Pre-coagulation coupled with sponge-membrane filtration for organic matter removal and membrane fouling control during drinking water treatment

Lijuan Deng[a,b,*], Huu-Hao Ngo[c], Wenshan Guo[c], Hongwei Zhang[a,b,*]

[a] State Key Laboratory of Separation Membranes and Membrane Process, Tianjin Polytechnic University, Tianjin 300387, China

[b] School of Environmental and Chemical Engineering, Tianjin Polytechnic University, Tianjin 300387, China

[c] Centre for Technology in Water and Wastewater, School of Civil and Environmental Engineering, University of Technology Sydney, Sydney, NSW 2007, Australia

*Corresponding author, Email: hwzhang@tju.edu.cn; Tel: +86-13502171853

Email: lijuan19850317@gmail.com; Tel: +86-18171272998

Abstract

A new hybrid system was developed in this study for the treatment of drinking water consisting of pre-coagulation using polyaluminium chloride (PACl) and membrane filtration (MF) with sponge cubes acting as biomass carriers (P-SMF). When compared to a conventional MF (CMF) and a MF after coagulation by utilizing PACl (P-MF), better removal of nutrients, UV_{254} and dissolved organic carbon (DOC) (> 65%) was obtained from the P-SMF. The accumulation of biopolymers (including polysaccharides and proteins), humic substances, hydrophilic organics, and other small molecular weight (MW) organic matter in the CMF led to the most severe membrane fouling coupled with the highest pore blocking and cake resistance. Pre-coagulation was ineffective in eliminating small MW and hydrophilic organic matter.

Conversely, the larger MW organics (i.e. biopolymers and humic substances), small MW organics and hydrophilic organic compounds could be removed in significantly larger quantities in the P-SMF by PACl coagulation. This was achieved via adsorption and the biodegradation by attached biomass on these sponges and by the suspended sludge. Further analyses of the microbial community indicated that the combined addition of PACl and sponges generated a high enrichment of *Zoolgloea*, *Amaricoccus* and *Reyranella* leading to the reduction of biopolymers, and *Flexibacter* and *Sphingobium* were linked to the degradation of humic substances. Moreover, some members of *Alphaproteobacteria* in the P-SMF may be responsible for the removal of low MW organics. These results suggest that the pre-coagulation process coupled with adding sponge in the MF system is a promising technology for mitigating membrane fouling.

Key words: Drinking water treatment; Membrane filtration; Coagulation; Sponge; Microbial community; Membrane fouling

1. Introduction

Membrane filtration has become a promising technology for the treatment of drinking water. However, membrane fouling induced by natural organic matter (NOM) (e.g. humic acid, biopolymers) and microorganisms is still a major obstacle for the wider application of membrane technologies. Chemical coagulation is a pretreatment method that can improve water quality, mitigate membrane fouling and eliminate some organic matter, especially hydrophobic fractions of NOM with a larger molecular size. Nevertheless, biopolymers' (polysaccharides and proteins) contribution to irreversible fouling was not effectively reduced. Also the accumulation of

48 bacteria, any remaining biopolymers, hydrophilic NOM and low molecular weight (MW)
49 organic matter on the membrane through operational processes was responsible for the
50 occurrence of membrane fouling (Gao et al., 2011a; Matilainen and Sillanpää, 2010).

51 Current studies have employed further treatment processes to enhance the removal of
52 fouling materials in membrane tanks. It was reported that Fe/Mn (Fe(II)/K_2MnO_4 (combination
53 of pre-oxidant and coagulant) as a pretreatment for ultrafiltration (UF): limited transmembrane
54 pressure (TMP) development; reduced bacterial activity and the associated extracellular
55 polymeric substances (EPS); altered organic matter properties; decreased levels of EPS within
56 cake layer; and lowered MW organic matter (< 10,000 Da) in membrane pores (Yu and Graham,
57 2015a). An integrated coagulation-UF system with a sand layer around the submerged membrane
58 module successfully retarded the cake layer formation and inner membrane fouling. This was
59 ascribed to the fact that the removal of deposited flocs in the sand layer by the backwash process
60 led to fewer bacteria on the flocs' surface, and less generation and accumulation of both
61 biopolymers and EPS by the membrane (Yu and Graham, 2015b). Yu et al. (2016) discovered
62 that the coagulation-UF process with addition of a submersible ultraviolet (UVC) lamp (pulsed
63 UV in 1 min on and 31 min off cycles at 3.17×10^{-2} W/cm^2) in the membrane tank at a low flux
64 of 20 L/m^2·h, did not equate to any measurable increment in TMP. In fact, this presented with
65 smaller concentrations of bacteria and soluble microbial products (SMP), and considerably less
66 organic matter in membrane pores.

67 In recent years, the combination of biomass carriers with membrane technology has been
68 taken into account for enhancing performance when treating drinking water. The performance of
69 the attached growth membrane bioreactor (aMBR) with 15% polyvinyl alcohol gel (PVA-gel) as
70 the carrier and conventional membrane filtration reactor (MF) for polluted surface water

71 treatment was evaluated by Li et al. (2017). They reported that compared to the MF system,
72 aMBR clearly performed better in terms of organic matter removal, less membrane fouling and
73 longer operating time. Conversely, some studies combined coagulation and PAC addition prior
74 to membrane filtration for drinking water treatment. Tian et al. (2010) directly added
75 polyaluminium chloride (PACl) and powdered activated carbon (PAC) into the submerged MBR
76 (MCABR), which successfully removed dissolved organic matter (DOM) better through the
77 synergetic effect of membrane separation, biodegradation by microorganisms, coagulation by
78 PACl and PAC adsorption from slightly polluted surface water. Yu et al. (2014) pointed out that
79 pre-coagulation by alum by continuously adding PAC at a low dosage before UF (CAUF)
80 enhanced the DOM removal (especially proteinaceous materials), and minimized reversible and
81 irreversible fouling in a short-term operation (< 20 days). However, after 20 days, a higher TMP
82 development rate in the CAUF was observed due to the accumulation of microorganisms and the
83 associated EPS in the cake layer.

84 Hu et al. (2014) added PACl as the coagulant into micro-polluted surface water, which was
85 collected as influent for a PAC-MBR. The PAC-MBR with the optimal PAC dosage (e.g. 2 g/L)
86 could minimize membrane fouling and improve effluent water quality, while removing
87 intermediate MW organic fraction (1-10 kDa) by PAC adsorption/biodegradation effect and
88 larger MW organic fraction (> 10 kDa) by membrane rejection. However, the overdose of PAC
89 (e.g. 3 g/L) caused less organic material to be removed, more rapid flux decline and worse
90 membrane fouling. Moreover, sludge discharge or PAC replacement should be conducted to
91 maintain low fouling propensity after a certain number of operational days. Observed here was
92 the fact that membrane fouling of the PAC-MBR with pre-coagulation was significantly affected

by internal fouling. This system should be operated at a low flux rate in combination with effective physical cleaning protocols (Shao et al., 2014).

Previous studies indicated that sponge as attached growth media in a long-term sponge-submerged MBR successfully demonstrated its superiority in improving treatment performance. It also enhanced sludge characteristics and mitigated membrane fouling when treating synthetic domestic wastewater (Deng et al., 2014). In view of the potential advantages of using sponge in wastewater treatment, this study explored the feasibility of long-term operation of membrane filtration (MF) systems with sponge addition after coagulation by PACl (P-SMF) for the treatment of drinking water. Treatment performance was investigated in a conventional MF (CMF), a MF with pre-coagulation (P-MF) and a P-SMF, in terms of nutrient and organic matter removal. In all of the proposed MF systems, detailed analyses were conducted on characteristics of influent, effluent, suspended sludge, foulants extracted from membrane surfaces and membrane pores (e.g. MW distribution, hydrophilic components, EPS) along with the microbial community to explain membrane fouling behaviors and mechanisms.

2. Materials and methods

2.1. Synthetic drinking water source

The synthetic drinking water was prepared by mixing domestic sewage with local tap water at a volumetric ratio of 1:40 and 1 mg/L humic acid, which stimulated the slightly polluted drinking water sources. Tapwater was retained overnight to completely remove residual chlorine before adding humic acid to domestic sewage. Water quality of synthetic drinking water sources is summarized in Table 1. Additionally, the temperature and pH of the prepared raw water were 20.1 ± 2.3 ºC and 7.25 ± 0.36 over the entire study period, respectively.

Table 1.

2.2. Experimental set-up and operational conditions

Fig. S1 illustrates the experimental set-up of polyaluminium chloride (PACl) coagulation-membrane filtration (MF) with sponge addition (P-SMF), PACl coagulation-MF (P-MF) and a conventional MF (CMF), which were operated in parallel throughout the whole experiment. The effective working volume for each membrane tank of MF systems was 2 L. For the P-SMF and P-MF, PACl as the coagulant was added to the synthetic drinking water at a dosage of 10 mg/L. Furthermore, the membrane tank of the P-SMF was filled with 6% of polyester-polyurethane porous sponge cubes (dimensions being 10 mm × 10 mm × 10 mm in length, width and height, respectively, density of 28-45 kg/m^3, cell count of 90 cells/in). Prior to the continuous membrane filtration experiment, the sponge cubes were acclimatized for 15 days to ensure the enrichment of attached biomass on the sponge. In the membrane tank, a hollow fiber ultrafiltration (UF) membrane module was used, consisting of polyvinylidene fluoride (PVDF) membranes which had a pore size of 0.07 μm and an effective surface area of 0.20 m^2. Aeration was supplied by a soaker hose air diffuser underneath the membrane modules at the bottom of the tank. Activated sludge collected from a local wastewater treatment plant was put in the membrane tank at an initial sludge concentration of 1.50 g/L, 1.52 g/L and 1.49 g/L for the P-SMF, P-MF and CMF, respectively. During the operation, there was no sludge waste (infinite sludge retention time (SRT)). Filtration flux of membrane permeate withdrawn from the membrane module was consistently controlled at 10 L/m^2·h, resulting in a hydraulic retention time (HRT) of 1 h. A backwash mode was implemented to physically control membrane fouling during the experiment within a 58 min filtration cycle and 2 min backwash. When the experiment ended at TMP of 35.0

kPa, the membrane was removed from the tank and put in chemical solutions, specifically HCl (0.5%), NaOH (0.4%) and NaClO (0.2%) in sequence.

2.3. Analysis methods

Ammonium (NH_4-N), nitrite (NO_2-N), nitrate (NO_3-N) and phosphorus (PO_4-P) concentrations of influent and effluent samples were determined with standard methods (APHA, AWWA, WEF, 1998) using a HACH DR6000 UV VIS spectrophotometer (HACH Co., USA). These concentrations of suspended solids in the membrane tank as mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were quantified based on standard methods (APHA, AWWA, WEF, 1998). The measurement of UV absorbance at 254 nm, UV_{254}, of 0.45 mm filtered solutions was done utilizing the above-mentioned HACH spectrophotometer. Dissolved organic carbon (DOC) was determined using a total organic carbon (TOC) analyzer (TOC-LCPH, Shimadzu, Japan). The quantification of bacteria concentration as the Heterotrophic Plate Count (HPC) was done using the yeast extract agar method (ISO6222, 1999). Extracellular polymeric substances (EPS) and soluble microbial products (SMP) extracted from suspended sludge and cake layer in the membrane tank were analyzed for proteins (EPS_P, SMP_P) and polysaccharides (EPS_C, SMP_C) (Deng et al., 2014; Frølund et al., 1996; Raunkjer et al., 1994). After removing the cake layer from the membrane surface, membrane fibers were taken and soaked in 0.01 mol/L NaOH (pH = 12) to extract foulants from membrane pores (Kimura et al., 2009).

