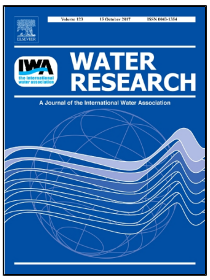
Impact of ozonation and biological activated carbon filtration on ceramic membrane fouling

Accepted Manuscript



Impact of ozonation and biological activated carbon filtration on ceramic membrane fouling

Khaled Ibn Abdul Hamid, Peter Sanciolo, Stephen Gray, Mikel Duke, Shobha Muthukumaran

PII:	S0043-1354(17)30745-5
DOI:	10.1016/j.watres.2017.09.012
Reference:	WR 13206
To appear in:	*Water Research*
Received Date:	23 May 2017
Revised Date:	24 August 2017
Accepted Date:	04 September 2017

Please cite this article as: Khaled Ibn Abdul Hamid, Peter Sanciolo, Stephen Gray, Mikel Duke, Shobha Muthukumaran, Impact of ozonation and biological activated carbon filtration on ceramic membrane fouling, *Water Research* (2017), doi: 10.1016/j.watres.2017.09.012

Impact of ozonation and biological activated carbon filtration on ceramic membrane fouling

Highlights

1. BAC improved the permeability of the CMF by removing a large proportion of biopolymer
2. O3 improved permeability and permeate quality of CMF to a greater extent than BAC
3. O3 removed biopolymers (100%) and HS (84%) to obtain greater permeability of CMF
4. Inclusion of BAC between O3 treatment and ceramic filtration was detrimental

Impact of ozonation and biological activated carbon filtration on ceramic membrane fouling

Khaled Ibn Abdul Hamid[a,b]*; Peter Sanciolo*[a,b]*; Stephen Gray*[a,b]*; Mikel Duke*[a,b]*; Shobha Muthukumaran*[a,b,*]

[a.] College of Engineering and Science, Victoria University, PO Box 14428, Melbourne, VIC 8001, Australia; E-Mail: khaled.ibnabdulhamid@live.vu.edu.au; peter.sanciolo@vu.edu.au; stephen.gray@vu.edu.au; mikel.duke@vu.edu.au; shobha.muthukumaran@vu.edu.au

[b.] Institute for Sustainability and Innovation, Victoria University, PO Box 14428, Melbourne, VIC 8001, Australia

[*] Author to whom correspondence should be addressed; E-Mail: shobha.muthukumaran@vu.edu.au Tel.: +61-3-9919-4859.

ABSTRACT

Ozone pre-treatment (ozonation, ozonisation) and biological activated carbon (BAC) filtration pre-treatment for the ceramic microfiltration (CMF) treatment of secondary effluent (SE) were studied. Ozone pre-treatment was found to result in higher overall removal of UV absorbance (UVA_{254}) and colour, and higher permeability than BAC pre-treatment or the combined use of ozone and BAC (O3+BAC) pre-treatment. The overall removal of colour and UVA_{254} by ceramic filtration of the ozone pre-treated water was 97% and 63% respectively, compared to 86% and 48% respectively for BAC pre-treatment and 29% and 6% respectively for the untreated water. Ozone pre-treatment, however, was not effective in removal of dissolved organic carbon (DOC). The permeability of the ozone pre-treated water through the ceramic membrane was found to decrease to 50% of the original value after 200 minutes of operation, compared to approximately 10% of the original value for the BAC pre-treated, O3+BAC pre-treated

water and the untreated water. The higher permeability of the ozone pre-treated water was attributed to the excellent removal of biopolymer particles (100%) and high removal of humic substances (84%). The inclusion of a BAC stage between ozone pre-treatment and ceramic filtration was detrimental. The O3+BAC+CMF process was found to yield higher biopolymer removal (96%), lower humic substance (HS) component removal (66%) and lower normalised permeability (0.1) after 200 minutes of operation than the O3+CMF process (86%, 84% and 0.5 respectively). This was tentatively attributed to the chemical oxidation effect of ozone on the BAC biofilm and adsorbed components, leading to the generation of foulants that are not generated in the O3+CMF process. This study demonstrated the potential of ozone pre-treatment for reducing organic fouling and thus improving flux for the CMF of SE compared to O3+BAC pre-treatment.

Keywords: ozonation, BAC filtration, ceramic membrane, secondary effluent, biopolymers, humic substances.

1 Introduction

The application of MF membranes to treat SE from wastewater treatment plants has focused on membranes made of polymeric materials (Lehman and Liu 2009). Recently, however, the application of membranes made of ceramic materials in wastewater treatment is growing. Although the price per square meter of active filtration layer are typically higher for ceramic membranes than for polymeric membranes (Ciora Jr and Liu 2003), the ability of ceramic membrane to effectively pair with different pre-treatment options have made them an emerging concept in the wastewater treatment technology to offset this higher material cost (Dow et al. 2013). One well known example is coagulation pre-treatment which aggregates particulates prior to membrane filtration, preventing

particles from entering into membrane pores and depositing on the membrane surface (Gaulinger 2007, Hendricks 2006). Thus, the permeate quality in the MF system is enhanced by coagulation pretreatment (Carroll et al. 1999, Hiraide 1992, Mo and Huang 2003, Vickers et al. 1995, Xia et al. 2004).

