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Removal of micropollutants by membrane bioreactor under temperature variation

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Abstract

The effects of controlled temperature variation in the range of 10 – 45 °C were assessed in a lab-scale MBR that treated synthetic municipal wastewater spiked with selected micropollutants. The effects were evaluated with respect to total organic carbon (TOC) and total nitrogen (TN) removal, micropollutant removal, sludge growth, level of soluble microbial products (SMP) in the mixed liquor and membrane fouling. Overall, the temperature shifts caused high variation in the TOC and TN levels in the reactor supernatant, however that in membrane-permeate was relatively more stable, substantiating the robustness of the MBR process. Results regarding the removal of micropollutants at ambient temperature (20 °C) demonstrate an apparent correlation between hydrophobicity, chemical structures and the removal of micropollutants. Temperature variation below and above 20 °C, especially the operation under 45 °C appeared to significantly influence the removal of certain less hydrophobic (Log D < 3.2) micropollutants possessing strong electron withdrawing functional groups. The removal of most hydrophobic compounds (Log D > 3.2) was stable under the temperature range of 10 – 35 °C, however, deteriorated at 45 °C. The temperature shifts were also associated with higher levels of SMP in the mixed liquor which appeared to trigger membrane fouling as evidenced by a rapid increase in transmembrane pressure.

Keywords: micropollutants, membrane bioreactor (MBR), temperature, operating condition, water recycling.

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1 Introduction

In recent years, the applications of membrane bioreactors (MBR) for the treatment of both municipal and industrial wastewater have increased dramatically. In particular, MBR has been recognized as a key treatment process to facilitate wastewater reclamation and water recycling practice [1-2]. At the same time, the occurrence of micropollutants such as pharmaceutically active compounds and endocrine disrupting chemicals in raw and treated domestic wastewater has been identified as a significant environmental health concern [3]. Although most of these contaminants remain unregulated, there is a growing consensus among the scientific community and water authorities regarding their optimized removal during wastewater to protect public health and the environment. Not surprisingly, there has been a significant scientific interest regarding the removal efficiency of micropollutants by MBR treatment [4-9].

Previous studies have indicated significant variation in the removal of micropollutants by MBR, ranging from near complete removal for some compounds (e.g. ibuprofen and bezafibrate) to almost no removal for several others (e.g. carbamazepine and diclofenac) [5, 8-9]. The reasons for such variation are not yet fully understood. Recent studies, therefore, have focused on elucidation of underlying principles of micropollutant removal in MBR and formulation of strategies to enhance micropollutant removal [7, 10-11]. With the aim of finding avenues to enhance micropollutant removal, the effect of operational parameters such as hydraulic retention time, sludge retention time [9] and pH [8, 12] on the removal efficiency of micropollutant in MBR have been specifically targeted.

Temperature fluctuation in biological wastewater treatment processes can result from seasonal or diurnal (e.g. in arid and semi arid areas) variations, and from the operation of batch units in upstream industrial processes [13]. Because microbial growth and activity [14] as well as solubility and other physicochemical properties of organics [4] are significantly affected by temperature conditions, temperature variability have been related to deterioration in bulk water quality parameters and system instability [4, 13]. The effects have been dependent on the temperature stability and the magnitude of any fluctuations, and have been linked to sludge deflocculation and decreased sludge metabolic activity. Nevertheless, systematic studies on the effects of temperature variation on micropollutant removal in either conventional activated sludge (CAS) process or MBR remain very scarce. Most of the observations of variation of micropollutant removal with ambient temperature have been

anecdotal and based on measurement of limited number of samples at full scale plants, and have been reported as relatively high effluent concentrations of certain micropollutants during low winter temperature or vice versa [15-16]. In addition to temperature, other factors like overall pollutant loading, precipitation and sunlight availability (important for photodegradation) can also influence the observed seasonal variations in effluent concentration; therefore in the absence of a controlled experimental design the effect of temperature cannot be accurately ascertained. It is also noteworthy that the few available studies [17-19] that have specifically investigated the effect of temperature on micropollutant removal by lab-scale biological reactors have been restricted to a temperature range of below 30 °C. Information on micropollutant removal performance beyond these limits is important as municipal wastewater plants can experience higher levels of temperature. These include situations when high temperature industrial effluent is mixed with municipal wastewater or in the cases of arid and semi arid areas where the diurnal temperature during the summer can vary from 30 to 55 °C [20]. It is also important to note that temperature-dependent soluble microbial products (SMP) levels in the mixed liquor may have significant implications on floc structure, sludge settleability and potentially on membrane fouling [21]. However, to date there has been no comprehensive study to investigate simultaneously the potentially interrelated effects of temperature variation on the mixed liquor characteristics, bulk organics and micropollutants removal and membrane fouling.

This study aims to investigate the effects of controlled temperature transients on the performance of a lab-scale MBR. The effects of controlled temperature shifts (20, 10, 20, 35 and 45 °C, respectively) were assessed in terms of TOC and TN removal, micropollutant removal, sludge growth, level of SMP in the mixed liquor and membrane fouling. Special focus was given on the intricate relationship between physiochemical properties of the micropollutants and their removal by MBR during operation under normal ambient temperature (20 °C) as well as the potential deterioration due to temperature fluctuations.

2 Materials and Methods

2.1 Model micropollutants and synthetic wastewater

A set of 22 compounds representing four major groups of micropollutants, namely pharmaceutically active compounds, pesticides, hormones and industrial chemicals were selected in this study. The selection of these model compounds was also based on their

widespread occurrence in domestic sewage and their diverse physicochemical properties (e.g. hydrophobicity and molecular weight). The effective hydrophobicity of these compounds varies significantly as reflected by their Log D values at pH 8 (see Supplementary Table S1). A combined stock solution was prepared in methanol, kept in a freezer and used within a month. Once stable operation had been achieved (see section 2.2) micropollutants were continuously introduced to the feed solution to achieve a concentration of approximately 5 μg L^{-1} of each selected compound. The actual measured concentration in the feed was somewhat lower than that added, the exact value depending on the sensitivity of detection of the specific compound (see section 2.3). However, periodic chemical analysis of the influent samples confirmed the accuracy and consistency of this dosing process throughout the duration of the experiment.

A synthetic wastewater as utilized in a previous study [7] was modified as mentioned below to simulate medium strength municipal sewage. The concentrated synthetic wastewater was prepared and stored in a refrigerator at 4^{o}C. It was then diluted with MilliQ water on a daily basis to make up a feed solution containing glucose (400 mgL^{-1}), peptone (100 mgL^{-1}), urea (35 mgL^{-1}, KH_2PO_4 (17.5 mgL^{-1}), $MgSO_4$ (17.5 mgL^{-1}), $FeSO_4$ (10 mgL^{-1}), and sodium acetate (225 mgL^{-1}).