Three-dimensional excitation emission matrix **(**EEM**)** spectrophotometry served to determine dissolved organic matter (DOM) characteristics using a fluorescence spectrophotometer (RF-6000, Shimadzu, Japan). It was conducted at different emission

wavelengths ranging from 200 to 550 nm at 5 nm increment and excitation wavelengths from 200 to 450 nm at 5 nm increment with a scanning speed of 2000 nm/min. The determination of hydrophilic and hydrophobic organic components was carried out with resins of Superlite DAX-8 (Supelco, USA) and Amberlite XAD-4 (Rohm and Hass, Germany), which fractionated NOM into strongly hydrophobic organic matter that was subsequently adsorbed by DAX-8. Weakly hydrophobic (or transphilic) organic matter was adsorbed by XAD-4 and hydrophilic organic matter which passed through both resins (Qu et al., 2012). Molecular weight distribution of samples was determined by high-performance size exclusion chromatograph (HPSEC) using a high performance liquid chromatogram (HPLC) (Shimadzu 20A Prominence LC system, Shimadzu, UK). It was equipped with UV/VIS detection (SPD-20A, Shimadzu, UK) at 254 nm. HPSEC was undertaken using a BioSep-SEC-s3000 column (Phenomenex, UK) 300 × 7.8 mm (inner diameter (ID)) and Security Guard™ Cartridge fitted with a GFC 3000 disc 4 × 3.0 mm (ID). The mobile phase of 0.01 mol/L sodium acetate was employed at a flow rate of 1 mL/min. Then the samples were injected with a volume of 500 µL.

At the experiment's completion, the individual fouling component for the fouled membrane was determined based on the resistance-in-series model and Darcy's equations (Choo and Lee, 1996):

$$J = \Delta P/\mu R \qquad (1)$$

$$R_T = R_M + R_C + R_P \qquad (2)$$

where R_T is total resistance, R_M is the intrinsic membrane resistance, R_C is the cake resistance, and R_P is the pore blocking resistance.

Fouled membrane and clean membrane were characterized by Fourier Transform Infrared Spectroscopy (FTIR, Nicolet iS50, Thermo Fisher Scientific, USA). Scanning electronic

185 microscopy (SEM) (Hitachi S4800, Japan) observations were undertaken for fouled membranes
186 and a clean membrane sample, which could refer to the protocol proposed by Tian et al. (2010).
187 A confocal laser scanning microscopy (Leica TCS SP8, Leisa, Germany) was used to observe the
188 surface of the fouled membrane. SYTO 63 (20 μM, Thermo Fisher Scientific, USA), Fluorescein
189 isothiocyanate (FITC) (10 g/L, sigma) and ConA (0.25 g/L, sigma) were employed to stain total
190 bacterial cells, proteins and polysaccharides of foulants on the membrane surface, respectively
191 (Chen et al., 2006). Suspended sludge, cake layer on membrane surface and attached biomass of
192 sponge were sent to GENEWIZ to determine the microbial community of samples using high-
193 throughput sequencing.
194
195 **3. Results and discussion**
196 *3.1. Treatment performance of the CMF, P-MF and P-SMF*
197 Nitrogen and phosphorus removals were also compared among the CMF, P-MF and P-SMF
198 as shown in Table 1. All of the MF systems were efficient in removing NH_4-N, reaching 85.87 ±
199 4.78% for the CMF, 92.12 ± 3.26% for the P-MF, and 97.16 ± 2.98% for the P-SMF,
200 respectively. Influent NO_2-N was eliminated by approximately 50% for both the CMF and P-MF,
201 while the P-SMF demonstrated higher NO_2-N removal efficiency of 68.42 ± 3.65% and
202 significant elimination of NO_3-N by 71.55 ± 1.36%. These results indicated that the CMF could
203 accomplish effective nitrification, while the addition of PACl wielded only a negligible impact
204 on nitrogen removal. Furthermore, sponge addition enhanced the removal of nitrogen by creating:
205 firstly, aerobic/anoxic conditions at the outer layer of the sponge; and secondly, anoxic/anaerobic
206 conditions at the sponge's inner layer (Chu and Wang, 2011; Guo et al., 2008). In the CMF, PO_4-
207 P removal of 32.16 ± 7.24% was mainly realized by phosphorus uptake by phosphate

accumulating organisms (PAOs) (Guo et al., 2010). The P-MF removed 92.54 ± 6.05% of PO_4-P, which was almost 3 times higher when compared to the CMF. This could be attributed to the chemical coagulation precipitating as insoluble Al-phosphates and adsorption of phosphate ions onto the positively charged $Al(OH)_3$ colloids coupled with phosphorus uptake by phosphate accumulating organisms (PAOs) (Özacar et al., 2003; Polanska et al., 2005). Slightly more PO_4-P was removed in the P-SMF (95.72 ± 4.61%), suggesting that phosphate removal was mainly achieved by PACl coagulation and phosphorus uptake.

During the whole study period no sludge withdrawal occurred. When the experiment was completed, MLSS levels increased to 2.67, 2.34 and 1.67 g/L at biomass growth rate of 0.040, 0.050 and 0.002 g/L·d for the CMF, P-MF and P-SMF, respectively. MLVSS concentrations reached a higher value for the CMF (2.15 g/L) and P-MF (1.91 g/L) than for the P-SMF (1.39 g/L). In the P-SMF, adding sponge could notably curtail suspended sludge concentration by stunting microorganism growth in activated sludge through adsorption onto and inside sponge cubes (Deng et al. 2014). For the effluents, suspended solids were virtually undetected in any of them (Turbidity < 0.06 NTU) together with notably low bacterial concentrations (< 6 CFU/mL in the effluents). This was achieved mainly by membrane rejection, PACl coagulation and retention by sponge for attached biomass growth.

3.2. Membrane fouling development and fouling materials in membrane tanks

The TMP variation versus operational time for the CMF, P-MF and P-SMF is illustrated in Fig. 1. The CMF displayed a gradual increase in TMP from 5.5 to 12.0 kPa within the first 15 days and then rapidly rose to 35.0 kPa until day 29. It gave rise to the fastest fouling rate of 1.03 kPa/d. As to the P-MF, a slow initial TMP increment was observed for the 22-day operation,

after which the TMP increase was much quicker for the remaining period. This resulted in a relatively lower fouling rate of 0.64 kPa/d. TMP in the P-SMF increased to 35.0 kPa after 86 days at the lowest fouling rate of 0.34 kPa/d. These results suggested that the CMF was most seriously subjected to membrane fouling, which could be alleviated to some degree after PACl addition. The pre-coagulation coupled with sponge addition significantly prolonged filtration duration and increased membrane filterability.

Fig. 1.

The key factors contributing to membrane fouling are dissolved organic matter (DOM) from influent and EPS and SMP associated with bacteria. UV_{254} and DOC removals in the CMF, P-MF and P-SMF are summarized in Table 1. Referring to the CMF, UV_{254} and DOC removals were lower than 20%, while the corresponding values increased to 52.16 ± 4.92% and 47.83 ± 4.32% in the P-MF, respectively. Under the operational conditions in this study (influent pH 7.25 ± 0.36), adsorption of humic-like substances on $Al(OH)_3$ crystals by sweep flocculation was responsible for NOM removal with $Al(OH)_3$ fraction as the main products (Kabsch-Korbutowicz, 2005). The application of sponge further improved UV_{254} and DOC removals in the P-SMF, reaching 74.71 ± 3.67% and 68.30 ± 5.36%, respectively. The MW distributions of DOM obtained from HPSEC analysis (Fig. 2) revealed that similar patterns were observed for influent and effluent samples, while the peaks corresponding to humic substances, biopolymers and small MW organic substances decreased for all MF systems to various degrees. The CMF effluent exhibited some decline in peaks corresponding to biopolymers, humic substances and small MW organic matter.

253 Suggested here is the possibility that biopolymers and humic substances accumulated in the
254 CMF, which gave rise to the severest membrane fouling. Additionally, some small MW organics
255 passed through membrane pores, resulting in certain levels of the corresponding organics being
256 left in the effluent. On the other hand, the cake layer could retain small MW organics, while only
257 a few of them were deposited on the membrane pores as documented in Section 3.3.1.
258 Compared to the CMF, peaks related to biopolymers and humic substances of effluent were
259 further decreased in the P-MF, except for small MW organics. It indicated that the pre-
260 coagulation process could reduce some biopolymers/EPS and humic substances, but it exerted
261 only a slight effect on removals of small MW organic matter. Similar findings by Chen et al.
262 (2017) and Lai et al. (2015) also pointed out that the coagulation process exerted greater effects
263 on these higher than lower MW organic matter. In the P-SMF, biopolymers and humic
264 substances could be removed by membrane separation, PACl coagulation, adsorption on sponge,
265 and biodegradation with the attached biomass on the sponge and suspended sludge in the
266 membrane tank. Moreover, the elimination of small MW organics was linked to the presence of
267 sponge (Ngo et al., 2008) and some microorganisms in membrane tanks. The bacteria
268 contributing to the removal of biopolymers, humic substances and small MW organic matters are
269 described in Section 3.4.
270 **Fig. 2.**
271
272 EPS of mixed liquor was characterized by EEM spectroscopy to further elucidate the effects
273 of organic matter on membrane fouling (Fig. 3). Six key fluorescence peaks referred to as
274 fluorophores A, C, T_1, T_2, B and D were found. Humic-like substances were demonstrated by
275 peaks A and C. Tryptophan-like (peak T) and tyrosine-like (peak B) materials were indicated as

276 protein-like fluorophores (Baker et al., 2003; Lee et al., 2008). The presence of peak D at Ex/Em
277 of 270-280/300-310 nm suggests the presence of SMP-like substances. It was observed that in
278 the CMF, intensities of peaks B, T_1, and T_2 were stronger than those of peaks D, A and C,
279 confirming that mixed liquor mainly contained protein-like and SMP-like materials. Comparing
280 the HPSEC and EEM results for the CMF, humic substances were more likely to be adsorbed on
281 the membrane surface or in the membrane pores. In contrast, all peaks declined in the P-MF and
282 P-SMF. Furthermore, the reduction in intensities of peaks associated with the protein- and SMP-
283 like substances in the P-SMF was greater than that in the P-MF. These results confirmed that
284 fouling components (including biopolymers and humic substances) of mixed liquor could be
285 more effectively removed with a combination of pre-coagulation and sponge addition in
286 comparison to the pre-coagulation process alone.
287 **Fig. 3.**
288
289 Compositions of EPS and SMP in suspended sludge contributing to membrane fouling were
290 designed for all MF systems for different TMP ranges (Table 2). During the period of gradual
291 TMP increment (≤ 12.0 kPa), EPS levels of the CMF, P-MF and P-SMF demonstrated narrow
292 ranges of 8.53-12.10 mg/L, 6.00-9.80 mg/L and 4.37-6.26 mg/L, respectively. When TMP
293 increased above 12 kPa (TMP jump), the CMF and P-MF exhibited a notable accumulation of
294 EPS, while the increase in EPS was not significant in the P-SMF. More specifically, a marginal
295 difference in EPS_C was observed between the CMF and P-MF within the ranges of 5.59-8.26 and
296 5.23-7.98 mg/L, respectively. EPS_P levels in the CMF were 7.21-8.96 mg/L, which were higher
297 than those for the P-MF (5.03-6.67 mg/L). For the P-SMF, both the EPS_C and EPS_P revealed a
298 slight variation at the lowest levels at 2.84-3.56 mg/L and 4.17-4.56 mg/L, respectively. SMP

299 contents were lower than EPS in all MF systems. The CMF possessed more SMP (2.82-8.87
300 mg/L) than the P-MF (2.13-6.47 mg/L) and P-SMF (0.82-2.52 mg/L).