Combination of coagulation and membrane filtration can improve not only the permeability of membrane but also the quality of produced water (Jang et al. 2006). Coagulation pretreatment in combination with ceramic MF was observed to reduce the rate of cleaning operations (Mallevialle et al. 1996). However, it was observed in a study that the irreversible fouling of low MW polysaccharide compounds cannot be reduced by coagulation (Lahoussine-Turcaud et al. 1990). The unfavorable results may occur when coagulation is applied prior to polymeric MF membranes (Mallevialle et al. 1996). The partial removal of natural organic matter (NOM) by adding coagulant chemicals result in suppressing fouling in MF membranes. As the chemical residuals are required to be minimized to ensure the safe water quality, incorporation of ozonation can be an alternative solution to reduce membrane fouling.

When used as a pre-treatment of MF ceramic membrane, ozone can provide higher permeate flux without any damage of ceramic membrane (Lehman and Liu 2009). Higher flux leads to lower capital cost and therefore is a key part in the affordability of ceramic membranes for water treatment. The higher permeate flux obtained by ozone pre-treatment can be attributed to the significant reduction of membrane fouling which is strongly dependent upon ozone concentration and hydrodynamic conditions (Kim et al. 2008, Yu et al. 2016b). During characterization of NOM in a combined ozone-ceramic membrane process it was observed that the flux increase (25%) for ozone pre-treated water was attributable to the decomposition of NOM (Park et al. 2012). Another study on the effect of ozonation and CMF of SE (pilot plant in Chino, California) showed that

ozone pre-treatment is effective at degrading colloidal NOM which is likely responsible for the majority of membrane fouling (Lehman and Liu 2009). Ozone was also found to improve the permeate flux of samples taken from Lake Lansing (Haslett, Michigan) through a titania-coated ceramic membrane, which was attributed to the formation of •OH or other radicals at the membrane surface and oxidative degradation of foulants on the membrane surface (Karnik et al. 2005).

Ozone pre-treatment can, however, also worsen membrane fouling (Zhu et al. 2009). The negative effect of ozone has been attributed to the increase in the quantity of large organic molecules after ozonation. Ozone pre-treatment can kill microorganisms in the feedwater, thereby releasing cell debris which can foul the membrane. Moreover, ozone pre-treatment can break down high molecular weight (MW) dissolved organic matter (DOM) to low MW components (Nguyen 2012) that can facilitate bacterial regrowth, resulting in accelerated membrane bio-fouling (Miettinen et al. 1998, van Der Kooij et al. 1989). The contradictory and inconclusive performance of ozone on UF membrane fouling observed in previous studies can be explained by the dependence of ozone effect on both the nature of raw water and ozone dose (Yu et al. 2017).

The inclusion of a BAC stage after ozonation has the potential to overcome fouling due to bacterial regrowth that may be facilitated by ozonation. When contaminants are removed in BAC filtration system, two main parallel mechanisms are involved. The adsorption due to the presence of adsorption sites on the activated carbon (Walker and Weatherley 1999) and biodegradation due to microbial activity developing in the gaps of the media (Lu et al. 2013, Rattier 2012, Servais et al. 1992). The synergistic effect of adsorption and biodegradation may result in the removal of organic matter including micro-pollutants, halogenated hydrocarbons, and taste and odour compounds (Velten et

al. 2007). Moreover, the activated carbon in the BAC column can be used over several reactivation cycles without having to be replaced for fresh carbon. This reduces the environmental burden related to the disposal of spent carbon (Van Der Hoek et al. 1999). Consequently, the BAC filtration system requires low energy requirement and operating cost (Walker and Weatherley 1999).

Numerous studies exist on the effect of combined ozonation and BAC treatment on water quality. The combination of ozonation and BAC process has shown higher reduction of biological regrowth potential and better removal of disinfection byproduct (DBP) precursor than ozonation alone (Cipparone et al. 1997, van Der Kooij et al. 1989). The application of ozone on SE transforms larger molecules of DOM into smaller ones, thus increasing the biodegradability of the organic matter (Amy et al. 1987, Volk et al. 1993). The DOC which can be removed by biodegradation is known as biodegradable dissolved organic carbon (BDOC). The BDOC produced in ozonation process can be removed by subsequent BAC treatment (Siddiqui et al. 1997). Combined ozonation and BAC is recommended for the drinking water treatment by many studies (Geismar et al. 2012, Huck et al. 1992, Kong et al. 2006, Price 1993, Toor and Mohseni 2007, Van Der Hoek et al. 1999, Xu et al. 2007, Yapsakli and Çeçen 2010). Combined ozonation and BAC has also been used in wastewater treatment. While treating SE of wastewater, the combined ozone and BAC were found to achieve 58, 90, 25, 75 and 90% removal efficiencies of chemical oxygen demand (COD), NH_3–N, total organic carbon (TOC), UVA_{254} and colour respectively (Wang et al. 2008) and 50, 90, 70 and 95% removal efficiencies of dissolved organic carbon (DOC), trace organic chemicals, non-specific toxicity and estrogenicity respectively (Reungoat et al. 2012).