2.2 Laboratory-scale MBR system and operation protocol

A laboratory scale MBR system was employed in this study. The system consisted of a glass reactor with an active volume of 9 L, a continuous mixer, two air pumps, a pressure sensor, and influent and effluent pumps. Two ZeeWeed-1 (ZW-1) hollow fiber ultrafiltration (0.04 μm) membrane modules supplied by Zenon Environmental (Ontario, Canada) were submerged into the reactor. Each module had an effective membrane surface area of 0.047 m^2. The membrane modules were operated under an average flux of 4.3 $Lm^{-2}h^{-1}$ on a 14 minute suction and 1 minute rest cycle to provide relaxation time to the membrane modules. An electrical magnetic air pump (Heilea, model ACO 012) with a maximum air flow rate of 150 L min^{-1} was used to aerate the MBR system via a diffuser located at the bottom of the reactor. High temperature can have a significant impact on dissolved oxygen (DO) concentration in the reactor. Therefore the DO concentration in the reactor was monitored daily by a DO probe and kept constant at 2 ± 1 mgL^{-1} by controlling the air flow rate. In addition a continuously operated mixer ensured homogeneous mixing of the liquor and prevented the settling of biomass. A small air pump was also used to provide a constant air

flow through the membrane modules to reduce fouling and cake formation. Transmembrane pressure was continuously monitored using a high resolution pressure sensor (±0.1 kPa) which was connected to a personal computer for data recording. A stainless steel heat exchanging coil was connected to a temperature controlling unit (Neslab RTE 7, Thermofisher Scientific, Australia) and directly submerged into the reactor to maintain the mixed liquor temperature at the desired level. The mixed liquor pH was stable around 7.8±0.1.

The MBR was seeded with activated sludge from another lab-scale MBR system which had been in continuous operation for over 3 years [7]. The hydraulic retention time was set at 24 hours, corresponding to a permeate flux of 4.3 $Lm^{-2}h^{-1}$. Apart from the samples for mixed liquor suspended solid (MLSS), mixed liquor volatile suspended solid (MLVSS) and extracellular polymeric substance (EPS) analysis, no sludge was withdrawn from the MBR at any stage of this study. The sludge retention time (SRT), taking into account the amount of sludge withdrawn for MLSS, MLVSS and EPS samples, was approximately 630 d. After an initial start up period of two months under a temperature of 20.0±0.1^{o}C, stable operation of the MBR in terms of TOC and TN removal had been achieved. At this point, micropollutants were added to the synthetic wastewater and the operating temperature was regulated to different set points of 20, 10, 20, 35 and 45 °C, respectively. At the end of each phase the MBR temperature was changed at a rate of 5 °C day^{-1} to a new temperature set point (See supplementary figure S2). The system was operated for two weeks at 45 °C and for three weeks at all other set points. During the entire operation, all other operating parameters remained the same. Micropollutant analysis (see section 2.3) on duplicate samples was conducted at least once each week to monitor the removal efficiency. The membrane modules were cleaned by ex-situ soaking and backwashing with NaOCl before the start of the investigation with temperature shifts. Membrane cleaning was also conducted just before the initiation of operation at 35 °C and when the system was operated at 45 °C. Further details regarding membrane cleaning will be discussed in section 3.3.

As mentioned earlier, diurnal or seasonal variation in bioreactor temperature can happen, and this study was designed to capture the effect of such changes on MBR performance rather than to report steady state removal performance under different temperatures, which would require acclimatization of the biomass under specific temperatures [19]. Our experimental design is in line with a previous study by Morgan-Sagastume and Allen [13].

2.3 Micropollutant analysis

The micropollutants in feed and permeate samples were extracted using 6 mL 200 mg Oasis HLB cartridges (Waters, Milford, MA, USA). The cartridges were pre-conditioned with 7 mL dichloromethane and methanol (1:1, v/v), 7 mL methanol, and 7 mL reagent water respectively. The feed and permeate samples (500 mL each) were adjusted to pH 2 – 3 and then loaded onto the cartridges at a flow rate of 15 $mLmin^{-1}$. The cartridges were then rinsed with 20 mL Milli-Q water and dried with a stream of nitrogen for 30 min. The trace organic compounds were eluted from the cartridges with 7 mL methanol followed by 7 mL dichloromethane and methanol (1:1, v/v) at a flow rate of 1 – 5 $mLmin^{-1}$, and the eluents were evaporated to dryness under a gentle stream of nitrogen in a water bath at 40 °C. The extracted residues were then dissolved with 200 µL methanol solution which contained 5 µg bisphenol A-d_{16} and transferred into 1.5 mL vials, and further evaporated to dryness under a gentle nitrogen stream. Finally, the dry residues in the vials were derivatized by addition of 100 µL of BSTFA (1% TMCS) plus 100 µL of pyridine (dried with KOH solid), which were then heated in a heating block at 60 – 70 °C for 30 min. The derivatives were cooled to room temperature and subjected to GC-MS analysis.

Analyses of the micropollutants were conducted using a Shimadzu GC-MS QP5000 system, equipped with a Shimadzu AOC 20i autosampler. A Phenomenex Zebron ZB-5 (5% diphenyl – 95% dimethylpolysiloxane) capillary column (30 m × 0.25 mm ID, d_f = 0.25 µm) was used. Helium carrier gas was maintained at a constant flow rate of 1.3 mL min^{-1}. The GC column temperature was programmed from 100 °C (initial equilibrium time 1 min) to 175 °C via a ramp of 10 $°Cmin^{-1}$ and maintained 3 min, 175 – 210 °C via a ramp of 30 °C, 210 – 228 °C via a ramp of 2 $°Cmin^{-1}$, 228 – 260 °C via a ramp of 30 °C, 260 – 290 °C via a ramp of 3 °C min^{-1} and maintained 3 min. The injector port and the interface temperature were maintained at 280 °C. Sample injection (1 µL) was in splitless mode.

For qualitative analysis, MS full-scan mode from m/z, 50 – 600 was used, apart from the mass spectrum, the relative retention times of each compound was used for confirmation of the compound. Quantitative analysis was carried out using selected ion monitoring (SIM) mode. For each compound, the most abundant and characteristic ions were selected for quantitation. The selected ions of the analyzed compounds after silyl derivatization are in agreement with those reported elsewhere [22-23].

195 Standard solutions of the analytes were prepared at 1, 10, 50, 100, 500 and 1000 ng mL^{-1}, and
196 an internal instrument calibration was carried out with bisphenol A- d_{16} as internal standard.
197 The calibration curves for all the analytes had a correlation coefficient of 0.99 or better.
198 Detection limits were defined as the concentration of an analyte giving a signal to noise (s/n)
199 ratio greater than 3 (see Supplementary Table S3). The Limit of Reporting was determined
200 using an s/n ratio of greater than 10.

201 Removal efficiency was calculated as $R = 100 \times \left(1 - \frac{C_{Eff}}{C_{Inf}}\right)$, where C_{Inf} and C_{Eff} are influent
202 and effluent (permeate) concentrations of the micropollutants, respectively. It is noteworthy
203 that complete degradation of an organic compound may follow different pathways and
204 undergo several steps. Therefore, the term removal here does not necessarily indicate
205 complete degradation of the trace organics, but rather a loss of the specific trace chemical
206 molecule, either by a chemical change or sorption to solid surfaces.

