMX to occupy. However, as the concentration of
314 both SMX and CBZ in feed was raised to 750 $\mu\text{g/L}$, CBZ occupied more adsorption sites
315 (competitive adsorption) and was better removed, even though it possesses a more recalcitrant

316 structure. The competitive adsorption of CBZ over SMX is also manifested by the lower and
317 more stable concentration of CBZ in the supernatant (Figure 2).

318 **4. Conclusion**

319 Improved removal of sulfamethoxazole and carbamazepine by a PAC-amended MBR system
320 was demonstrated. The removal of these compounds was dependent on their hydrophobicity and
321 loading as well as the PAC dosage. $64\pm 7\%$ removal of sulfamethoxazole, which has been
322 reported as more biodegradable of the two micropollutants, was registered in contrast to
323 negligible removal of carbamazepine under no or low (0.1 g/L) PAC concentration. A
324 sustainable and significantly improved performance in the removal of both compounds was
325 observed, when a high dosage of 1.0 g/L of PAC was utilised. The removal efficiencies of
326 sulfamethoxazole and carbamazepine increased to 82 ± 11 and $92\pm 15\%$, respectively.

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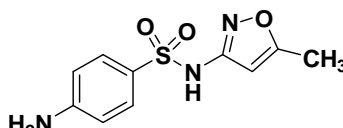
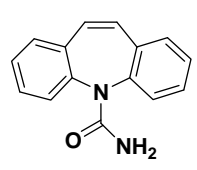
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398 LIST OF TABLES

399 **Table 1:** Chemical properties of the selected micropollutants.

Micropollutant	Sulfamethoxazole (SMX)	Carbamazepine (CBZ)
Structure		
Molecular weight (g/mol)	253.3	236.3
Log <i>D</i> (at pH8)	0.9	2.67
Solubility (g/L) at 25 °C and pH 8	16	0.22
Dissociation constant (pK_a)	1.39 & 5.81	-0.49 & 13.94

400

401 **Table 2:** PAC adsorption isotherm (at 25°C) constants for sulfamethoxazole (SMX) and carbamazepine
 402 (CBZ).

Freundlich isotherm constants				Langmuir isotherm constants		
	K	1/n	R ²	q _m [mg/g]	K ₁	R ²
	[(mg/g)/ (mg/L) ^{1/n}]					
SMX	166	0.26	0.94	282	1.44	0.97
CBZ	225	0.17	0.87	287	7.70	0.94

Freundlich isotherm: $q_e = KC_e^{1/n}$; Langmuir isotherm: $1/q_e = (1/q_m K_1)(1/C_e) + 1/q_m$;

q_e =equilibrium mass of compound sorbed on unit mass of adsorbent, C_e =equilibrium concentration of compound in liquid, q_m =maximum adsorption capacity, K = partitioning coefficient. **Note:** Batch test data with MBR sludge fitted neither of the isotherms; however considering single data points, a maximum adsorption of 0.017 and 0.020 mg/g were estimated for SMX and CBZ, respectively.

403

404 **Table 3:** Basic biological performance of the MBR system.

TOC removal (%)	TN removal (%)	MLSS (g/L)	Permeate turbidity (NTU)	UV ₂₅₄ absorbance of the permeate (cm ⁻¹)	
				Before PAC addition	After PAC addition
92±5	96±5	12±1	<0.2	0.125	0.005

405

406 **Table 4:** Concentrations of sulfamethoxazole (SMX) and carbamazepine (CBZ) in permeate under
407 different operating conditions.

Day of operation	PAC conc. in MBR, g/L	Micropollutant conc. in feed, µg/L	Concentration in permeate, µg/L ^a	
			SMX	CBZ
1-32	0	750	280±55	660±87
33-48 ^b	0.1	750	447±96	494±226
49-64 ^c	0.1	100	18±10	190±80
65-72	1.0	100	10±10	22±10
73-92	1.0	750	127±80	80±55

^a Values indicate mean concentration±standard deviation.

^b Accidental low temperature in MBR from day 21-30 caused variable removal of both SMX and CBZ.

^c Removal of CBZ was more sensitive to accidental low temperature in MBR during day 46-53 even though the influent concentration was reduced; SMX showed stable removal due to its relative biodegradability.

408

409

410 LIST OF FIGURE CAPTIONS

411 **Figure 1:** TOC and micropollutants removal throughout the operation period: (a) TOC, (b)
412 sulfamethoxazole (SMX), and (c) carbamazepine (CBZ). P1 and P2 indicate points of PAC addition to
413 achieve final concentrations of 0.1 g/L and 1.0 g/L, respectively; T indicates periods of accidental low
414 temperature in MBR; horizontal bar in each graph indicates respective feed concentration.