The effect of combined ozonation and BAC treatment in water treatment processes involving membranes has also been studied. The combined effect of ozonation and BAC

pre-treatment was found to improve the permeate flux of a PVDF membrane for the treatment of activated sludge effluent (Nguyen and Roddick 2010). However, application of ozone and/or BAC as pre-treatments for ceramic membrane filtration has not been investigated for advanced treatment of SE (Li et al. 2005). Understanding the effect of combined ozone-BAC pre-treatment on the removal efficiency of the organic matters and reduction in membrane fouling would allow designing the optimized and economic treatment conditions. The goal of this investigation was to explore the impact of these pre-treatment approaches on waste water quality and ceramic membrane permeability.

2 Materials and methods

2.1 Raw water

Raw SE was collected from Melbourne Water's Western Treatment Plant, where more than 50% of this Australian city's sewage is treated by an activated sludge-lagoon process. The sample water was collected from the maturation lagoon overflow, before UV disinfection and chlorination, which corresponds to the water that would be fed to a membrane plant for reuse. The sample water was stored at 4°C until needed. Prior to all tests, the stored sample was warmed to room temperature (22±1°C) and pre-filtered using 10 μm paper filters (Advantec 5A).

2.2 Experimental equipment

A schematic representation of the experimental equipment is shown in Figure 1. An A2Z ozone generator was used to generate ozone. Pure oxygen was supplied to the generator at a flow rate of 2 L(NTP).min^{-1}. Ozone was injected in the feed sample at a flow rate of 1.4 L(NTP).min^{-1} through a stone diffuser. The BAC particles (Acticarb BAC GA1000N)

were obtained from an operating ozone – BAC system in Castlemaine water treatment plant, Castlemaine, Australia (Zhang et al. 2016). A BAC column with a height of 180 mm and diameter of 50 mm has been used in this test. The BAC feed was pumped at a flow rate of 15 mL.min^{-1}. The empty bed contact time (EBCT) of the column was 20 min.

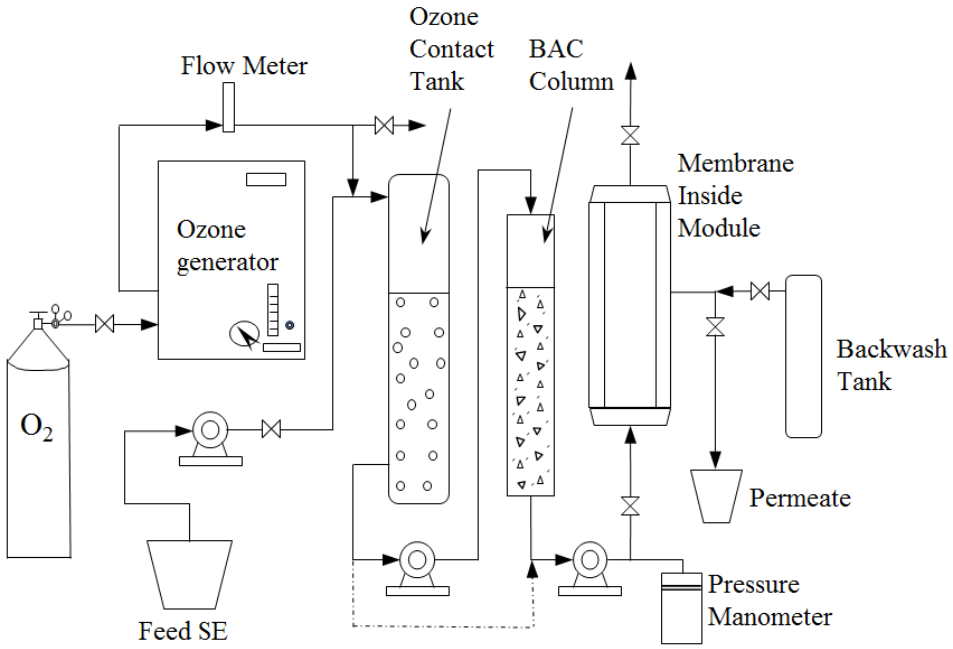


Figure 1: *Ozone-BAC+Ceramic membrane filtration equipment.*

A tubular ceramic membrane (Pall Corporation) with a nominal pore size of 100 nm was used (7 mm inner diameter, 25 cm length). The inside-out membrane has an aluminium oxide support layer with a zirconium oxide coating layer on it. A stainless steel Schumasiv membrane module was used to house the membrane. Stainless steel fittings (Swagelok) and high pressure tubes were used for connecting the membrane process components. The membrane feed was pumped using a low speed piston pump (Fluid Metering, Inc, QG 150) at a flow rate of 15 mL.min^{-1}. Pressure was monitored using a digital manometer (TPI 665). The temperature for all experiments was 22 ± 1°C. The specifications of the ozone generator, BAC column and membrane used in this study are given in Table 1.

Table 1: Operating conditions of different treatment steps.