207 *2.4 Other analytical methods*

208 Total organic carbon (TOC) and total nitrogen (TN) were analyzed using a Shimadzu
209 TOC/TN-V_{CSH} analyzer. TOC analysis was conducted in non-purgeable organic carbon
210 (NPOC) mode. Samples were kept at 4 °C until analyzed and calibrations were performed in
211 the range between 0 and 1000 mg L^{-1} and 0 to 100 mgL^{-1} for TOC and TN, respectively.
212 Mixed liquor samples taken from MBR were centrifuged (Allegra X-12R, Beckman Coulter,
213 USA) at 3270 g and the TOC and TN concentration in the supernatant was measured as an
214 indication of bioreactor performance (before membrane filtration). MLSS and MLVSS
215 contents in the MBR reactor were measured in accordance to the Standard Methods for the
216 Examination of Water and Wastewater [24]. The concentrations of EPS and soluble microbial
217 products (SMP) were determined by previously described methods [25]. pH was measured
218 using an Orion 4-Star Plus pH/conductivity meter.

219 3 Results and discussion

220 *3.1 TOC and TN removal*

221 Figure 1 depicts significant variation in the level of TOC and TN in the reactor supernatant
222 due to temperature variation below and over the initial acclimatization temperature (20 °C). It
223 is well known that most biological reactions are slower at low temperatures [19]. On the other

hand, the decay and lyses of bacteria under (near) thermophilic temperatures can heighten soluble microbial products release and simultaneously hinder metabolic activity, thereby increasing the concentration of soluble carbonaceous/nitrogenous compounds in the effluent. In a previous study by Sundaresan et al., [26] for a stepwise decrease of temperature from 35 to 5 °C the chemical oxygen demand (COD) removal performance of a submerged bed bioreactor treating domestic wastewater was stable up to 15 °C, however, deteriorated moderately at 10°C and significantly at 5°C. Furthermore, Morgan-Sagastume et al., [13] reported 20% deterioration in soluble COD removal by a laboratory scale sequencing batch reactor treating pulp and paper mill effluent due to a rapid temperature change from 35 to 45 °C. The significant variation observed in supernatant TOC and TN concentration in our study at temperatures below (10 °C) and over 20°C (i.e. at 35 and 45 °C) is hence not surprising. Of particular interest was the fact that despite the large fluctuations in supernatant TOC concentration (100±94 mg L^{-1}) the TOC concentration in the membrane permeate was consistently low (8±7 mg L^{-1}) and stable (Figure 1a). Our observation is in good agreement with other available MBR studies which also report more stable and improved permeate quality as compared to the reactor supernatant quality despite significant temperature shifts [20-21], possibly due to the retention of suspended and macro-colloidal organics on the membrane cake layer. Fractionation of the TOC comprising the cake layer over the membrane by techniques such as liquid chromatography organic carbon detection (LC—OCD) can provide detailed information on the type of substances retained on the membrane, however, that is beyond the scope of this study. On the other hand, as expected, in the absence of a denitrification zone within the MBR, the TN removal in our study was fairly low. No biological removal of TN (supernatant concentration exceeding that of the feed) during operation under 45 °C can be attributed to the release of nitrogen due to disintegration of biomass [13, 26] and also to decreased MLSS concentration (see section 3.3). Furthermore, as compared to the case of TOC, not much reduction in the TN concentration in permeate over the concentration in the supernatant was observed. Our observation is consistent with that of Al-Amri et al., [20] who also reported that physical removal by membrane filtration in MBR does not contribute to the removal of ammoniacal nitrogen as much as it does for COD.

[Figure 1]

3.2 Micropollutant removal

3.2.1 Removal at the temperature of initial acclimatization

The removal efficiency of the selected micropollutants at the ambient temperature (20 °C) has been plotted in Figure 2. Tadkaew et al., [7] have recently demonstrated that the classification of trace organics according to their intended use or origin can only be used to qualitatively predict the removal efficiencies of compounds having similar molecular features or physicochemical properties. In good agreement with the study by Tadkaew et al., [7] , in this study, 80 – 99% removal of all four hormones and four alkyl phenolic surfactant and industrial compounds (bisphenol A, 4-t-butyl phenol, 4-t-octyl phenol, and 4-n-phenol) were observed. These results are also consistent with previously published data [4-5, 7-8]. It is noteworthy that all the hormones and alkyl phenolic compounds possess significant hydrophobicity and the members of these groups share similar molecular backbone structures between them, which may, in part, explain the similarities of their removal efficiencies. On the other hand, owing to the difference in the molecular structure, removal efficiencies of the eleven pharmaceuticals and two pesticides (fenoprop and pentachlorophenol) tested varied widely even within the same class of therapeutic compounds. Therefore further discussion on removal efficiency will be based on physicochemical properties.

Previous studies have suggested that removal of the very hydrophobic (Log D > 3.2) compounds is probably dominated by sorption to the activated sludge followed by subsequent biodegradation in the reactor [7, 27]. Given the long sludge age in MBRs, the removal of micropollutants. which adsorb readily to the activated sludge, can be significantly enhanced and is usually high [7]. Similarly, we observed near-complete removal of all the compounds possessing a Log D >3.2 (Figure 2). According to a simple qualitative framework proposed by Tadkaew et al., [7] for compounds possessing lower hydrophobicity, functional groups play an important role in determining the extent of biodegradation and thus overall removal. They suggested that compounds possessing only electron withdrawing groups (EWG) may have removal efficiency below 20 %, and those containing only electron donating groups (EDG) may show more than 70 % removal, while the removal of the compounds containing both EWG and EDG may vary significantly. As discussed below, our results comply largely with the qualitative framework recently proposed [7].

In good agreement with the well-documented poor removal of the anti-depressant drugs carabamazepine and primidone [5], we observed less than 40% removal of these recalcitrant compounds. Notably carbamazepine contains a strong EWG (amide) while primidone contains in addition a weak EDG (methyl). Despite possessing amide in its structure, the presence of the strong EDG hydroxyl group has been noted as the reason of achieving excellent removal of the non-steroidal anti-inflammatory drug (NSAID) acetaminophen in other studies [6]. The reason of rather low (below 50 %) removal of acetaminophen in this study in comparison to several previous studies [4, 6, 28] could not be explained clearly; nevertheless this observation affirms the notion that presence of an amide group contributes significant recalcitrance to compound structure. Over 90 % removal of the antipruritic (anti-itching) medication salicylic acid is in line with previous reports [29] and can be attributed to the presence of strong EDG hydroxyl group along with the weak EWG carboxylic groups. On the other hand, all the compounds containing the weak EWG (carboxylic group)—weak EDG (methyl) combination, namely, the hypolipidemic agent gemfibrozil and the NSAIDs naproxen, ibuprofen and ketoprofen showed above 50 % to above 90 % removal. The relatively higher removal of ibuprofen and gemfibrozil may be attributed to their higher hydrophobicity. The observed removal efficiencies of these four compounds are also in line with the literature reports [28]. The low and highly variable removal of the nitroimidazole antibiotic metronidazole is in good agreement with the report of Beier et al. [30], and may be attributed to the presence of strong EWG nitro group in its structure.