301 These results suggest that membrane fouling is mainly associated with EPS_C and EPS_P of
302 mixed liquor. In the CMF, food supplied for the microorganisms (food to microorganism (F/M)
303 ratio of 0.086 d^{-1}) was extremely limited in the substrate available for microorganisms.
304 Consequently, the sludge's metabolic activity declined, while the endogenous metabolism, cell
305 lysis and cell hydrolysis occurred simultaneously with the release of EPS and SMP (Wu and Lee,
306 2011). These were reduced due to the addition of PACl by curtailing biomass growth (relatively
307 higher F/M ratio of 0.093 d^{-1}) and membrane separation. Having a more substantial reduction of
308 proteins rather than polysaccharides in the P-MF, indicates that the hydrophobic fraction of
309 biopolymers was more easily removed by PACl coagulation. Biopolymers (including proteins
310 and polysaccharides) could be remarkably eliminated by sponge addition in the P-SMF through
311 adsorption onto sponge and biodegradation by attached biomass of sponge (Deng et al., 2014).
312 Moreover, the lowest biomass growth (F/M ratio of 0.130 d^{-1}) limited the EPS and SMP
313 generation in the P-SMF.

314 **Table 2.**

315

316 *3.3. Foulants on the membrane surface and inside the membrane pores*

317 At the end of this experiment, membrane modules were removed from the reactor and
318 fouling resistances were analyzed for all MF systems (Table 3). Total fouling resistance (R_T) was
319 higher for the CMF and P-MF (4.86×10^{12} m^{-1} and 3.47×10^{12} m^{-1}, respectively), while the P-
320 SMF demonstrated the lowest R_T of 1.74×10^{12} m^{-1}. As for the CMF, R_T comprised 45.16% of
321 the cake layer resistance (R_C, 2.19×10^{12} m^{-1}), 40.32% of pore blocking resistance (R_P, $1.96 \times$

322 10^{12} m^{-1}) and 14.52% of clean membrane resistance (R_M, 0.71 × 10^{12} m^{-1}). PACl addition
323 reduced R_C and R_P, which accounted for 44.70% and 34.74% of R_T, respectively. For the P-SMF,
324 R_C of 1.74×10^{12} m^{-1} was almost one-second of that for the P-MF. Although there was a
325 significant decline of R_P to 0.21 × 10^{12} m^{-1} comprising 12.02% of R_T, the proportion of R_M
326 increased to 40.73% of R_T. These results suggested that both the cake layer and pore blocking
327 induced membrane fouling. Compared to the CMF, the pre-coagulation in the P-MF decreased
328 the R_C and R_P, which in turn were substantially reduced by the sponge, and this led to the highest
329 membrane permeability in the P-SMF. Characterization of the cake layer on the membrane
330 surface and pore blocking is further investigated in the following sections.
331 **Table 3.**
332
333 *3.3.1. Cake layer fouling*
334 At the end of the experiment, the cake layer was retrieved from the membrane surface and
335 its properties were analyzed in terms of EEM spectra, MW distributions and EPS compositions.
336 The EEM fluorescence spectra of the cake layer on the membrane surface (Fig. 4) revealed that
337 in the CMF, significantly high intensities were obtained for peaks represented by protein- (Peak
338 T_1, T_2 and B), SMP- (Peak D) and humic-like substances (Peak A and C), which promoted
339 severe cake fouling. After pretreatment by PACl addition, some of the peak intensities declined
340 with more substantial decrease in protein- and humic-like substances indicated by peaks A, C, B
341 and T_2. In the P-SMF, most peaks were not evident except for peak T_1 (protein-like substances).
342 The SEC results (Fig. 5) further supplemented the EEM fluorescence results. Cake layer from the
343 CMF retained more biopolymers, humic substances and small MW organics, leading to higher
344 R_C. In comparison to the CMF, foulants on the membrane surface of the P-MF possessed fewer

biopolymers, and humic substances, and presented a slight reduction in the peak of small MW organic matter.

All MW fractions of organics in the cake layer declined remarkably in the P-SMF. These outcomes indicate that cake fouling was mainly induced by the accumulation of biopolymers (including SMP- and protein-like substances), and humic-like substances on the membrane surface, and subsequently were eliminated by PACl coagulation to a certain degree. The accumulation of small MW organics within the cake layer in the P-MF could be ascribed to the coagulation process since it could not eliminate these components (Matilainen et al. 2010). The P-SMF clearly performed better in eliminating biopolymers, humic substances and small MW organics of the cake layer because the presence of PACl and sponge reduced organic matter in the suspended sludge.

Fig. 4.

Fig. 5.

Foulants on the membrane surface (cake layer) were further characterized by FTIR (Fig. S2). As for the new PVDF membrane, adsorption peaks close to 840, 873, 1070, and 1170 cm^{-1} were associated with the chemical bonds CF_2 and CH_2 (Enomoto et al., 1968). The peaks near 1640 cm^{-1} (amide I), 1510 cm^{-1} (amide II) and 1400 cm^{-1} (amide III) demonstrated the accumulation of protein or protein-like substances in the fouled membrane (Shirshova et al., 2006; Zhou et al., 2007). Additionally, the sharp band at about 2940 cm^{-1} indicated polysaccharides or polysaccharide-like components (Chefetz et al., 1998; Shirshova et al., 2006). The P-SMF exhibited the lowest intensity peaks which were attributable to protein- and polysaccharide-like materials, followed by the P-MF and CMF. Compositions of EPS and SMP (Fig. S3) were

368 evaluated to support these results. It was discovered that the levels of EPS_C and EPS_P in the cake
369 layer (13.67 ± 1.53 and 18.41 ± 2.51 mg/g cake layer, respectively) were remarkably high for the
370 CMF. PACl addition as a pretreatment did not significantly decrease the EPS_C level, but it did in
371 fact reduce the EPS_P level by approximately 46%, respectively obtaining 10.79 ± 1.53 and 9.94 ±
372 1.38 mg/g of the cake layer. In the P-SMF, EPS_C and EPS_P values decreased to 2.43 ± 0.19 and
373 3.68 ± 0.32 mg/g of cake layer, respectively. Levels of SMP_C and SMP_P in the CMF (9.83 ± 1.19
374 and 6.34 ± 0.84 mg/g cake layer, respectively) were higher than those of the P-MF (8.76 ± 0.78
375 and 4.28 ± 0.56 mg/g cake layer, respectively) and P-SMF (2.18 ± 0.23 and 2.09 ± 0.18 mg/g
376 cake layer, respectively). These results indicate that the cake layer formation was partly induced
377 by the deposition of biopolymers (polysaccharides and proteins) on the membrane surface. Pre-
378 coagulation was better at removing the hydrophobic fraction of biopolymers (proteins) from
379 foulants on the membrane surface. The addition of sponge further reduced the biopolymers in the
380 cake layer formation process, resulting in the lowest R_C in the P-SMF.

381 To further clarify and support the results obtained above, SEM images and CLSM images
382 for all MF systems were taken from the fouled membrane. When compared to the clean
383 membrane, much more irregular and denser cake layer formed on the membrane surface in the
384 CMF, where many more biopolymers (including polysaccharides and proteins) and bacteria were
385 detected (Figs. S4(b) and (c)). After pre-coagulation involving the addition of PACl, the cake
386 layer of the P-MF contained less bacteria and biopolymers (Figs. S4(d) and (e)). Compared to the
387 CMF and P-MF, a flatter and smoother membrane surface was observed in the P-SMF, on which
388 the fewest deposits (biopolymers and bacteria) were evident as illustrated in Figs. S4(f) and (g).
389 These results suggest that the coexistence of biopolymers and bacteria could promote the

390 formation of a thick cake layer, which can be restricted by pre-coagulation and/or sponge
391 addition.
392
393 *3.3.2. Pore blocking*
394 The internal foulants from the CMF demonstrated stronger intensities of peaks T_1, T_2, B and
395 D than peaks C and A, and this indicated that pore blocking was mainly influenced by protein-
396 and SMP-like substances, followed by humic-like substances (Fig. 6(a)). Although the PACl
397 addition could reduce intensities of peaks A, C, T_1, T_2 and B associated with humic- and protein-
398 like substances somewhat, SMP-like substances as represented by peak D were still clearly
399 visible (Fig. 6(b)). This indicated that some protein- and SMP-like substances, which could be
400 deposited and/or accumulated in the membrane pores, were removed in the P-MF. Subsequently,
401 the combined addition of PACl and sponge notably eliminated all peaks related to protein-,
402 SMP- and humic-like substances in the P-SMF in comparison to other MF systems (Fig. 6(c)).
403 Apart from this, the location of peaks T_1 and T_2 in EEM spectra of organics extracted from the
404 membrane pores in both of the P-MF and P-SMF, were blue-shifted (20-30 nm) to shorter
405 wavelengths along the emission axis. A blue shift is associated with the elimination of particular
406 functional groups (e.g. carbonyl, hydroxyl and amine), or less evidence of π-electron systems,
407 and furthermore reduced the number of aromatic rings and conjugated bonds in a chain structure
408 (Swietlik et al., 2004).
409 The SEC results (Fig. 7) further suggested that biopolymers and humic substances were
410 deposited in large numbers in the membrane pores of the CMF. The pre-coagulation process
411 reduced these foulants to some degree in the P-MF. Further addition of sponge in the P-SMF
412 substantially reduced adsorption of larger MW organics (biopolymers and humic substances)

413 into the membrane pores through adsorption and biodegradation. Since the majority of small
414 MW organics penetrated the membrane pores and formed part of the cake layer (as discussed in
415 Sections 3.2 and 3.3.1), they only remained in the membrane pores in small amounts. The
416 coagulation process could not effectively remove small MW organic matter, while adding
417 sponge in the P-SMF prompted a substantial reduction in these organic materials, thus producing
418 the lowest R_P.
419 **Fig. 6.**
420 **Fig. 7.**
421
422 In this study, the hydrophilicity of organic matter plays a key role in membrane fouling. As
423 shown in Fig. 8, the CMF eliminated about 43% of the hydrophilic organic matter, while the
424 various concentrations of either strong hydrophobic and/or weak hydrophobic fractions slightly
425 changed in the effluent sample (Table S1). As the membrane module used in this study
426 comprised hydrophilic PVDF membranes, hydrophilic organic matter was more easily deposited
427 and/or adsorbed into the membrane pores. It resulted in the severest membrane pore blocking
428 and the highest R_P in the CMF. After pre-coagulation by the PACl, the proportions of strongly
429 hydrophobic and weakly hydrophobic compounds were reduced by 57.37 ± 2.94% and 50.13 ±
430 2.61%, respectively. Both the P-MF and CMF effluents displayed similar levels of hydrophilic
431 organic matter, which suggested the pre-coagulation process was better at removing strongly
432 hydrophobic and some weakly hydrophobic matter than hydrophilic organic matter (Matilainen
433 et al., 2010), thus giving rise to relatively higher R_P in the P-MF. The considerable increase in
434 the removal of strongly hydrophobic, weakly hydrophobic and hydrophilic fractions of organic
435 matters (> 70%) was obtained for the P-SMF effluent. It demonstrated that when compared to the

436 P-MF, the combined addition of sponge and PACl noticeably eliminated hydrophobic and
437 hydrophilic organic components, and thus proved to be more effective in ameliorating pore
438 blocking as indicated by the lowest R_P.