Process Stage	Parameters	Conditions
Membrane	Filtration area	0.0055 m^2
	Pore size	100 nm
	Filtration mode	Dead end
	Pump flow rate	15 $mL.min^{-1}$
	Flux	180 $L.m^{-2}.h^{-1}$
	Backwash frequency	30 min
	Backwash pressure	4 bar
Ozone	Gas flow rate	1.4 $L.min^{-1}$
	Mass concentration	0.11 $g.L^{-1}$
	Production rate	13.05 $g.L^{-1}$
BAC	Empty bed contact time	20 min
	Flow rate	15 $mL.min^{-1}$
	BET surface area of particles	502 $m^2.g^{-1}$
	Depth of bed	180 mm

2.3 Experimental procedure

SE was used as the feed for the O3 and/or BAC and/or CMF treatments. The membrane was operated in inside-out mode as the active layer was on the inside of the ceramic tube, in a conventional pressurized configuration using a direct filtration (dead-end) constant flux mode to replicate the operation of real plants by the water industry. Each filtration was conducted for at least 200 minutes. Transmembrane pressure (TMP) was continuously monitored and recorded for every 5s. The TMP was temperature corrected to a reference temperature of 20°C using Equation 1 and Equation 2 (EPA 2005),

$$P_{T=20} = P_{abs} \times \frac{\mu_{T=20}}{\mu_T} \quad (1)$$

$$\mu_T = 1.784 - (0.0575 \times T) + \left(0.0011 \times T^2\right) - (10^{-5} \times T^3) \quad (2)$$

Where, $P_{T=20}$ is the pressure at 20°C (Pa), P_{abs} is the absolute pressure (Pa), $\mu_{T=20}$ is the viscosity of water at 20°C and μ_T is the viscosity of water at temperature T. Hydraulic (liquid) backwashing was performed periodically via pressurized DI water and a series of valves. The backwash was set to occur after every 30 min of filtration at a backwash pressure of 4 bar. Samples were collected before and after each filtration steps to investigate different water quality parameters. During the O3+BAC+CMF experiment, the measured residual ozone was between 0.3 and 0.5 mg.L^{-1} prior to BAC column. During the O3+CMF experiment, measured residual ozone was 2 to 3 mg.L^{-1} prior to ceramic membrane. The higher concentration of residual ozone in the O3+CMF experiment was to allow the ceramic membrane to facilitate any potential catalytic reaction with residual ozone. In order to remove the accumulated organic and inorganic materials, the membrane was cleaned hot water for 10 minutes firsts. After that, 2% (w/v) NaOH was used to clean the membrane for 20-30 minutes at a temperature of 75-80°C with a subsequent hot water cleaning. Finally the membrane was cleaned with 2% w/w nitric acid for 20-30 minutes at a temperature of 75-80°C with a subsequent hot water cleaning (Pall 2006). The effectiveness of the cleaning procedure was confirmed by performing clean water test at 180 L.m^{-2}.h^{-1} for a minimum of one hour and achieving a TMP of 15 kPa ± 2 kPa.

The normalised permeability and the unified membrane fouling indices (UMFI) were used to quantify the fouling potential on the ceramic membrane. All TMP data points

192 which were already temperature corrected using Equation 1 and 2, were used to calculate
193 permeability or specific flux ($L.m^{-2}.h^{-1}.kPa^{-1}$) using Equation 3. The normalised
194 permeability, J'_s was then calculated by dividing $J/\Delta P$ by the initial or clean membrane
195 condition as shown in Equation 4.

$$J_s = \frac{J}{\Delta P} \tag{3}$$

$$J_s^{'} = \frac{\left(\frac{J}{\Delta P}\right)_{V_s}}{\left(\frac{J}{\Delta P}\right)_0} \tag{4}$$

196 Where J_s is the membrane permeability ($L.m^{-2}.h^{-1}.kPa^{-1}$), V_s is the specific volume ($L.m^{-2}$).
197 UMFI was determined experimentally by obtaining normalized specific flux at given
198 specific permeate volume. The procedure is described in detail in elsewhere (Huang et al.
199 2009). UMFI was calculated as the ratio of the difference in $1/J'_s$ to the difference in V_s
200 measured between the beginning of a filtration cycle to a specific endpoint as shown in
201 Equation 5.

$$UMFI = \frac{J_s^{'-1} - 1}{V_s} \tag{5}$$

202

203 If the endpoint chosen was at the completion of the filtration cycle, the UMFI calculated
204 represents the total fouling rate ($UMFI_T$) observed in this cycle. In multi-cycle filtration,
205 hydraulically irreversible fouling refers to the fouling that cannot be reversed by
206 backwashing with deionised water. Hydraulically irreversible fouling potentials were

evaluated by $UMFI_I$, which was calculated by selecting the endpoint at the beginning of subsequent filtration cycle. Hydraulically reversible fouling potentials $UMFI_R$ were obtained by subtracting $UMFI_I$ from $UMFI_T$ (Huang et al. 2009).

2.4 Analytical method

The SE UVA_{254}, DOC, colour and constituent molecular weight distribution were determined before and after different treatments. The UVA_{254} was measured using a HACH spectrophotometer (DR 5000) with a 1 cm quartz cell. DOC was measured using a Shimadzu Total Organic Carbon Analyzer (TOC-VCSH), which was equipped with an auto-sampler. DOC concentration was indirectly obtained by subtracting the two directly measured parameters: the total carbon (TC) and the inorganic carbon (IC). All samples were filtered through 0.45 μm cellulose acetate membrane filter prior to the DOC analysis. Colour was measured in PtCo units using HACH spectrophotometer (DR 5000) with a 10 cm quartz cell. The excitation-emission spectrums were measured using a Perkin-Elmer LS-55 Fluorescence Spectrometer, which used a xenon excitation source. The scans were performed from 200 to 550 nm at increments of 5 nm. The total number of scans per sample in the spectrometer was 70.