No specific report on the removal of the halogenated herbicide fenoprop by CAS or MBR could be found. However in line with the recalcitrance of the phenoxy carboxylic acid herbicides to biological treatment processes [31], a rather poor removal of that compound was achieved in this study. The removal efficiency of the other halogenated compounds (diclofenac, pentachlorophenol and triclosan) was in line with literature reports [5, 32]. Hai et al. [10] have recently demonstrated a combined effect of halogen content (ratio of molecular weight of the chlorine atoms to that of the whole compound) and hydrophobicity on the removal of halogenated trace organics by MBR. They suggested that compared to halogen content alone the ratio of halogen content to Log D, which incorporates two important physico-chemical properties, is a comparatively better index for prediction of removal. Although the set of halogenated compounds used in this study was not entirely the same as that used in the previous study, the observed trend remained the same. For example, although fenoprop (Halogen content = 0.39, Log D = -0.13) and triclosan (Halogen content = 0.37,

318 Log D = 4.76) possessed similar halogen contents, among the tested halogenated compounds,
319 they were removed with the lowest and the highest efficiency, respectively.

320 **[Figure 2]**

321 3.2.2 Removal during operation under controlled temperature variation

322 For the significantly hydrophobic (Log D > 3.2) phenolic and steroidal compounds, which
323 were removed with > 90% efficiency during operation under 20 °C, insignificant difference
324 in removal efficiency was observed in the temperature range of 10-35 °C (Figure 3). Similar
325 observations have been reported in the literature. Suzuki et al. [33] reported negligible change
326 in adsorption and decomposition of estrone and estradiol during batch tests at a temperature
327 as low as 5 °C. Zuehlke et al., [34] observed no seasonal variation in estradiol, estrone and
328 ehinylestradiol removal in real conventional activated sludge plant. Gabet-Giraud et al., [35]
329 also reported that estrone and 17β-estradiol removal under 10 and 20°C was similar. Suarez
330 et al., [17] observed that 17β-estradiol and 17α-ethinylestradiol removal was not significantly
331 different at 16 and 26 °C. Our results regarding the steroidal compounds removal are
332 consistent with the above reports. In contrast, Tanghe et al., [18] reported significant
333 deterioration in the removal capacity of nonylphenol by a laboratory activated sludge due to a
334 temperature shift from 28 to 10 °C, while we observed no apparent change in the range of 10-
335 35 °C. This discrepancy could possibly be attributed to the fact that for these readily
336 biodegradable compounds, MBR, in comparison to the activated sludge process, can achieve
337 more stable removal due to quicker response to operational perturbations [15].

338 Except for a few compounds (e.g. triclosan, 17β-estradiol acetate, 4-t-octylephenol) whose
339 removal remained stable, for all other hydrophobic compounds, significantly lower removal
340 efficiency was observed at 45 °C. The reduced removal efficiency of the micropollutants in
341 the near-thermophilic (45 °C) range corresponds well with the higher variability of the TOC
342 and TN removal performance in that regime in our study. Contradictory reports on the effect
343 of a thermophilic temperature regime on micropollutants removal during anaerobic digestion
344 of sludge can be found in the literature [36-37]. No reports on specifically micropollutant
345 removal under aerobic thermophilic conditions could be found. However, LaPara et al., [38]
346 reported that mesophilic biological treatment was superior in COD removal than a
347 thermophilic aerobic biological treatment for a pharmaceutical wastewater. They argued that
348 the predicted advantages of thermophilic treatment, such as, rapid biodegradation rates and
349 low growth yields without loss of physiological function were not valid in the system they

studied. Sludge disintegration under thermophilic temperatures can cause release of micropollutants from the sludge phase to the water phase, thereby increasing the concentration in the effluent. In addition, in our study, the observed MLSS concentration drop (see section 3.3) beyond 20 °C may have been another reason of deteriorated removal performance in the near-thermophilic regime. It is also interesting to note that sorption along with biodegradation plays an important role in the overall removal of the significantly hydrophobic compounds. For most compounds, equilibrium sorption decreases with increasing temperature [39]. It is possible that hindered adsorption, sludge disintegration and metabolic activity were simultaneously responsible for the lower removal of the significantly hydrophobic compounds at 45 °C.

A similar trend of reduced removal at the near-thermophilic temperature of 45 °C was observed in case of the less hydrophobic compounds (Log D < 3.2), and can be explained again by the disrupted metabolic activity typically associated with operation under such elevated temperature. In addition, a comparatively more pronounced variation between removals in the lower temperature regimes was observed. Comparing the removal performance in summer and winter Sui et al., [15] suggested that for the easily biodegradable compounds MBR performance can be expected to show less susceptibility to ambient temperatures as compared to conventional activated sludge process. However, compounds, which were moderately removed in MBR (e.g. diclofenac), showed seasonal variation. Nevertheless, no removal was achieved regardless of the season or the treatment processes for the recalcitrant micropollutants such as carbamazepine. A similar observation was also reported by Castiglioni et al., [40]. Our results corroborate well with the trends reported in literature. The compounds that are usually well removed by MBR (e.g. salicylic acid, ibuprofen, gemfibrozil, pentachlorphenol and estriol) and exhibited a removal efficiency of over 80% at 20 °C in this study, showed negligible variation at 10 and 35 °C. Lower and/or more variable removal at 10 °C was observed for certain compounds (e.g. ketoprofen, naproxen, metronidazole) which are reported to be moderately recalcitrant to MBR treatment [7, 10]. The removal of carbamazepine at 20 °C in this study was originally low, nevertheless higher than that reported in real plants [5, 15] and plummeted further both above and below the temperature of initial acclimatization (20 °C), indicating the extreme sensitivity of this recalcitrant compound removal to the operating conditions.

In the absence of relevant temperature-dependent removal efficiency related information in the literature, it, however, remains unexplainable why the highest removal efficiency of certain compounds were achieved at the two end values of temperature ranges tested i.e., at 10 °C (primidone and diclofenac) and 45 °C (fenoprop and acetaminophen), respectively, despite the fact that the sludge was originally acclimatized at 20 °C. Nevertheless, it is noteworthy that except for acetaminophen, the other three compounds (fenoprop, primidone, and diclofenac), which exhibited rather unexpected behavior (Figure 3), have also been widely reported to show low and highly variable removal in MBR [7, 10].

It is noteworthy that this study aims to capture the effect of dynamic temperature transient conditions (e.g., diurnal variation) on micropollutant removal by MBR. The removal performance may be different if longer acclimatization period under each temperature regime is applied. However, that is beyond the scope of this study.