439 **Fig. 8.**

440

441 *3.4. Microbial communities during the operational period*

442 The microbial community in the suspended sludge (SS), cake sludge (CS) and attached
443 biomass of the sponge (ABS) in all MF systems was investigated, in order to explain the effects
444 of pre-coagulation and/or sponge addition on microbial community varieties.

445 At the phylum level (Fig. 9(a)), the microbial community in all MF systems was dominated
446 by *Proteobacteria* in SS (43.33-56.51%) and in CS (40.88-55.23%), which proved to be more
447 abundant in the CMF and P-MF. *Proteobacteria* as a group of Gram-negative bacteria possessed
448 bacterial lipopolysaccharides located on their outer surface as the major components, which
449 enabled bacteria to more easily be deposited on the membrane surface (Tang et al., 2016). Thus
450 more abundant *Proteobacteria* in the CMF and P-MF might be responsible for the more severe
451 membrane fouling. Additionally, all samples were represented by *Bacteriodetes*, which
452 accounted for smaller proportions of total bacterial phylum in the CMF (13.36% (SS), and 18.62%
453 (CS)), and the P-MF (18.67% (SS), and 19.08% (CS)) than those in the P-SMF (28.4% (SS),
454 27.76% (CS), and 17.33% (ABS)). Since *Bacteriodetes* were related to the degradation of
455 carbohydrates and proteins (Buchanana and Gibbens, 1984), larger amounts of biopolymers in
456 the CMF and P-MF could be partially ascribed to fewer *Bacteroidetes*. Other subdominant phyla
457 in all samples were *Nitrospirae* (10.62-27.78%), followed by *Acidobacteria* (0.42%-9.52%),
458 *Actinobacteria* (0.34%-4.71%), *Gemmatimonadetes* (0.46%-2.64%), *Verrucomicrobia* (0.46%-

2.37%), *Chloroflexi* (0.23%-4.14%) and *Ignavibacteriae* (0.38%-4.27%). Previous studies have reported large amounts of *Actinobacteria* as filamentous bacteria in the MBR, in activated sludge processes and when using membrane biofilm (Miura et al., 2007a; Kwon et al., 2011). *Actinobacteria* occupied a larger proportion of the total bacterial community in SS samples of the CMF (4.71%), followed by the P-MF (3.29%), and P-SMF (2.71%). This could be another possible reason for the highest fouling rate in the CMF. PACl and/or sponge addition stimulated an increase in *Chloroflexi* from 1.74% to 3.16%, and 4.14% in SS, respectively. *Chloroflexi* demonstrated its capacity for degradation of the SMP including soluble carbohydrates and cellular materials (Miura et al., 2007b). Thus less SMP in the P-MF and P-SMP might be ascribed to a larger amount of *Chloroflexi*.

Fig. 9.

At the class level (Fig. 9(b)), *Nitrospira* was observed in the 10.37%-28.76% range in all samples. *Betaproteobacteria* and *Gammaproteobacteria* which were attributed to phylum *Proteobacteria* ruled the microbial community with a relative abundance of 18.08%-36.70% in the CMF, and 15.35%-33.87% in the P-MF. These amounts were higher than those reported for the P-SMF (9.21%-26.57%). *Betaproteobacteria* and *Gammaproteobacteria* have been often reported as the prominent groups in membrane systems for wastewater treatment (Duan et al., 2009; Fu et al., 2017; El-Fadel et al., 2017). *Gammaproteobacteria* promoted their attachment to the membrane surface, which induced biofouling (Gao et al., 2014a). *Alphaproteobacteria* could initiate biofouling by pre-attaching to a new membrane and subsequent colonization on the membrane, which promoted the attachment of many more other species on the membrane (Gao et al., 2011b). In addition, it emerged that *Alphaproteobacteia* and *Deltaproteobacteria* were

482 better enriched in SS of the CMF (5.03% and 6.56%, respectively) and P-MF (3.67% and 5.86%,
483 respectively) than the P-SMF (2.59% and 4.02%, respectively). Overall, the highest relative
484 abundance of *Alphaproteobacteria*, *Betaproteobacteria* and *Gammaproteobacteria* was
485 associated with the severest membrane fouling in the CMF. On the other hand, more abundant
486 *Sphingobacteriia* were detected in the P-SMF (14.35% in SS, 21.01% in CS and 3.61% in ABS)
487 in comparison to the CMF (9.22% in SS and 15.57% in CS) and P-MF (6.72% in SS and 12.30%
488 in CS). Biopolymers were evidently less abundant in the P-SMF, which might be due to the fact
489 that some members belonging to *Sphingobacteriia* favored the degradation of macromolecules,
490 i.e. polysaccharides, proteins (Fu et al., 2017).
491 The bacterial community structure was further analyzed at genus level to clarify different
492 membrane fouling behaviors in the three MF systems (Fig. 9(c)). The bacterial community of CS
493 was similar to that of SS, indicating the microbial community in CS mainly derived from SS.
494 Since this study was conducted under conditions of infinite SRT, *Nitrospira* as the dominant
495 NOB member could be enriched in SS (24.13%-30.12%) without sludge withdrawal and ABS
496 (28.76%). As well, one member of AOB, genus *Nitrosomonas* accounted for 3.22%-5.36% of the
497 SS and 12.74% of ABS samples, respectively. As a result, the nitrification process proved to be
498 effective in all MF systems. The relative abundance of *Zoogloea* and *Rhizobium* in SS samples
499 was higher for the P-SMF (6.17% and 6.23%, respectively) than the P-MF (2.76% and 3.54%,
500 respectively) and CMF (0.57% and 1.36%, respectively). Additionally, *Zoogloea* and *Rhizobium*
501 as denitrifying microorganisms were highly enriched in ABS samples (2.79% and 8.59%,
502 respectively) of the P-SMF with preferential accumulation of *Acidovorax* (denitrifiers) (Nielsen
503 et al., 2009). Consequently, the P-SMF realized more effective denitrification than the other MF
504 systems. In the CMF, *Thiothrix* was strongly enriched in SS (20.76%) as the second most

505 abundant genus, members of which caused serious membrane fouling, biofilm formation and
506 irreversible fouling. This process also induced the occurrence of filament-caused sludge bulking
507 (Gao et al., 2014a and 2014b). Moreover, the genus *Xanthomonas* constituting 10.89% and 6.69%
508 of the total bacterial community in SS and CS of the CMF, respectively, was the biopolymer-
509 producing bacteria, which could also significantly affect membrane fouling development (Jinhua
510 et al., 2006).

511 Some other bacteria were also detected in the CMF, for example *Comamonas* (2.36% (SS)
512 and 5.64% (CS)) and *Ferruginibacter* (3.58% (SS) and 3.67% (CS)). These were easily
513 deposited on aerobic membrane surfaces with the accumulation of dense organic matter (Xiong
514 et al., 2016). In contrast, the relative abundance of *Thiothrix*, *Xanthomonas, Ferruginibacter* and
515 *Comamonas* was lower for the P-MF and P-SMF. Yet, on the other hand, it was observed that the
516 combined addition of PACl and/or sponge prompted an increase in proportions of
517 *Flavobacterium,* especially for CS (2.51% for P-MF and 3.62% for P-SMF) and ABS samples
518 (3.79%). Bacteria in the *Cytophagae-Flavobacteria* group belonging to *Flavobacterium* was
519 reported to utilize protein, N-acetylglucosamine and chitin, and degrade part of the high
520 molecular mass fraction of the DOM (Ma et al., 2013a). These results indicate that PACl and/or
521 sponge addition could mitigate membrane fouling in MF systems.

522 The abundance of a microbial community involved in membrane fouling reduction was also
523 compared between the P-MF and P-SMF. It has been reported that *Zoogloea* (Class
524 *Betaproteobacteria*) made possible the formation of characteristic cell aggregates which were
525 embedded in extracellular gelatinous matrices, since zoogloeal matrices were favorable for
526 sludge flocculation. Additionally, they adsorbed fine particles which ameliorated membrane
527 fouling (Ma et al., 2013b). Therefore, less membrane fouling in the P-SMF might be related to

528 higher enrichment in species of *Zoogloea* in SS at 6.17% compared to that in the P-MF (2.76%).
529 Larger proportions of *Amaricoccus* (Class *Alphaproteobacteria*), which reduced polysaccharides
530 by using polysaccharides as substrate (Maszenan et al., 1997), were discovered in the P-SMF
531 (8.63% (SS), 7.86% (CS) and 5.37% (ABS)) at amounts much larger than in the P-MF (3.62%
532 (SS) and 5.63% (CS)). *Reyranella* (Class *Alphaproteobacteria*) is a kind of protein degrader
533 (Inaba et al., 2017) that exhibited higher relative abundance of 5.29%-7.32% in the P-SMF
534 compared to the P-MF (4.13%-5.46%). Thus, higher abundance of *Amaricoccus* and *Reyranella*
535 in the P-SMF could contribute to the reduction of biopolymers (polysaccharides and proteins),
536 resulting in slower membrane fouling development than the P-MF.
537 It was found that the diversity of microbial communities was highest in the P-SMF,
538 including *Flexibacter* (Class *Sphingobacteriia*) and *Sphingobium* (Class *Alphaproteobacteria*) at
539 the relative abundance of 3.74% and 3.45% (SS), 5.65% and 6.36% (CS) and 6.54% and 6.12%
540 (ABS), respectively. These genera could degrade high-molecular DOC fractions and humic
541 matter, and break refractory DOC and aromatic compounds (Basta et al., 2005; Hutalle-
542 Schmelzer et al., 2010). The genus *Woodsholea* (Class *Alphaproteobacteria*) for hydrolysis of
543 organic substrates (Abraham et al., 2004) was better enriched in SS at 0.36% and ABS at 2.61%
544 in the P-SMF, which have might partly contributed to the removal of small amount of MW
545 organic matter. Moreover, these low MW organics could be eliminated by some unclassified
546 bacteria attributed to Class *Alphaproteobacteria* in the P-SMF (Cottrell and Kirchman, 2000).
547 Overall, the least membrane fouling in the P-SMF was explained by a shrinkage in the size of the
548 bacterial community causing biofouling or release of biopolymers. Conversely, an increase
549 occurred in the proportions and diversity of microbial community for degrading fouling materials
550 in the suspended sludge and cake layer.

551

552 *3.5. Economic feasibility of the P-SMF and recommendation for future studies*

553 The initial investment includes membrane fibers (< $5), reactors (< $30), and aeration
554 supplied by the public laboratory. Moreover, the cost of sponge used in this study was extremely
555 low (< $0.1). The selected PACl at low dosage was a cost-effective coagulant. As the P-SMF
556 could be operated for almost 90 days, it was not necessary for chemical cleaning and membrane
557 replacement to be frequently conducted. Additionally, the reagents for chemical cleaning (i.e.
558 HCl, NaOH and NaClO) are not expensive. Overall, the P-SMF system was an economically
559 feasible option for drinking water treatment.