The molecular weight distributions of the wastewater components were achieved by Liquid Chromatography (LC) analyses with a PDA and fluorescence detector in series. The LC Method was performed using a TSK gel column (G3000 SW, C-No.SW3600482) at room temperature with a phosphate buffer (10 mM KH_2PO_4 + 10 mM Na_2HPO_4) as the mobile phase. The column was operated with a flow-rate of 0.5 $mL.min^{-1}$ and a 50 mL injection volume. This was coupled with sequential on-line detectors consisting of a UV visible photodiode array (λ = 200 - 800 nm) and a fluorescence detector (RF-10AXL).

231 The fluorescence excitation (Ex) and emission (Em) wavelengths of 280 nm/352 nm
232 (Ex/Em) were used for detection of protein-like compounds, and 330 nm/425 nm (Ex/Em)
233 for detection of humic substances. Polystyrene sulphonate (PSS) molecular weight
234 standards of 3420, 4600, 6200, 15650 and 39000 Da were used to calibrate the LC
235 column.

236 The concentrations of dissolved ozone in the experimental reaction solutions were
237 determined by the Indigo Method (Bader and Hoigné 1981). The method is based on
238 decolourization of the indigo reagent by ozone, where the loss of colour is directly
239 proportional to the ozone concentration. High purity indigo trisulfonate (>80%, Sigma
240 Aldrich) was used as the indigo reagent which has a molar absorptivity of about 20,000
241 $M^{-1}cm^{-1}$ at 600 nm. To measure the residual ozone the absorbance of indigo trisulfonate
242 after reaction with sample was subtracted from that of an ozone free blank. The
243 absorbance at 600 nm was measured using a DR 5000 spectrophotometer (HACH).

244

245 ## 3 Results and Discussion

246 ### *3.1 Raw water characterization*

247 The characteristics of the raw SE used in these experiments is compared to those in the
248 literature in Table 2. The pH, UVA_{254}, conductivity and COD values of the sample were
249 found to be very similar to literature values. The colour, turbidity and the total dissolved
250 solid (TDS) of the sample were found to be lower than the literature values. However, the
251 DOC of the sample was found to be higher than the literature values. The dissimilarity is
252 due to the different types of secondary treatment in different treatment plants.

253

254 **Table 2:** Characteristics of SE used in this work, and comparison to
255 other studies reported in literature.

Parameters	Values	Other studies
pH	7.7-7.9	7.3 (Zheng et al. 2010), 7.8 (Kalkan et al. 2011), 7.4-8 (Pramanik et al. 2016)
UVA_{254}, cm^{-1}	0.218±0.02	0.14 (Zhu et al. 2012). 0.22 (Kalkan et al. 2011), 0.34 (Nguyen and Roddick 2010)
Colour, Pt-Co	35-37	109 (Nguyen and Roddick 2010), 56-85 (Pramanik et al. 2016)
Turbidity, NTU	0.9±0.1	7.3 (Zhu et al. 2012), 1.5 (Zheng et al. 2010)
Conductivity, µS cm^{-1}	1665±35	1065 (Nguyen and Roddick 2010), 1620-1950 (Pramanik et al. 2016)
Total dissolved solid (TDS), $mg.L^{-1}$	883±5	1038 (Fan et al. 2008)
Dissolved organic carbon (DOC), $mg.L^{-1}$	13±0.5	11.7 (Zheng et al. 2010), 11.4 (Kalkan et al. 2011)
Chemical oxygen demand (COD), $mg.L^{-1}$	27.9±1	27 (Fan et al. 2008), 52.5 (Wang et al. 2008)

256 The fluorescence excitation-emission matrix (EEM) spectra of the SE are shown in Figure
257 2. Two major peak locations (280 nm/352 nm, 330 nm/425 nm, Ex/Em) were found in
258 the matrix. Fluorescence peaks with Em < 380 nm represent protein-like substances
259 (tyrosine and tryptophan), and fluorescence peaks with Em > 380 nm represent humic-
260 like substances were used (Chen et al. 2003, Ishii and Boyer 2012, Murphy et al. 2011,
261 Wang and Zhang 2010). Her *et al.* used two pairs of excitation and emission wavelengths
262 specific to protein-like and fulvic-like humic substances (HS) at Ex: 278 nm/Em: 353 nm
263 and Ex: 337 nm/ Em: 423 nm respectively for the fluorescence detector (Her et al. 2003).

Additionally, Salanis *et al.* has shown that tryptophan containing proteins fluoresce at Ex: 278-280 nm/Em: 320-350 nm (Salanis et al. 2011). Excitation and emission wavelengths of 278 and 353 nm were selected for detecting tryptophan containing protein substances, and 330 and 425 nm were selected for detecting fulvic like humic substances.