[Figure 3]

3.3 Sludge characteristics and membrane fouling

A significant impact of temperature on MLSS concentration was observed during operation at 35 and 45 °C (Figure 4). In this study, in the absence of sludge withdrawal, the MLSS concentration steadily rose for the first two months of operation under 10-20 °C, however, rather sharply decreased to the initial level when the temperature was elevated beyond 20 °C. Al-Amri et al., [20] reported a similar observation. They attributed the MLSS reduction at elevated temperatures of 35 °C and 45 °C to the changes in ambient temperature experienced by the microorganisms (biomass shock). Dias et al., [41] hypothesized that at higher temperatures, the cells utilize a large fraction of the energy to maintain their vital functions and not only to synthesize new cellular material, hence, causing reduction in the biomass growth. While the MLVSS/MLSS ratio in this study remained stable, the lower level of MLSS during operation under 35 and 45 °C can possibly suggest lower level of metabolism within the reactor, which may partially explain the lower level of removal of some micropollutants in the near thermophilic temperature regime.

[Figure 4]

EPS and SMP levels in the mixed liquor may have significant implications on floc structure, sludge settleability and potentially on membrane fouling. In this study apart from the initial

412 stage, the EPS level was rather stable throughout operation under the temperature shifts
413 (Figure 5). On the other hand, the protein content of SMP showed significant increase at
414 operating temperatures lower or higher than 20 °C, with the significant increase observed
415 during operation under near-thermophilic (45 °C) conditions. Our observation regarding
416 variation of EPS and SMP levels with operating temperature is in good agreement with the
417 available literature reports. Zhang et al., [21] reported a relatively stable total EPS
418 concentration in sludge when MBR temperature was increased from 40 °C to 45 °C. Al-
419 Amri et al. [20] observed relatively steady level of EPS until 55 °C. Furthermore, in line with
420 our observation, available reports suggest that deflocculation of MBR sludge and heightened
421 SMP release occurs both during operation under low (e.g. 13 °C) [42] and high (e.g.
422 thermophilic) [20-21] temperature conditions.

423 **[Figure 5]**

424 An interesting similarity of variation of TMP and SMP levels with changes in MBR operating
425 temperature was discernible in this study. TMP remained stable for the first three weeks of
426 operation (20 °C) and started to increase when the reactor temperature was reduced to 10 °C
427 (Figure 6). This suggests that the heightened level of SMP initiated fouling and once fouling
428 had occurred, TMP continued to rise gradually even when the temperature was returned to 20
429 °C. TMP increase at a more accelerated rate was observed during operation at higher
430 temperatures, especially 45 °C, possibly due to the further increased level of SMP. Our
431 results demonstrate a significant correlation of TMP rise with that of SMP (protein) and
432 suggest that while more aggravated fouling may occur during operations both below or over
433 20 °C, fouling can become very severe at the higher temperatures (35 °C and 45 °C).
434 Previously Abenayaka et al., [43] linked membrane fouling under thermophilic condition to
435 higher protein generation within the reactors. In fact while SMP level can increase either
436 under or beyond 20 °C, higher viscosity of sludge at low temperature promotes particle
437 deposition on membrane, and hence, physically reversible fouling dominates at low
438 temperature (e.g. 13 °C) [42, 44], while physically irreversible fouling can be expected to
439 develop more rapidly in the high-temperature period [44]. This may explain the observed
440 sharp increase in TMP during operation under 45 °C in this study.

441 **[Figure 6]**

4 Conclusion

In this study, variation in operating temperature (10 – 45 °C) exerted considerable effects on biological activity of MBR sludge which was initially acclimatized at 20 °C. Variations were observed regarding several basic parameters including TOC and TN removal, sludge generation and EPS and SMP production. In particular, the operation at 45 °C was characterized with significant drops in TOC and TN removal efficiency and MLSS concentration and heightened levels of SMP in the mixed liquor. Increased level of SMP both during temperature downshift and upshifts appeared to trigger accelerated TMP buildup. Despite significant variations in the bioreactor supernatant, TOC and TN concentrations in the membrane permeate remained relatively stable, possibly due to additional retention on membrane cake layer. The observed removal efficiency at 20 °C of the micropollutants selected in this study could be explained via a unique approach considering hydrophobicity (Log D) and presence of electron withdrawing and donating functional groups. With a few exception, operation at 45 °C clearly exerted detrimental effects on the removal efficiency of the micropollutants selected in this study. The removal of most hydrophobic compounds (Log D > 3.2) was stable during operations under the temperature range of 10 – 35 °C. On the other hand, for the less hydrophobic compounds (Log D < 3.2) a comparatively more pronounced variation between removals in the lower temperature regimes (10 – 35 °C) was observed. Lower and more variable removal efficiency at 10 °C was observed for certain hydrophilic compounds which have been reported to be moderately recalcitrant to MBR treatment. This study provides unique insight into the effect of dynamic short term (e.g., diurnal) temperature variation on micropollutant removal by MBR treatment. However, further studies under prolonged microbial acclimatization under each temperature regime would be essential to know the steady state removal performance under mesophilic or thermophilic temperature regimes.

5 Acknowledgements

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594

595 ## LIST OF FIGURES

596 **Figure 1**: Variation of TOC (a) and TN (b) concentration in mixed liquor supernatant and
597 membrane-permeate along with controlled temperature shifts.

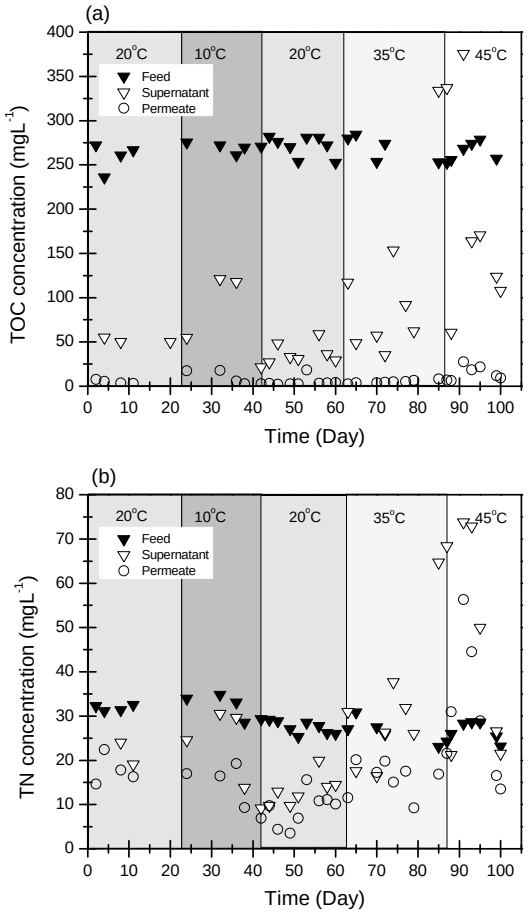
598 **Figure 2:** Removal of micropollutants at the temperature of initial acclimatization (20 °C).
599 Error bars represent the standard deviation of seven measurements.

600 **Figure 3:** Removal of micropollutants during operation with controlled temperature shifts.
601 The MBR was subject to five distinct phases wherein the temperature of the mixed liquor was
602 maintained in the following order: 20, 10, 20, 35 and 45 °C. The 45°C phase was maintained
603 for two weeks, while each of the other phases lasted for three weeks. Error bars represent the
604 standard deviation of seven and four measurements, in case 20 °C and other temperature
605 values, respectively.

606 **Figure 4**: Effect of operating temperature on the MLSS and MLVSS concentration.