560 Both HRT and filling ratio of sponge should be optimized so that the P-SMF system
561 performs better, in other words, it can operate for a much longer time. Detailed analyses should
562 focus on the specific genera affiliated with class *Alphaproteobacteria,* which is associated with
563 the removal of low MW organic matter. Duplicate experiments for this study should be
564 conducted to test whether the presence of microorganisms for the removal of humic substances is
565 successful or otherwise. Furthermore, the enrichment of microorganisms for the removal of low
566 MW organics and humic substances in the P-SMF constitutes a promising research topic. Further
567 studies should evaluate the performance of the P-SMF system for treating various drinking water
568 sources (e.g. ground water, surface water, river water). The effects of micropollutants (e.g.
569 pharmaceuticals, personal care products (PPCPs) and endocrine disrupting compounds (EDCs)
570 on the performance of the P-SMF system should be investigated so that the possibilities of
571 altering the microbial community during the treatment of drinking water can be assessed.

572

573 **4. Conclusions**

574 This study focused on the feasibility of the P-SMF during a long-term experiment involving
575 the treatment of drinking water. Enhanced nutrient, DOC and UV_{254} removals were realized by
576 PACl pre-coagulation and sponge addition in the P-SMF compared to the P-MF and CMF.
577 Larger MW organics (biopolymers and humic substances) and hydrophilic organic matter in the
578 CMF accounted for the fastest membrane fouling development, and the most serious cake layer
579 formation and pore blocking. The P-MF only eliminated larger MW organic matter, while the
580 coupled process of pre-coagulation by PACl and sponge addition in MF system considerably
581 enhanced the removal of larger and small MW organics, and hydrophilic organic matter. The P-
582 SMF indicated the most diverse microbial community, especially in the presence of *Zoolgloea*,
583 *Amaricoccus*, *Reyranella*, *Flexibacter* and *Sphingobium* and some microorganisms belonging to
584 *Alphaproteobacteria* for the reduction of fouling materials. Finally, it can be stated here that the
585 P-SMF demonstrated its superiority in alleviating membrane fouling and reducing R_P and R_C.
586

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593

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Table titles

Table 1. Water quality of influent and effluent samples from the P-SMF, P-MF and CMF

Parameters	Influent samples	P-SMF		P-MF		CMF	
		Effluent	Removal efficiencies	Effluent	Removal efficiencies	Effluent	Removal efficiencies
NH_4-N (mg/L)	3.68 ± 0.69	0.10 ± 0.02	97.16 ± 2.98%	0.29 ± 0.03	92.12 ± 3.26%	0.52 ± 0.05	85.87 ± 4.78%
NO_3-N (mg/L)	2.84 ± 1.27	0.808 ± 0.36	71.55 ± 1.36%	3.06 ± 0.24	—	3.03 ± 0.37	—
NO_2-N (mg/L)	0.125 ± 0.028	0.039 ± 0.001	68.42 ± 3.65%	0.058 ± 0.005	53.61 ± 5.83%	0.060 ± 0.46	52.03 ± 7.31%
PO_4-P (mg/L)	0.098 ± 0.006	0.004 ± 0.002	95.72 ± 4.61%	0.007 ± 0.002	92.54 ± 6.05%	0.066 ± 0.008	32.16 ± 7.24%
Turbidity (NTU)	3.23 ± 1.26	0.04 ± 0.01	98.76 ± 1.52%	0.05 ± 0.03	98.45 ± 1.36%	0.05 ± 0.03	97.83 ± 1.69%
Total bacterial concentration (CFU/mL)	(5.31 ± 1.42) × 10^5	3 ± 1	100%	4 ± 2	100%	5 ± 2	100%
UV254 (cm^{-1})	0.087 ± 0.008	0.022 ± 0.005	74.71 ± 3.67%	0.042 ± 0.005	52.16 ± 4.92%	0.075 ± 0.006	14.22 ± 5.76%
DOC (mg/L)	5.29 ±1.21	1.68 ± 0.48	68.30 ± 5.36%	2.76 ± 0.26	47.83 ± 4.32%	4.36 ± 0.49	17.52 ± 4.49%

Table 2. EPS and SMP compositions of mixed liquor in the P-SMF, P-MF and CMF at different TMP ranges

Concentrations [a]	P-SMF		P-MF		CMF	
	TMP ≤ 12 kPa	TMP 13-35 kPa	TMP ≤ 12 kPa	TMP 13-35 kPa	TMP ≤ 12 kPa	TMP 13-35 kPa
EPS_C (mg/L)	1.85-2.75	2.84-3.56	3.08-5.16	5.23-7.98	3.23-5.23	5.59-8.26
EPS_P (mg/L)	2.52-3.51	4.17-4.56	2.92-4.64	5.03-6.67	5.30-6.87	7.21-8.96
EPS (mg/L)	4.37-6.26	7.01-8.12	6.00-9.80	10.26-14.65	8.53-12.10	12.80-17.22
SMP_C (mg/L)	0.57-0.88	1.04-1.36	1.26-3.05	3.19-4.83	1.68-3.42	3.63-5.18
SMP_P (mg/L)	0.25-0.86	1.05-1.16	0.87-1.31	1.27-1.64	1.14-1.84	2.08-3.69
SMP (mg/L)	0.82-1.74	2.09-2.52	2.13-4.36	4.46-6.47	2.82-5.26	5.71-8.87

[a] EPS_C, polysaccharides based EPS; EPS_P, proteins based EPS; SMP_C, polysaccharides based SMP; SMP_P, proteins based SMP

Table 3. Fouling resistance distribution in the P-SMF, P-MF and CMF

Resistance distribution	P-SMF		P-MF		CMF	
	$10^{12} \times m^{-1}$	% of R_T	$10^{12} \times m^{-1}$	% of R_T	$10^{12} \times m^{-1}$	% of R_T
Total, R_T	1.74		3.47		4.86	
Cake layer, R_C	0.82	47.25	1.55	44.70	2.19	45.16
Pore blocking, R_P	0.21	12.02	1.21	34.74	1.96	40.32
Clean membrane, R_M	0.71	40.73	0.71	20.56	0.71	14.52

Figure captions

Fig. 1. TMP variation over operational time for the CMF, P-MF and P-SMF

Fig. 2. MW distribution of organic matter of influent and effluent for the CMF, P-MF and P-SMF

Fig. 3. EEM fluorescence spectra of EPS of mixed liquor from the CMF (a), P-MF (b) and P-SMF (c)

Fig. 4. EEM fluorescence spectra of organic matter of cake layer from the CMF (a), P-MF (b) and P-SMF (c)

Fig. 5. MW distribution of organic matter from cake layer for the CMF, P-MF and P-SMF

Fig. 6. EEM fluorescence spectra of organic matter extracted from membrane pores of the CMF (a), P-MF (b) and P-SMF (c)

Fig. 7. MW distribution of organic matter from membrane pores for the CMF, P-MF and P-SMF

Fig. 8. Removals of hydrophobic and hydrophilic components of organic matter by different MF systems

Fig. 9. Distribution of microbial community in suspended sludge (SS(CMF), SS(P-MF), SS(P-SMF)), cake sludge (CS(CMF), CS(P-MF) and CS(P-SMF)) and ABS at the phylum (a), class (b) and genus (c) levels

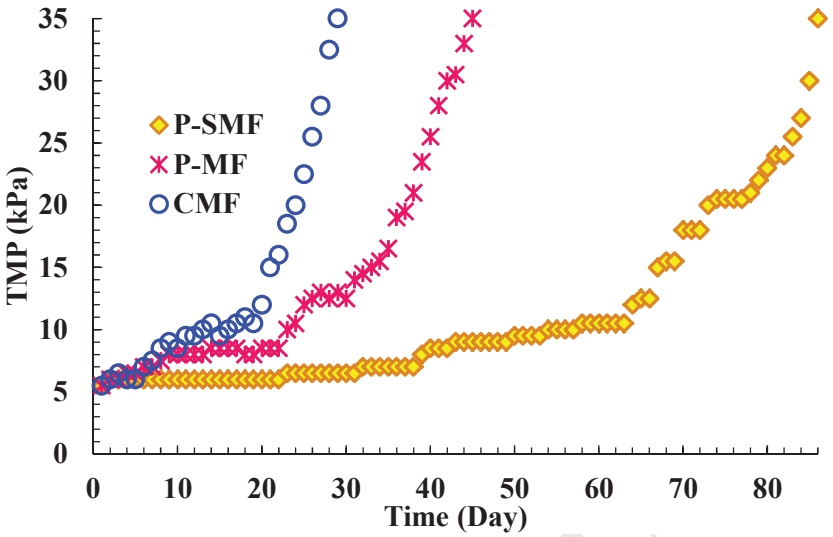


Fig. 1. TMP variation over operational time for the CMF, P-MF and P-SMF

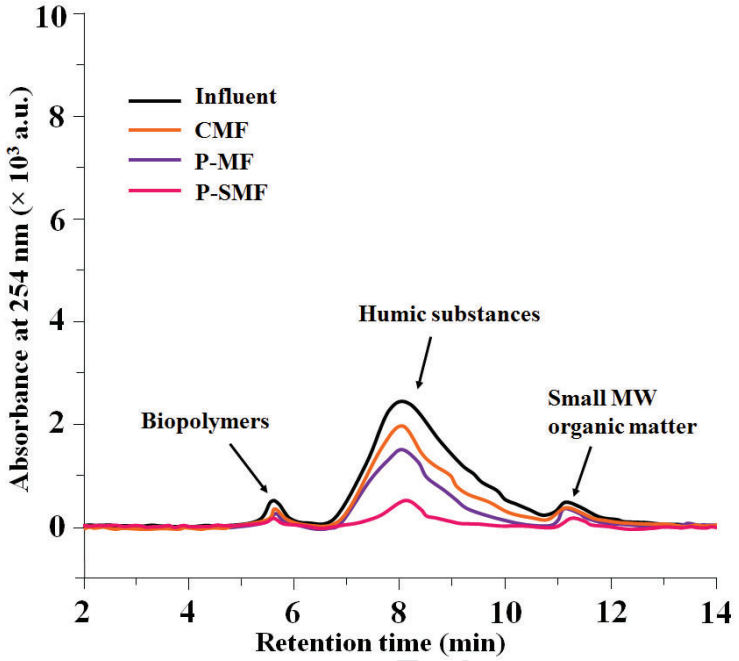
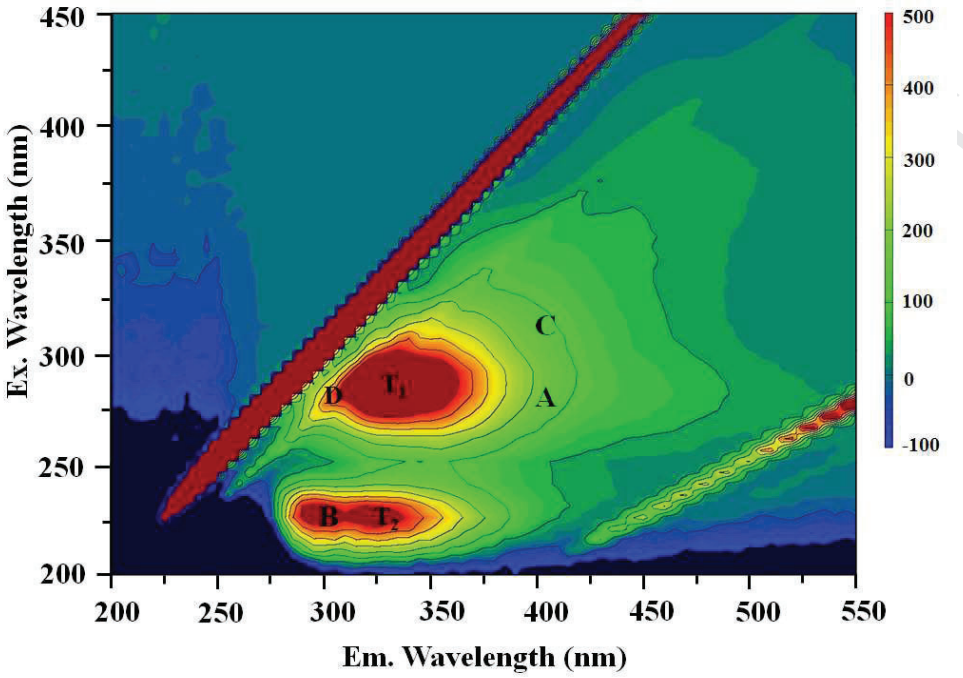