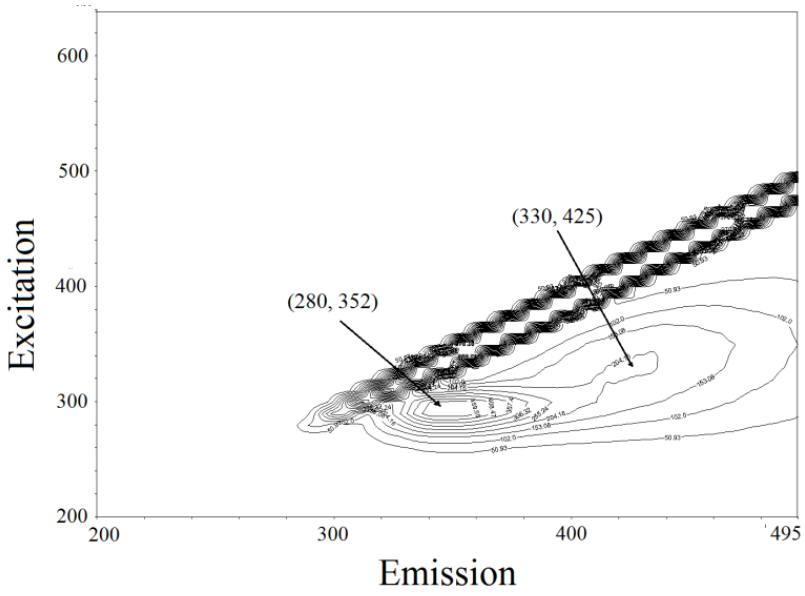


Figure 2: *EEM of SE feed solution.*

3.2 Effect of pre-treatment options on feedwater quality

The average removal percentages of DOC, UVA_{254} and colour by the individual application of BAC filtration and ozonation are compared to CMF in Figure 3. Both BAC and ozone were found to be more effective for removal of colour and UVA_{254} absorbance than CMF. This finding confirms the well-known effect of ozone and BAC treatment for improving treated water aesthetics (Pramanik et al. 2014). The DOC removal for the O3 and CMF options (4.6% and 5.3%) were lower than for BAC treatment (14%). This is consistent with literature studies that show that O3 treatment degrades large dissolved organic constituents to smaller compounds without removing them from solution

(Miettinen et al. 1998, Nguyen 2012, van Der Kooij et al. 1989, Von Gunten 2003), whereas the BAC treatment removes the organic constituents via adsorption and biodegradation (Lu et al. 2013, Rattier 2012, Walker and Weatherley 1999). Ozonation has been found to transform higher MW biopolymers into smaller compounds (Stüber et al. 2013). Ozone is known to decompose the humic substances into low MW substances (Camel and Bermond 1998, Takahashi et al. 1995, Von Gunten 2003). An increase in low MW compounds by ozonation was also found in a study conducted by Gonzalez *et al.* (González et al. 2013).

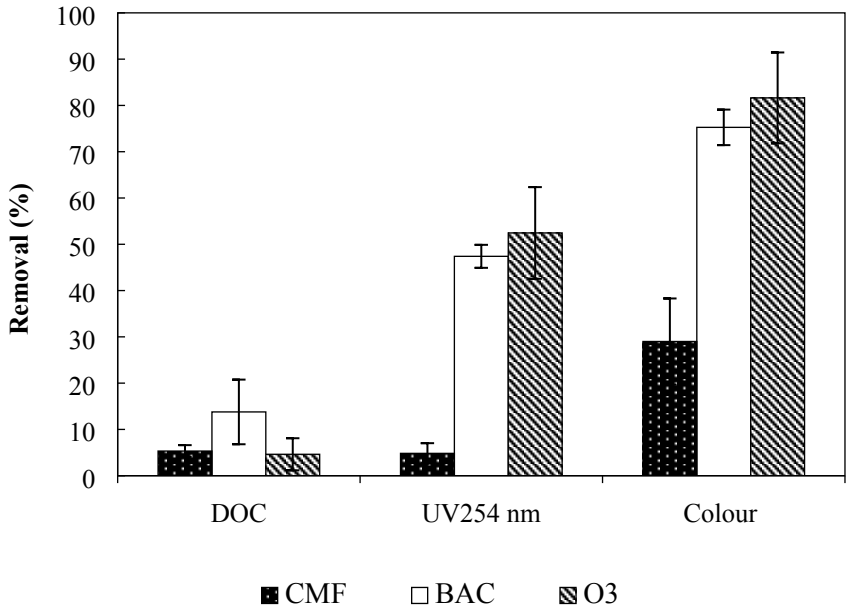


Figure 3: *Removal of DOC, UVA_{254} and colour by individual CMF, BAC filtration and ozonation processes.*

3.3 Effect of pre-treatment options on CMF permeate quality

The removal percentages of DOC, UVA_{254} and colour by the BAC+CMF, O3+CMF and O3+BAC+CMF options are compared to CMF alone in Figure 4(a). Overall, ozonation was the most effective pre-treatment, increasing the permeate UVA_{254} removal from 6%

296 (CMF alone) to 63% (O3+CMF) and the colour removal from 29% (CMF alone) to 97%
297 (O3+CMF). BAC treatment was slightly less effective (6% to 48% removal of UVA_{254}
298 and 29% to 86% removal of Colour). The inclusion of a BAC stage after the ozonation
299 (*i.e.*, the O3+BAC+CMF option) was found to be mildly worse than the ozone pre-
300 treatment alone (*i.e.*, the O3+CMF option) for both of these parameters.

301 The influence of each treatment step on the overall removal results shown in Figure 4(a)
302 are shown Figures 4(b), 4(c) and 4(d). It can be seen that the water quality changes that
303 occur during pre-treatment decrease the contribution of the CMF to the overall removal
304 result. The CMF colour removal achieved in the O3+CMF process (9%, Figure 4(c)), for
305 example, is less than the CMF colour removal achieved without pre-treatment (29%,
306 Figure 4(a)). The ozonation degrades wastewater components that would otherwise be
307 caught by the membrane, allowing them to pass through the membrane. Generally,
308 aromatic compounds are most reactive with ozone (Kasprzyk-Hordern et al. 2006, Park
309 et al. 2012).