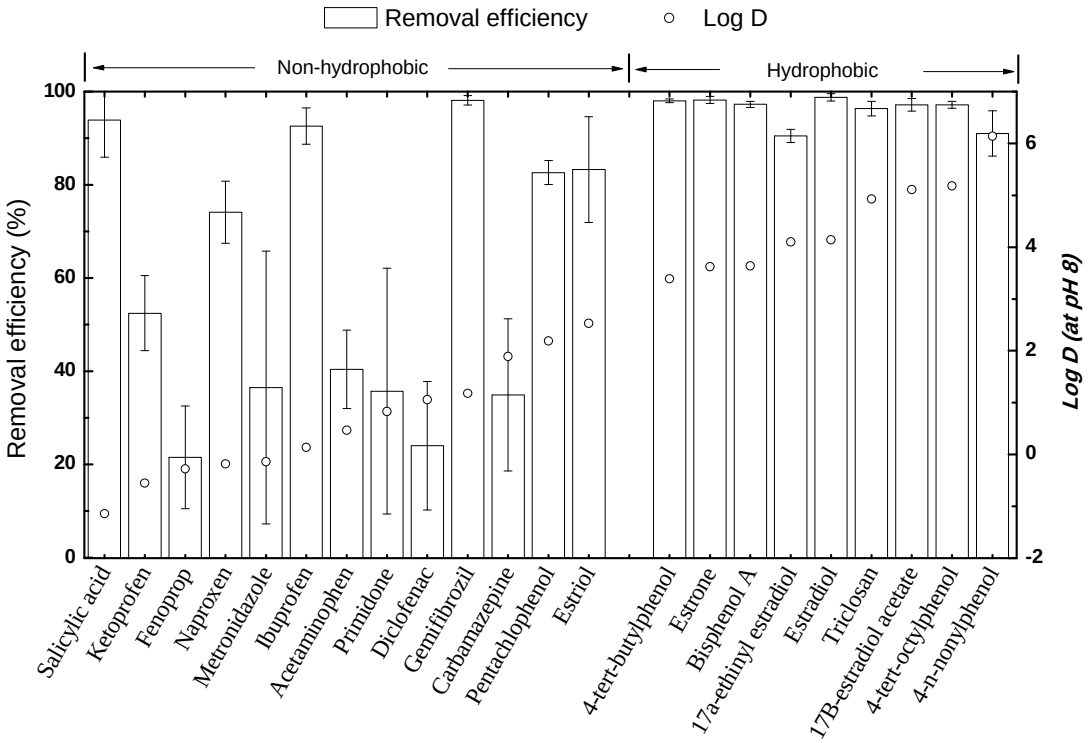
607 **Figure 5**: Variation of EPS (a) and SMP (b) content in mixed liquor as a function of
608 operating temperature.

609 **Figure 6**: Variation of transmembrane pressure (TMP) during operation under different
610 temperature regime.



609

610 **Figure 1**



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612 **Figure 2**

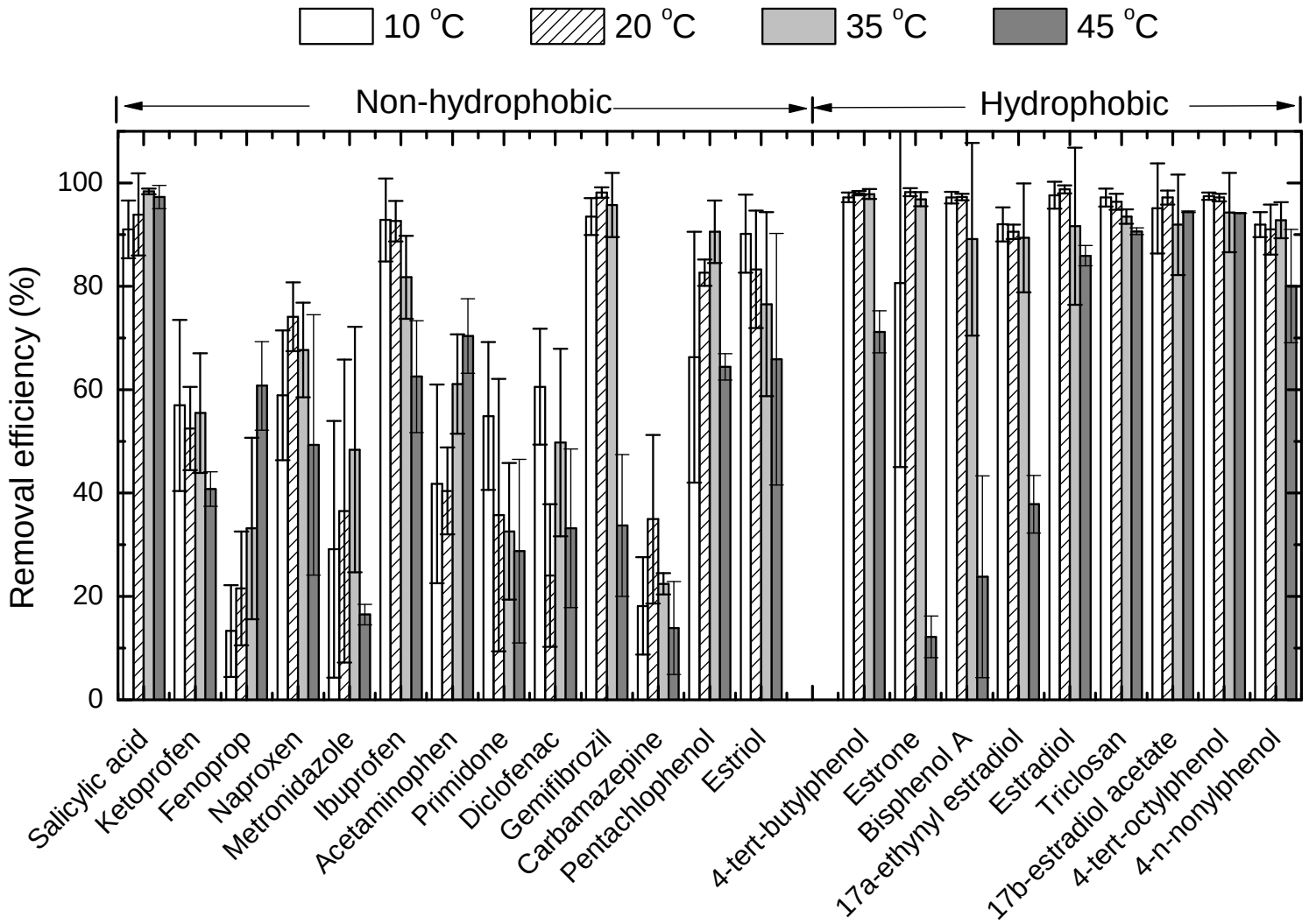
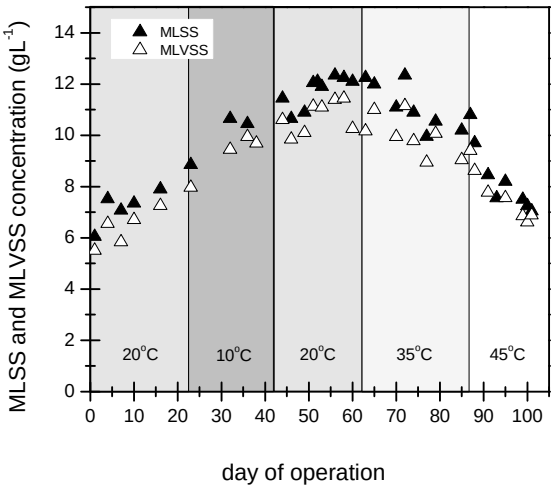