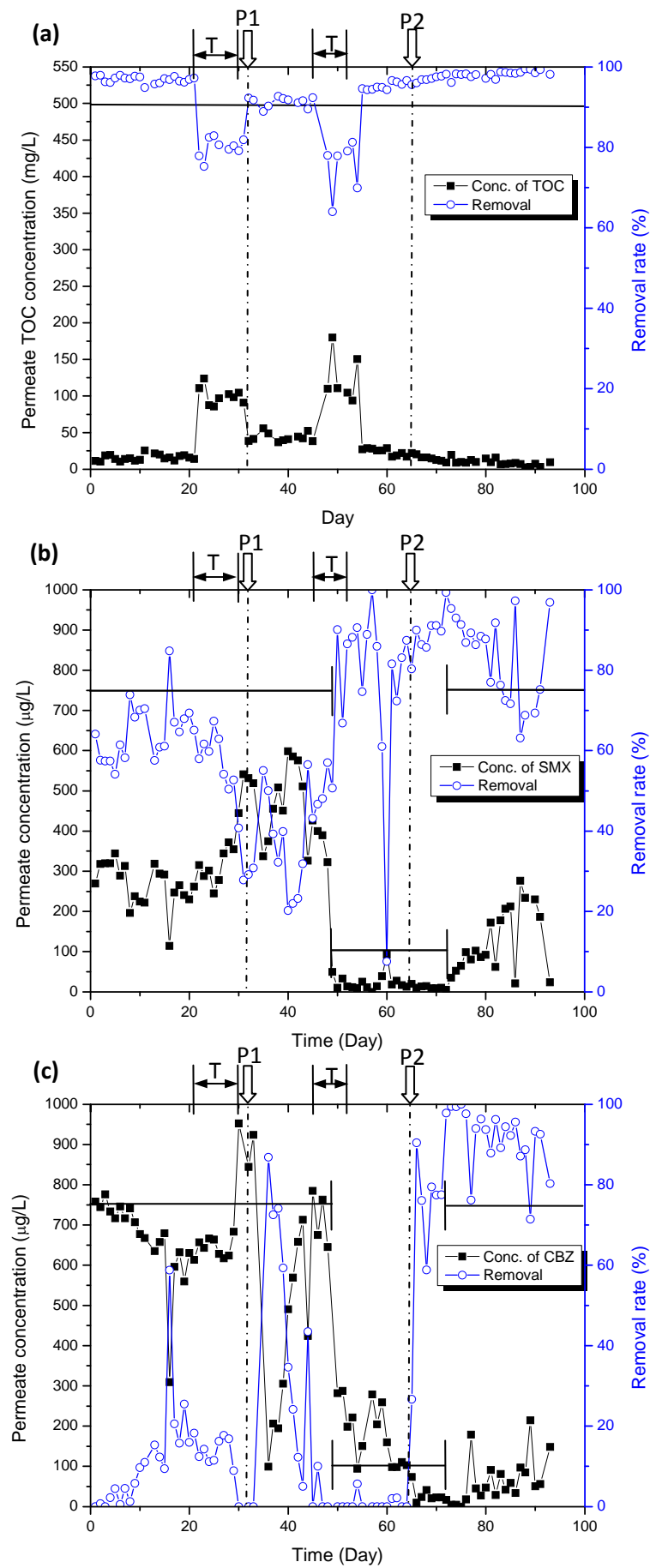
415 **Figure 2:** Relative concentrations of sulfamethoxazole (SMX) and carbamazepine (CBZ) in supernatant
416 and permeate before and after PAC addition in MBR. (Error bars represent the standard deviation of
417 available data points ($n \geq 5$). Only data corresponding to the highest feed micropollutant concentration
418 of 750 $\mu\text{g/L}$ have been included.

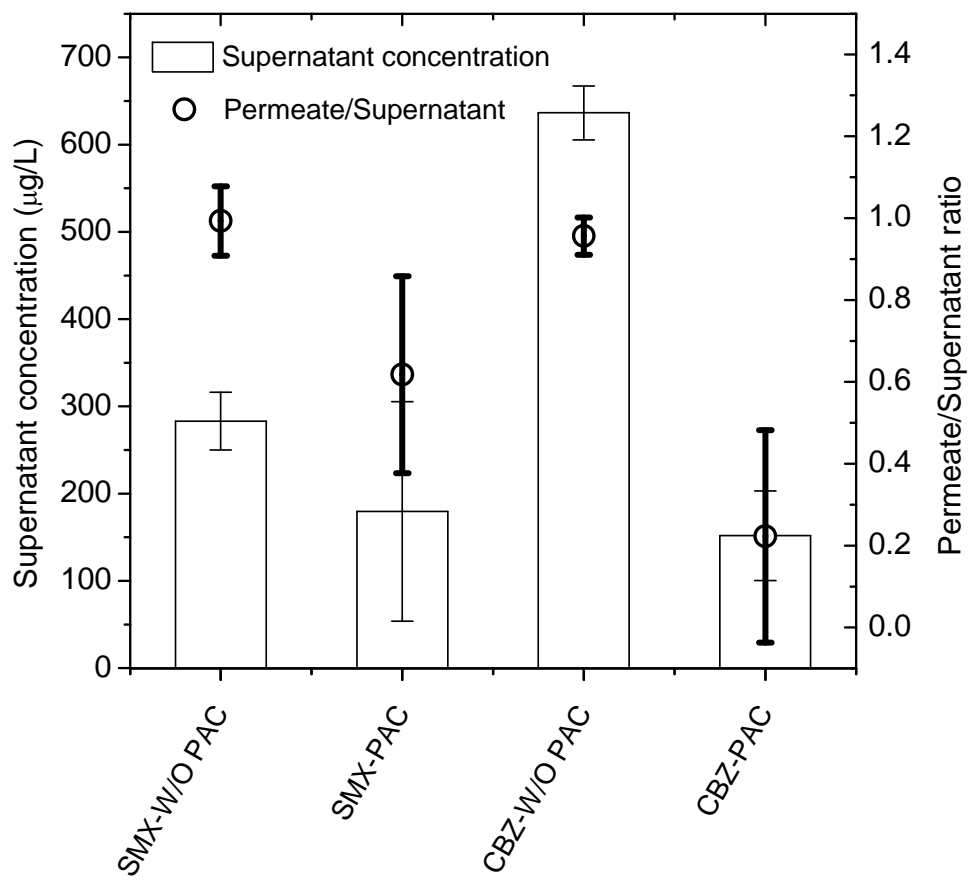
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420 LIST OF FIGURES

421

422 **Figure 1**





423

424 **Figure 2**