Fig. 2. MW distribution of organic matter of influent and effluent for the CMF, P-MF and P-SMF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Em. Wavelength (nm)
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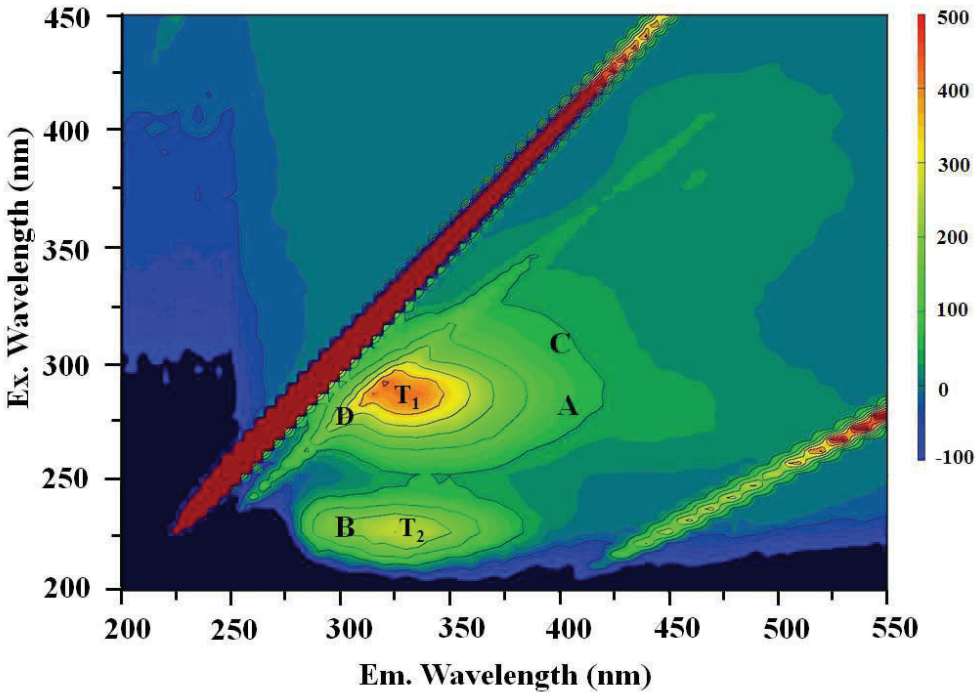
400
350
300
250
200
200
250
300
350
400
450
500
550
500
400
300
200
100
0
-100
C
D
T1
A
B
T2

(a)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Em. Wavelength (nm)
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500
400
300
200
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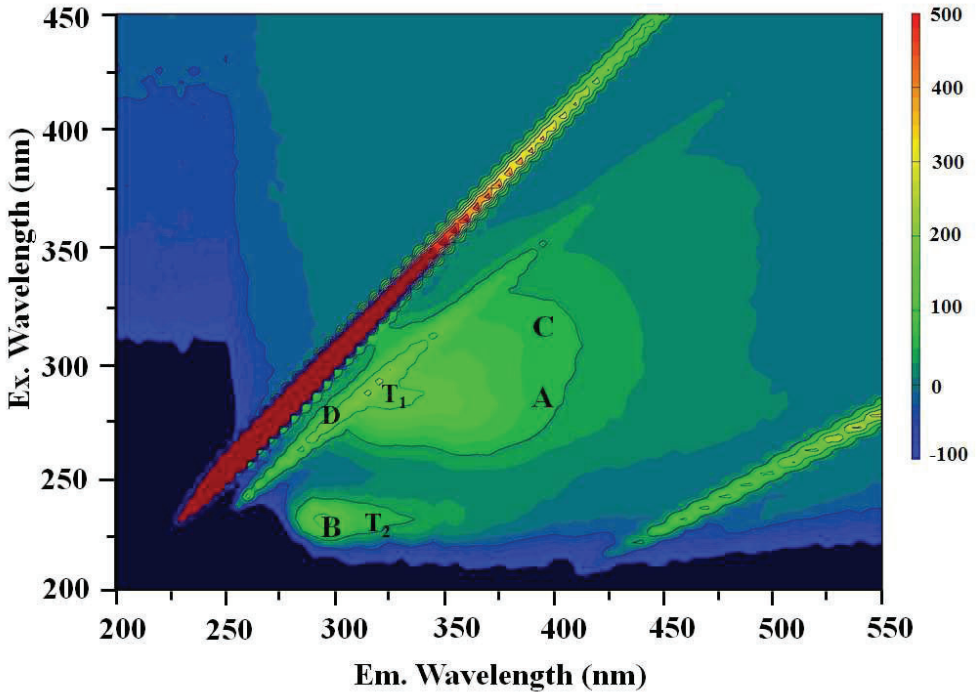
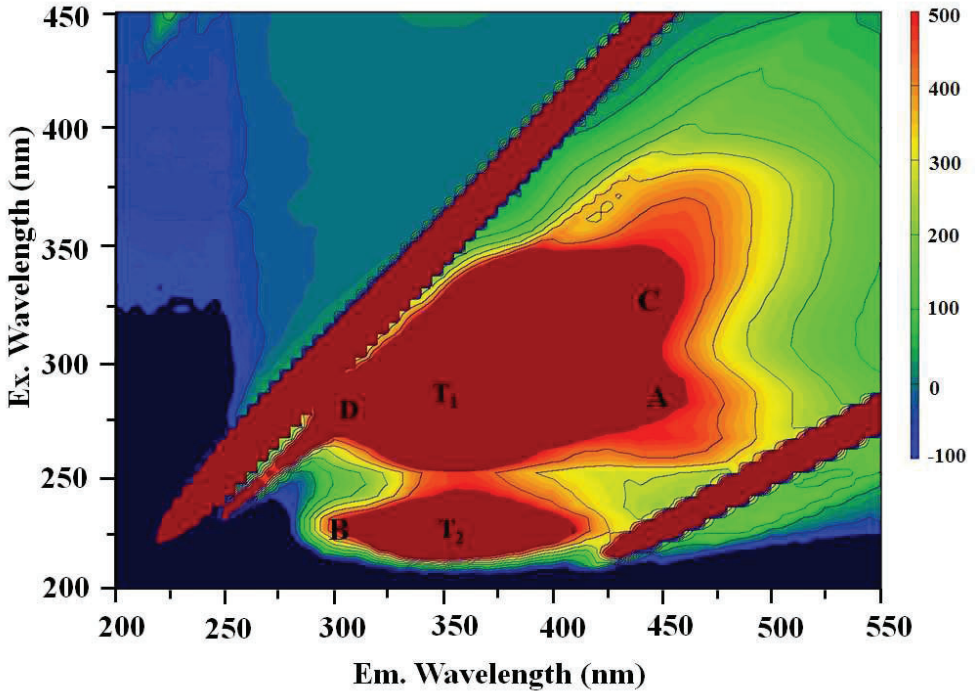
0
-100
C
D
T1
A
B
T2

(b)



(c)

Fig. 3. EEM fluorescence spectra of EPS of mixed liquor from the CMF (a), P-MF (b) and P-SMF (c)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400
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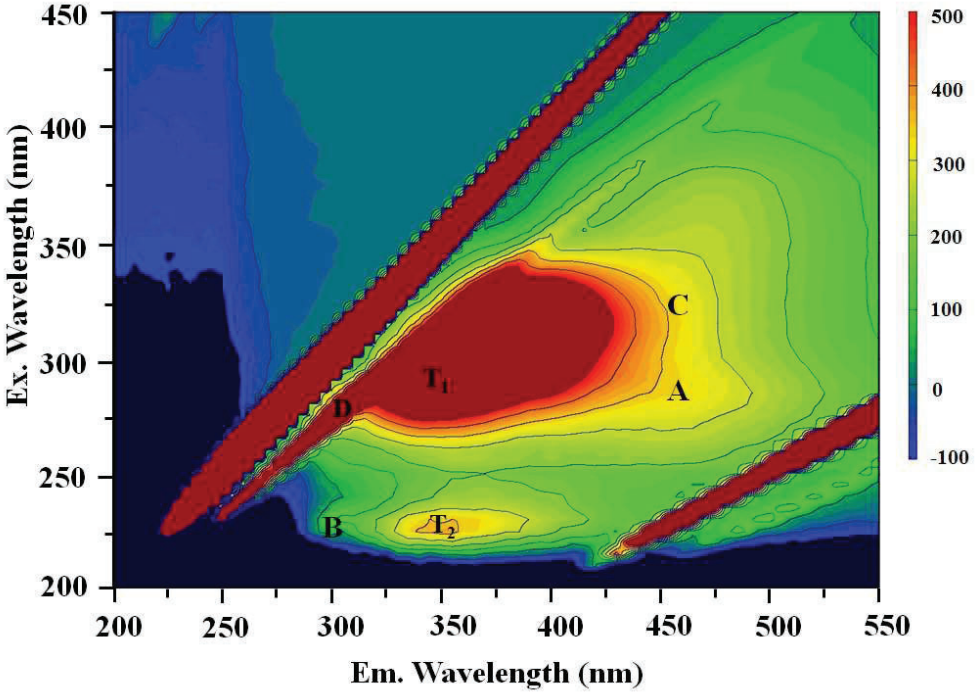
200
100
0
-100
C
A
D
T1
B
T2

(a)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Em. Wavelength (nm)
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250
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200
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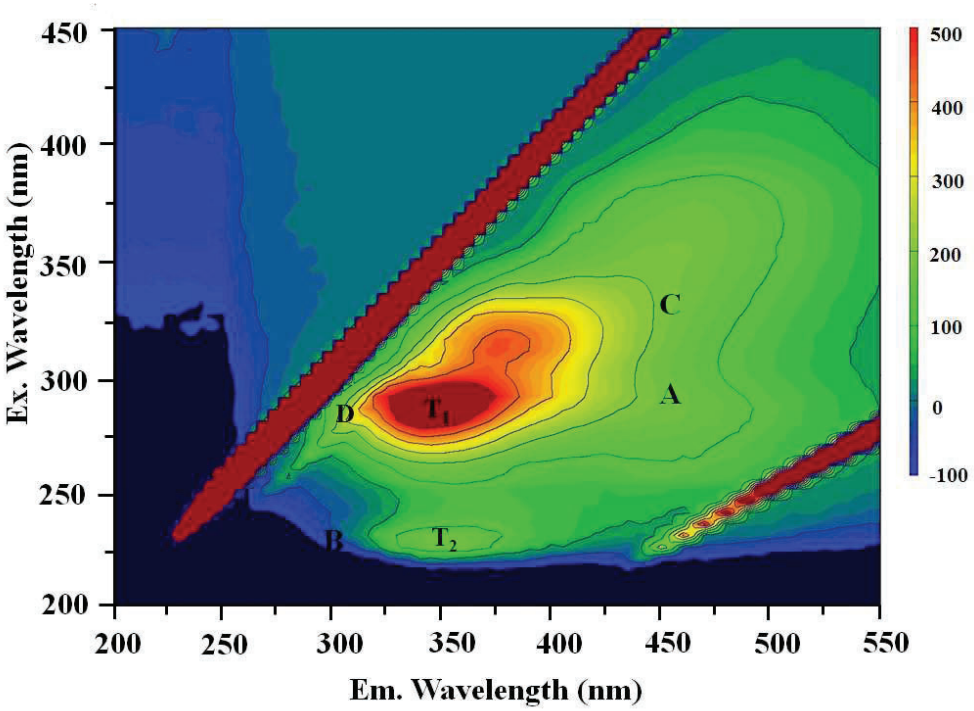
550
500
400
300
200
100
0
-100
C
A
D
T1
B
T2