10 °C
20 °C
35 °C
45 °C
Non-hydrophobic
Hydrophobic
Removal efficiency (%)
0
20
40
60
80
100
Salicylic acid
Ketoprofen
Fenoprop
Naproxen
Metronidazole
Ibuprofen
Acetaminophen
Primidone
Diclofenac
Gemifibrozil
Carbamazepine
Pentachlorophenol
Estriol
4-tert-butylphenol
Estrone
Bisphenol A
17a-ethynyl estradiol
Estradiol
Triclosan
17b-estradiol acetate
4-tert-octylphenol
4-n-nonylphenol

Figure 3



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626 **Figure 4**

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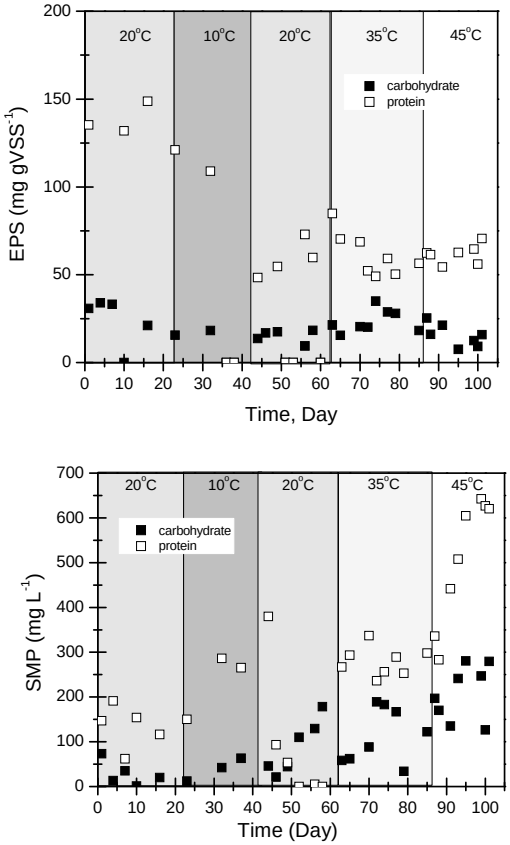

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629 **Figure 5**

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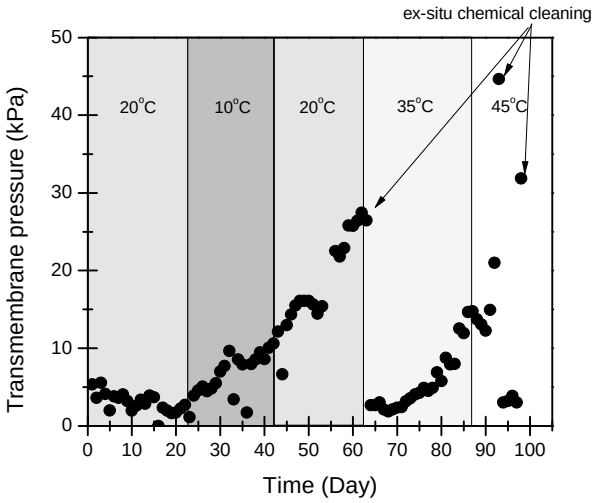

631

632 **Figure 6**

Removal of micropollutants by membrane bioreactor under temperature variation

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SUPPLEMENTARY DATA

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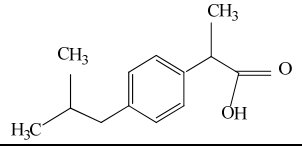
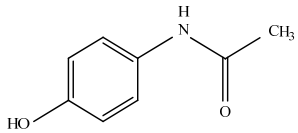
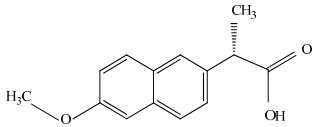
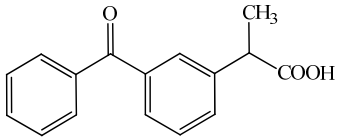
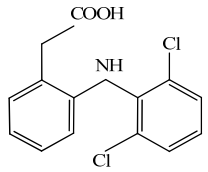
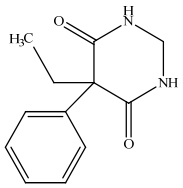
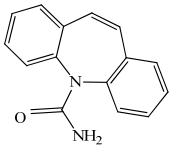
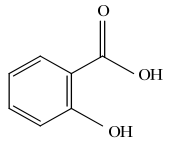
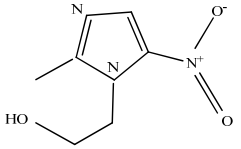
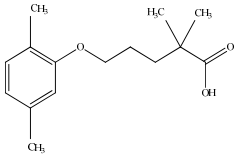
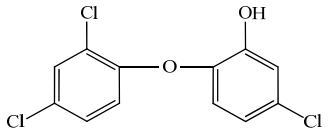
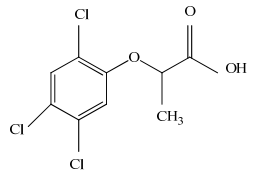
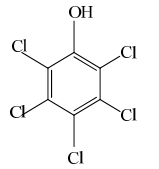
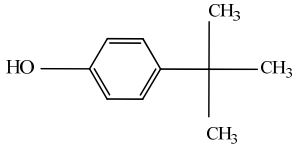
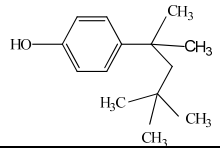
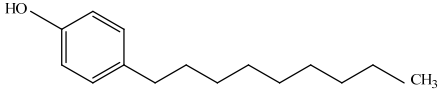
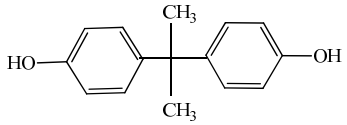
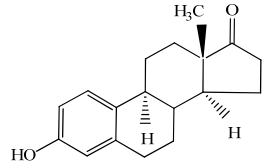
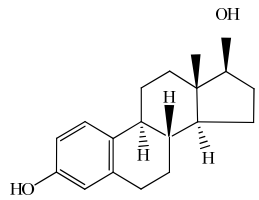
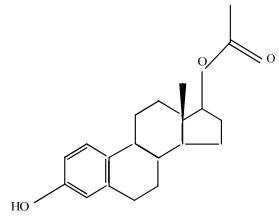
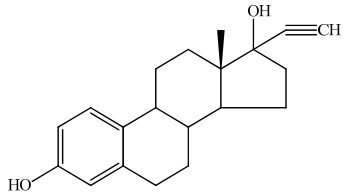
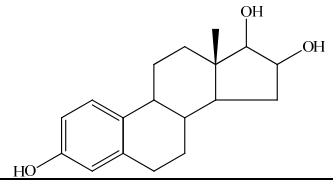
Table S1: Physicochemical properties of the selected micropollutants.