310 The DOC and colour removal by BAC filtration were found to be 13% and 69%
311 respectively (see Figure 4(b)). These removal values are marginally lower than those
312 observed by Pramanik *et al.* (2014). They studied the BAC filtration as a pre-treatment
313 for reducing the organic fouling of a MF membrane in the treatment of SE and found the
314 reduction in DOC and colour by the BAC stage were 32% and 78% respectively
315 (Pramanik et al. 2014). The removal of DOC can be attributed to the simultaneous
316 adsorption of bio-refractory compounds and bio-oxidation of biodegradable organic
317 matter by the BAC.

318 The removal of DOC by ozonation was low (7%) but ozonation effectively removed
319 UVA_{254} (63%) and colour (88%) (see Figure 4(c)) as observed by others in the literature.

Dow *et al.* investigated the performance of ceramic MF membrane to treat SE with ozone and/or coagulation pre-treatment (Dow et al. 2013) and found that ozone reduced DOC, UVA_{254} and colour by 5%, 52% and 85% respectively.

The measured contribution of each of the process stages to the overall removals by the O3+BAC+CMF option is shown in Figure 4(d). The negative value in the removal percentages of UVA_{254} for the ozonized effluent through BAC filtration was attributed to an increase in UVA_{254} resulting from improved clarity of the treated water by ozonation, enabling better light absorbance in the spectrophotometer (Dow et al. 2013). Ozone played a key role in removal of UVA_{254} and colour, and since BAC followed ozone, its removal contribution was not as strong as when BAC is used without ozone (Figure 4(b)).

Figure 4: *Removal of DOC, UVA_{254} and colour by* ***a.*** *all four sequences using ceramic membrane; unit contribution for each stages of* ***b.*** *BAC+CMF;* ***c.*** *Ozone+CMF;* ***d.*** *Ozone-BAC+CMF system.*

High performance liquid chromatography – size exclusion chromatography (HPLC-SEC) was used to study the chemical and physical changes taking place during treatment. The resulting apparent molecular weight distributions for the treated and untreated water are shown in Figure 5 and Figure 6.

These figures represent the fluorescence spectrum at 280 nm/352 nm (Ex/Em) for proportion of protein substances that contain tryptophan and 330 nm/425 nm (Ex/Em) for fulvic-like humic substances respectively. A small peak is observed at approximately 43 kDa (Figures 5(a-d)). Generally the biopolymers have a MW range of greater than 20 kDa (Nguyen and Roddick 2010, Penru et al. 2013). Myat *et al.* (2012) in a study of organic matter in wastewater observed a peak at 50 kDa (fluorescence spectrum at 278 nm/304 nm (Ex/Em)) and attributed this to proportion of protein substances that contain tryptophan (Myat et al. 2012). In Figures 6, multiple peaks are observed in the range of 0 to 5000 Da. Generally, the HS are ranged from 100 to 5,000 Da (Sutzkover-Gutman et al. 2010).

The rejections of tryptophan containing protein biopolymers and of HS by the different treatment steps relative to the feed water quality, calculated from the peak areas from Figure 5 and Figure 6, are shown in Table 3. The tryptophan containing protein biopolymers detected at 280 nm/352 nm (Ex/Em) were significantly removed by the CMF without pre-treatment (97%) while the HS detected at 330 nm/425 nm (Ex/Em) were only slightly removed by the membrane (7%). These removals are different to those obtained by others using polymeric membranes. Pramanik *et al.* found that the tryptophan containing protein biopolymer rejection and HS rejections were 20% and 10% rejection in their wastewater treatment using a hydrophilic PVDF membrane with a nominal pore size of 0.1 µm (Pramanik et al. 2015). The higher rejection of biopolymers by the CMF in this study (nominal pore also 0.1 µm) can be attributed to the narrower pore size

359 distribution of the ceramic membrane (Ishizaki et al. 1998). As ceramic membranes have
360 higher proportions of smaller pores and less larger pores, greater quantity of high MW
361 biopolymers can be rejected by CMF.

362 In the BAC+CMF process, a partial reduction of biopolymers (59%) and HS (50%) were
363 observed by BAC filtration. The high MW tryptophan containing protein biopolymers
364 may have been biodegraded by microorganisms formed in the BAC while the HS may
365 have been adsorbed by the activated carbon of the BAC (Pramanik et al. 2014, 2016).
366 Following the BAC, CMF effectively removed biopolymers (99% removal) but gave rise
367 to little additional HS removal (55%). Pramanik *et al.* studied the effect of BAC prior to
368 0.1 μm hydrophilic PVDF membrane while treating biologically treated SE (Pramanik et
369 al. 2016). It was observed that, for the BAC treated effluent, high MW biopolymers and
370 HS were retained by the membrane, playing an important role in membrane fouling.