(b)



(c)

Fig. 4. EEM fluorescence spectra of organic matter of cake layer from the CMF (a), P-MF (b) and P-SMF (c)

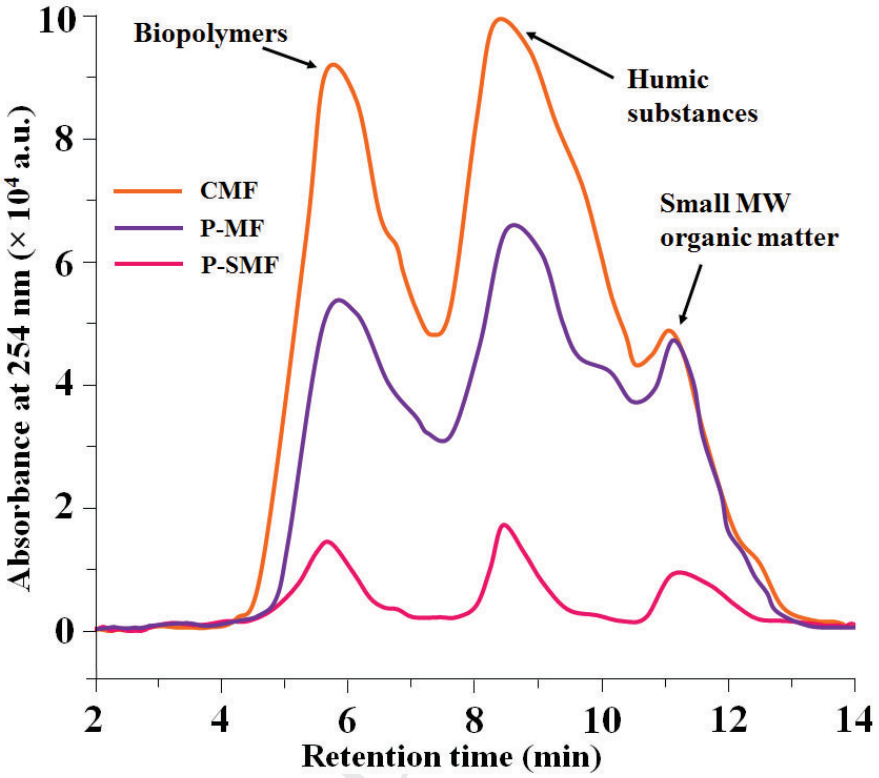
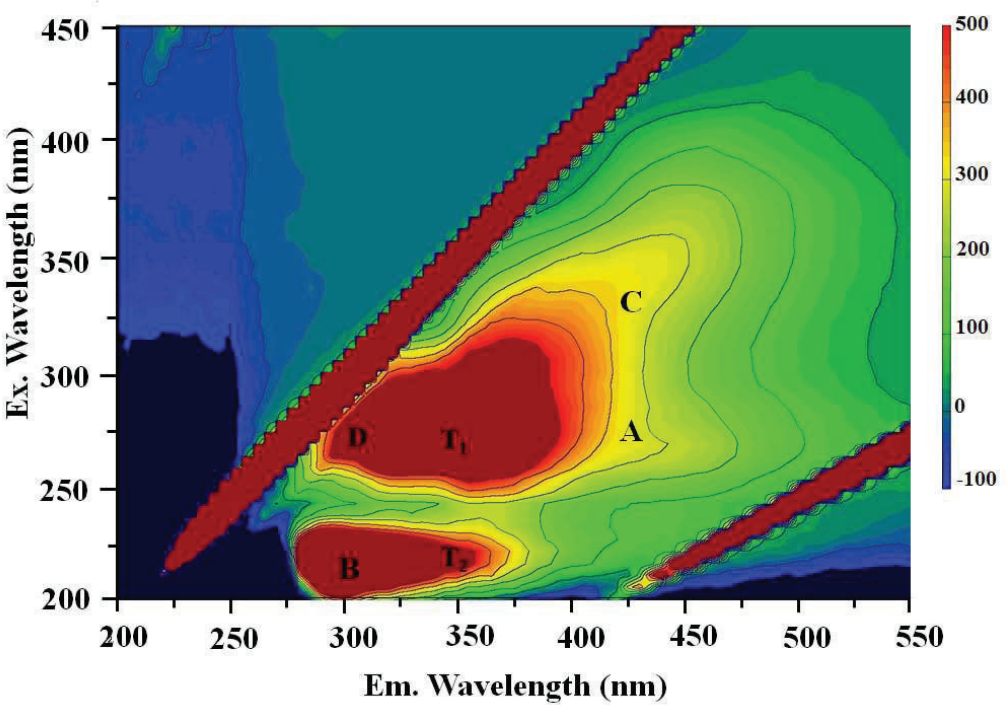


Fig. 5. MW distribution of organic matter from cake layer for the CMF, P-MF and P-SMF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Em. Wavelength (nm)
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200
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300
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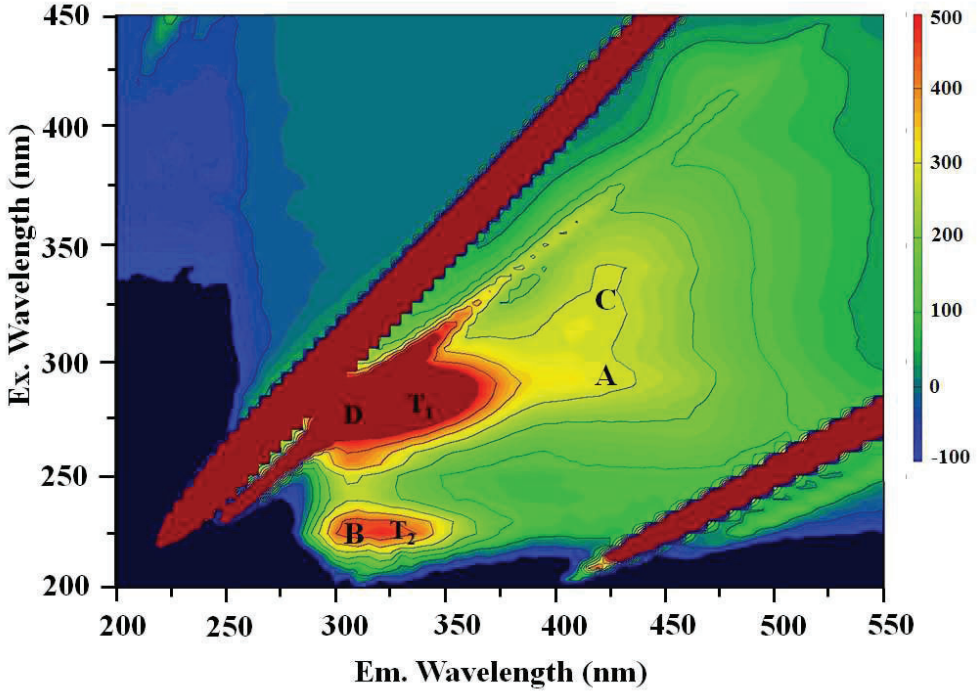
450
500
550
500
400
300
200
100
0
-100
C
A
D
T1
B
T2

(a)


Ex. Wavelength (nm)
Em. Wavelength (nm)
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400
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300
250
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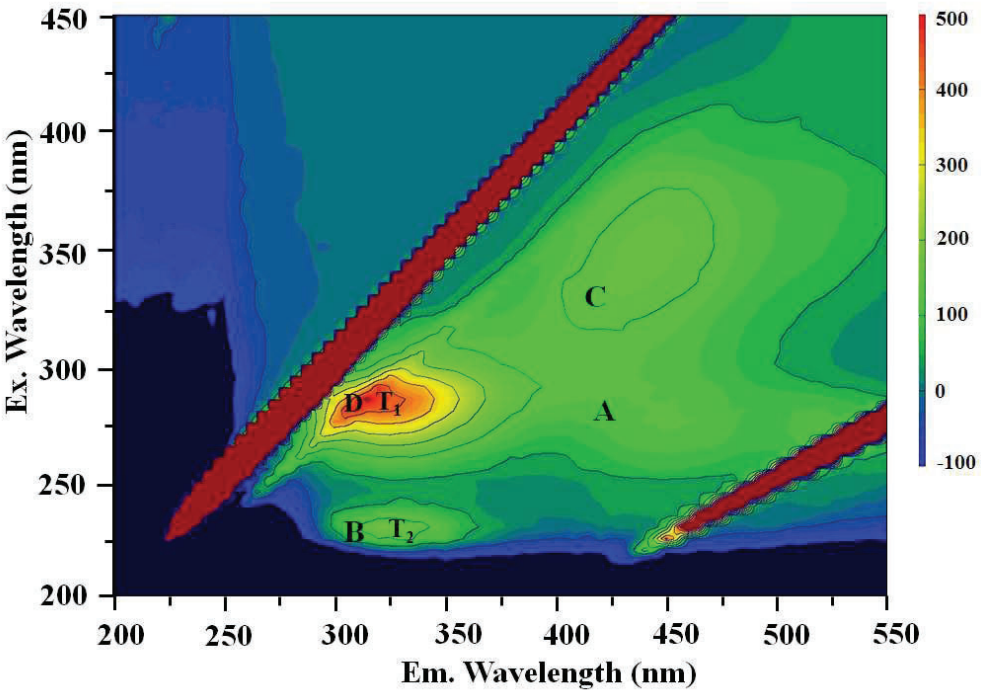
200
250
300
350
400
450
500
550
500
400
300
200
100
0
-100
C
A
D
T1
B
T2

(b)



(c)

Fig. 6. EEM fluorescence spectra of organic matter extracted from membrane pores of the CMF (a), P-MF (b) and P-SMF (c)

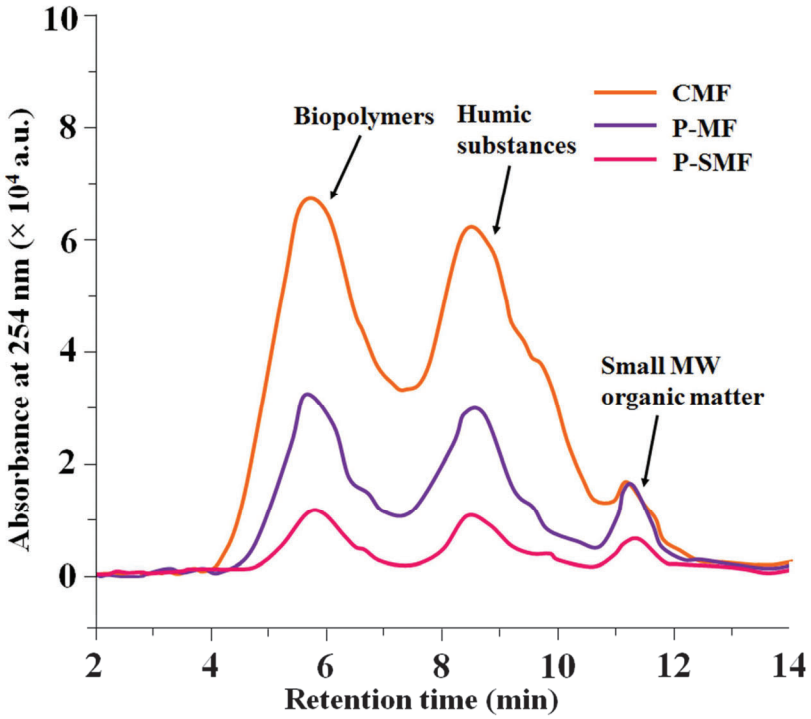


Fig. 7. MW distribution of organic matter from membrane pores for the CMF, P-MF and P-SMF