Category	Compound	CAS number	Molecular weight (g/mol)	Log K_{OW} [a]	Log D at pH 8 [a]	Dissociation constant (pKa)[a]	Water solubility (mg/L)[b]	Structure of compounds
Pharmaceutically active compounds	Ibuprofen ($C_{13}H_{18}O_2$)	15687-27-1	206.28	3.50 ± 0.23	0.14	4.41 ± 0.10	21	
	Acetaminophen ($C_8H_9NO_2$)	103-90-2	151.16	0.48 ± 0.21	0.47	9.86 ± 0.13 1.72 ± 0.50	14000	
	Naproxen ($C_{14}H_{14}O_3$)	22204-53-1	230.26	2.88 ± 0.24	-0.18	4.84 ± 0.30	16	
	Ketoprofen ($C_{16}H_{14}O_3$)	22071-15-4	254.28	2.91 ± 0.33	-0.55	4.23 ± 0.10	16	
	Diclofenac ($C_{14}H_{11}Cl_2NO_2$)	15307-86-5	296.15	4.55 ± 0.57	1.06	4.18 ± 0.10 -2.26 ± 0.50	2.4	

	Primidone ($C_{12}H_{14}N_2O_2$)	125-33-7	218.25	0.83 ± 0.50	0.83	12.26 ± 0.40 -1.07 ± 0.40	500	
	Carbamazepine ($C_{15}H_{12}N_2O$)	298-46-4	236.27	1.89 ± 0.59	1.89	13.94 ± 0.20 -0.49 ± 0.20	18	
	Salicylic acid ($C_7H_6O_3$)	69-72-7	138.12	2.01 ± 0.25	-1.14	3.01 ± 0.10	2240	
	Metronidazole ($C_6H_9N_3O_3$)	443-48-1	171.15	-0.14 ± 0.30	-0.14	14.44 ± 0.10 2.58 ± 0.34	9500	
	Gemifibrozil ($C_{15}H_{22}O_3$)	25812-30-0	250.33	4.30 ± 0.32	1.26	4.75	19	
	Triclosan ($C_{12}H_7Cl_3O_2$)	3380-34-5	289.54	5.34 ± 0.79	4.93	7.80 ± 0.35	10	

Pesticides	Fenoprop ($C_9H_7Cl_3O_3$)	93-72-1	269.51	3.45 ± 0.37	- 0.28	2.93	71	
	Pentachlorophenol (C_6HCl_5O)	87-86-5	266.34	5.12 ± 0.36	2.19	4.68 ± 0.33	14	
Surfactants and industrial chemicals	4-tert-butyphenol ($C_{10}H_{14}O$)	98-54-4	150.22	3.39 ± 0.21	3.39	10.13 ± 0.13	580	
	4-tert-octylphenol ($C_{14}H_{22}O$)	140-66-9	206.32	5.18 ± 0.20	5.18	10.15 ± 0.15	5	
	4-n-nonylphenol ($C_{15}H_{24}O$)	104-40-5	220.35	6.14 ± 0.19	6.19	10.15	6.35	
	Bisphenol A ($C_{15}H_{16}O_2$)	80-05-7	228.29	3.64 ± 0.23	3.64	10.29 ± 0.10	120	
	Estrone ($C_{18}H_{22}O_2$)	53-16-7	270.37	3.62 ± 0.37	3.62	10.25 ± 0.40	677	

Steroid hormones	17-β-estradiol ($C_{18}H_{24}O_2$)	50-28-2	272.38	4.15 ± 0.26	5.94	10.27	3.9	
	17-β-estradiol –acetate ($C_{20}H_{26}O_3$)	1743-60-8	314.42	5.11 ± 0.28	5.11	10.26 ± 0.60		
	17-α ethinylestradiol ($C_{20}H_{24}O_2$)	57-63-6	269.40	4.10 ± 0.31	4.10	10.24 ± 0.60	11.3	
	Estriol (E3) ($C_{18}H_{24}O_3$)	50-27-1	288.38	2.53 ± 0.28	2.53	10.25 ± 0.70	441	

[a] Data are obtained from SciFinder database https://scifinder.cas.org/scifinder/view/scifinder/scifinderExplore.jsf

[b] Water solubility are obtained form http://chem.sis.nlm.nih.gov/chemidplus/

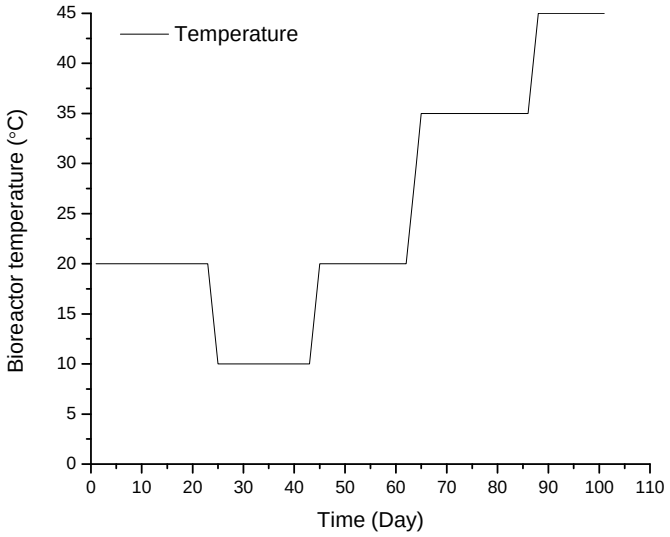


Figure S2: Controlled variation in the operating temperature of the MBR.

Table S3: Limit of detection of each compound during GC-MS analysis and average influent and permeate concentrations during operation under 20 °C as an example.

No.	Compound	Detection Limit (ng/L)	Average measured influent concentration (ng/L)	Average permeate concentration (ng/L)
1	4-tert-butylphenol	1	3900	80
2	Salicylic acid	1	3100	190
3	Ibuprofen	20	3900	290
4	Acetaminophen	20	2100	1240
5	Metronidazole	20	750	470
6	Primidone	10	3100	2000
7	Fenoprop	20	4770	3740
8	Pentachlorophenol	1	4450	770
9	Gemifibrozil	1	4670	90
10	Naproxen	1	4700	1220
11	Ketoprofen	20	3450	1640
12	Carbamazepine	10	4450	2800
13	Diclofenac	5	2380	1800
14	Triclosan	1	4700	170
15	4-tert-octylphenol	1	4000	110
16	4-n-nonylphenol	10	3190	290
17	Bisphenol A	1	4680	130
18	Estrone	5	2620	50
19	17-β-estradiol	5	2840	35
20	17-β-estradiol –acetate	5	2690	80
21	17-α ethinylestradiol	10	2730	260
22	Estriol	10	1200	200
I.S.	Bisphenol A-d_{16}	1		

I.S: Internal standard