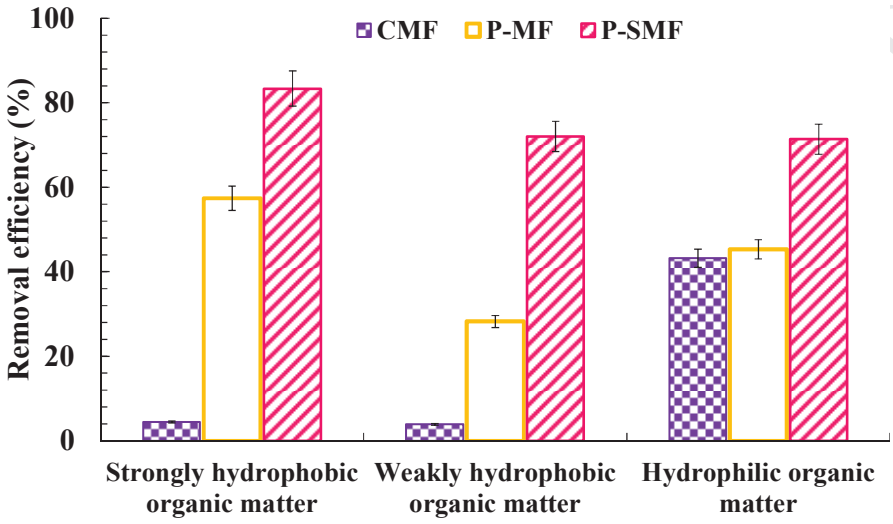
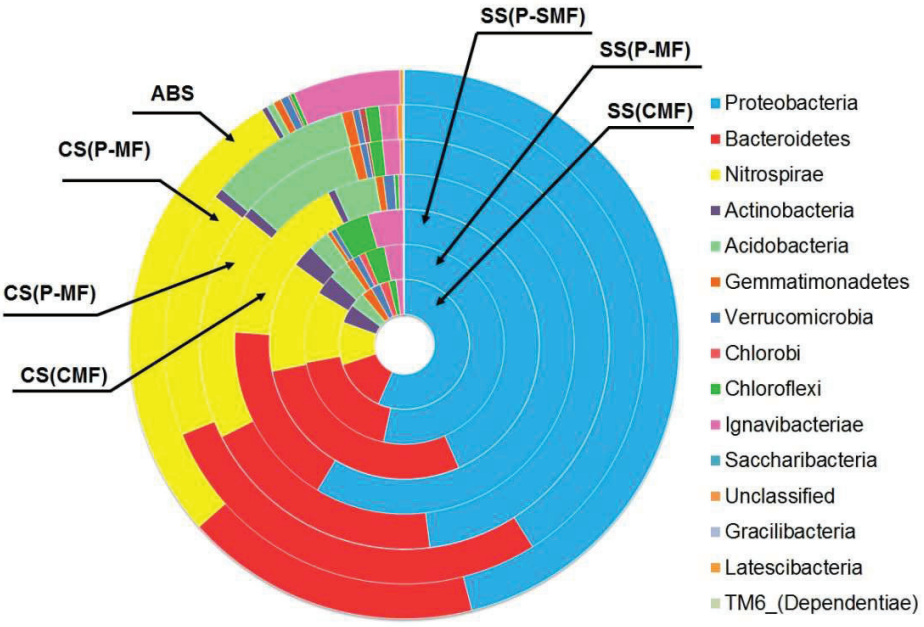
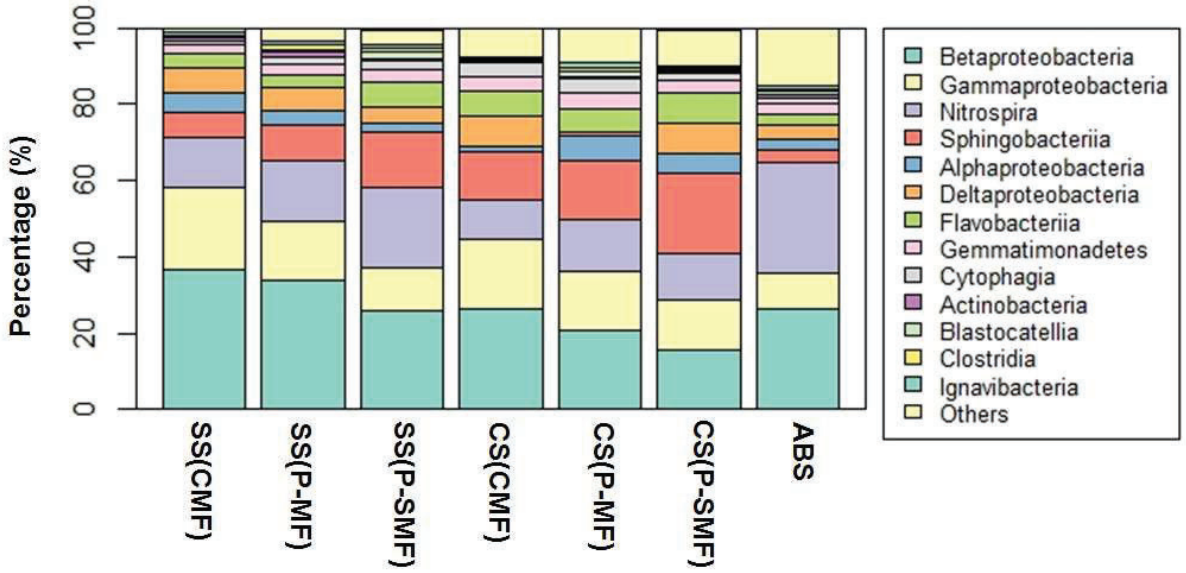


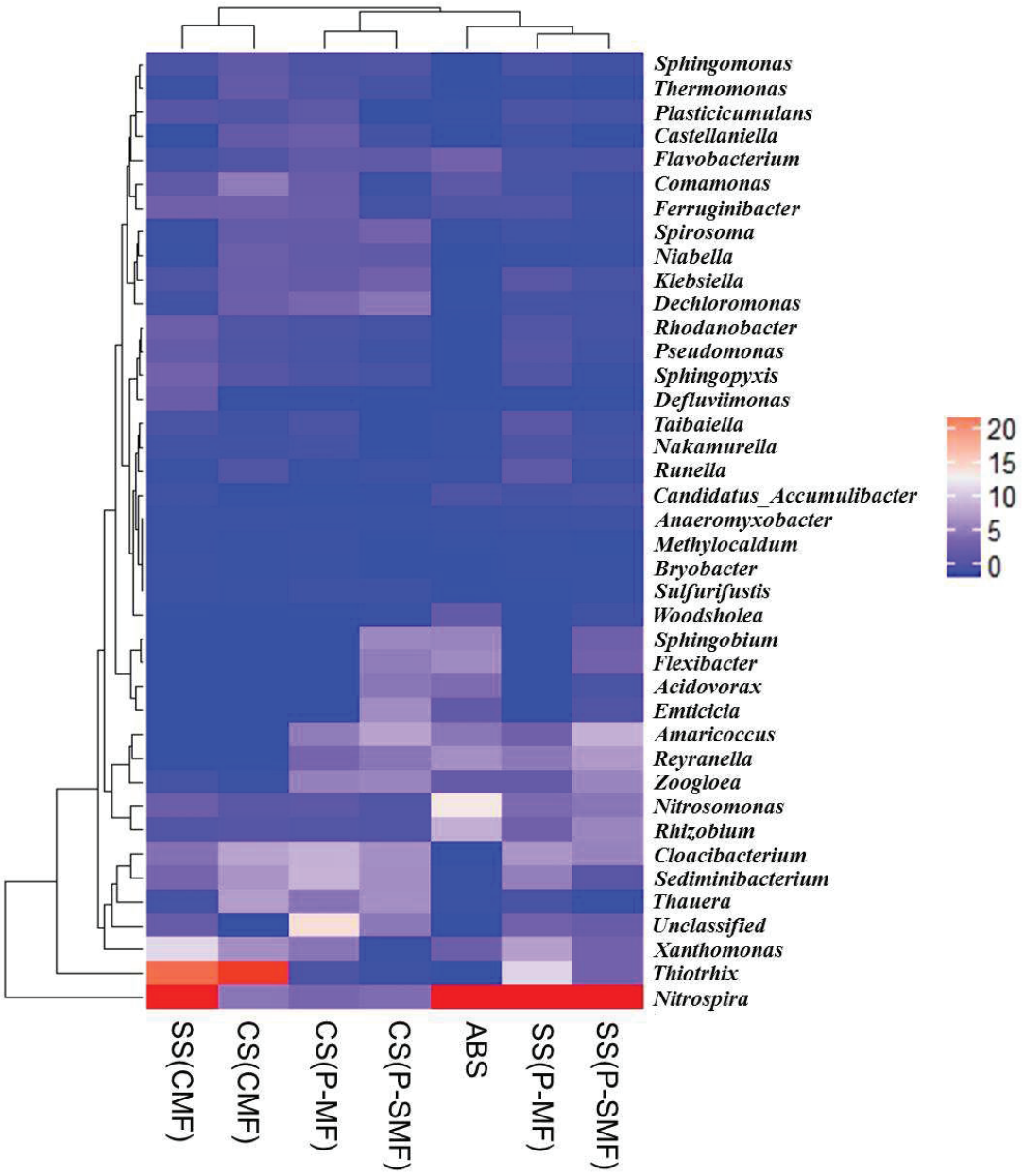
Fig. 8. Removals of hydrophobic and hydrophilic components of organic matter by different MF systems


SS(P-SMF)
SS(P-MF)
SS(CMF)
ABS
CS(P-MF)
CS(P-MF)
CS(CMF)
Proteobacteria
Bacteroidetes
Nitrospirae
Actinobacteria
Acidobacteria
Gemmatimonadetes
Verrucomicrobia
Chlorobi
Chloroflexi
Ignavibacteriae
Saccharibacteria
Unclassified
Gracilibacteria
Latescibacteria
TM6_(Dependentiae)

(a)


Percentage (%)
0
20
40
60
80
100
SS(CMF)
SS(P-MF)
SS(P-SMF)
CS(CMF)
CS(P-MF)
CS(P-SMF)
ABS
Betaproteobacteria
Gammaproteobacteria
Nitrospira
Sphingobacteriia
Alphaproteobacteria
Deltaproteobacteria
Flavobacteriia
Gemmatimonadetes
Cytophagia
Actinobacteria
Blastocatellia
Clostridia
Ignavibacteria
Others

(b)



(c)

Fig. 9. Distribution of microbial community in suspended sludge (SS(CMF), SS(P-MF), SS(P-SMF)), cake sludge (CS(CMF), CS(P-MF) and CS(P-SMF)) and ABS at the phylum (a), class (b) and genus (c) levels