371 In the O3+CMF process, a high amount of biopolymers were removed by ozonation
372 (100%). This was also found in literature studies (Filloux et al. 2012). The removal effect
373 of ozone is attributed to the transformation of biopolymers into smaller compounds
374 (Stüber et al. 2013). Ozonation, with or without CMF, significantly reduced the quantity
375 of HS (84% removal). The significant removal of this fraction can be attributed to the
376 high aromaticity of the HS components (González et al. 2013). The biopolymer
377 components removal after ceramic filtration, however, was lower (86%) than before
378 ceramic filtration (100%). This suggests that some of the degraded biopolymer
379 components combine to form larger MW species as they are forced through the membrane
380 pores (Kim et al. 2007).

381 In the O3+BAC+CMF process, samples taken after the ozonation stage showed that this
382 stage removed a high proportion of biopolymers and HS (100% and 83% respectively).

383 Samples taken after the BAC stage, however, exhibited lower removals (75% and 66%
384 respectively), indicating that the BAC is adding biopolymers and HS to the process
385 stream. These increases can be attributed to the chemical oxidation and release by the
386 ozone of the adsorbed material and biofilms on the BAC. Ceramic filtration after
387 O3+BAC pre-treatment then removes most of the biopolymers (96%) but does not
388 improve the HS component removal.

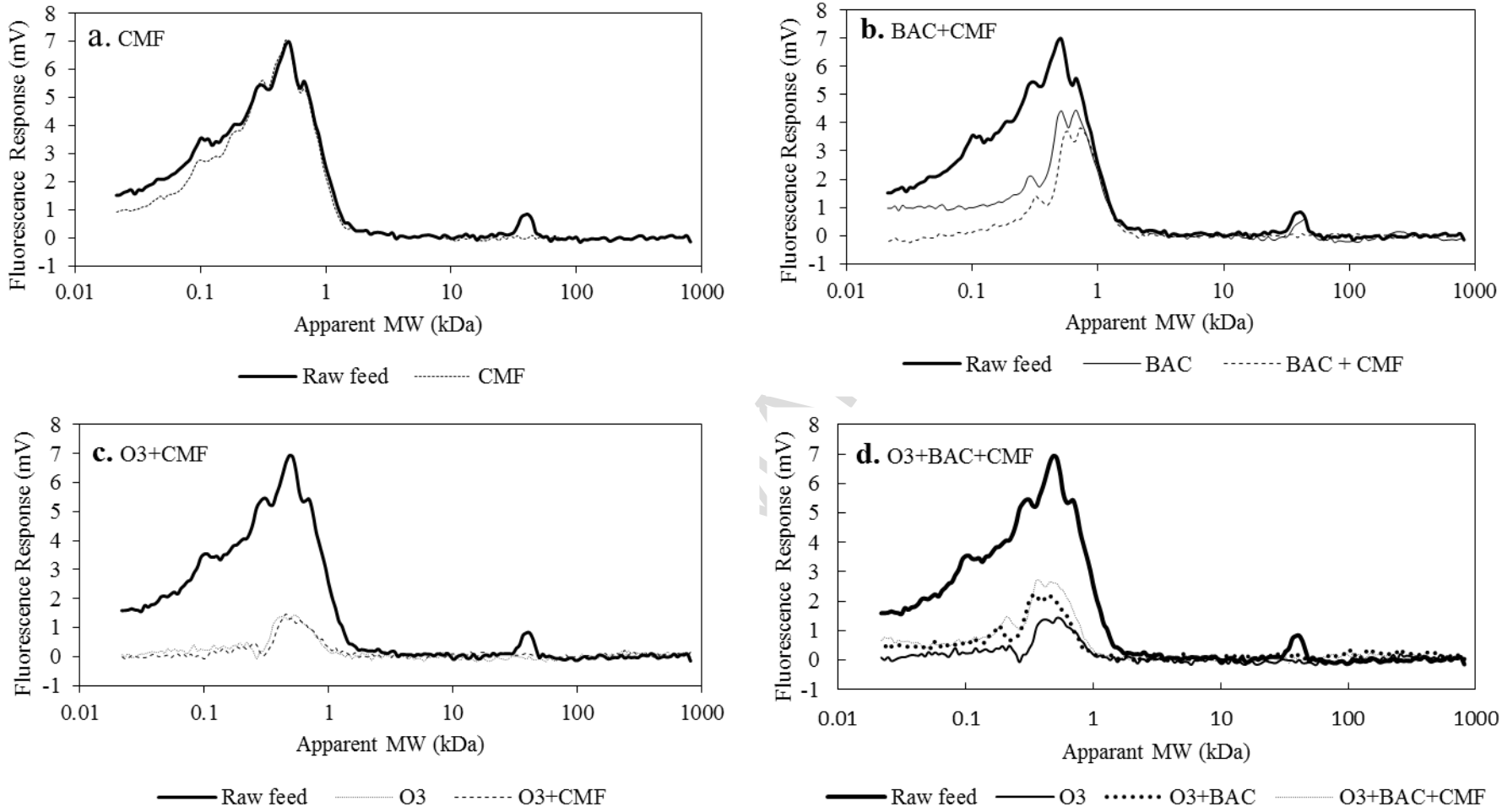


Figure 5: *Fluorescence spectrum at 280 nm/352 nm (Ex/Em) for treatment by* ***a.*** *CMF alone;* ***b.*** *BAC+CMF;* ***c.*** *ozone-CMF;* ***d.*** *ozone-BAC+CMF system.*

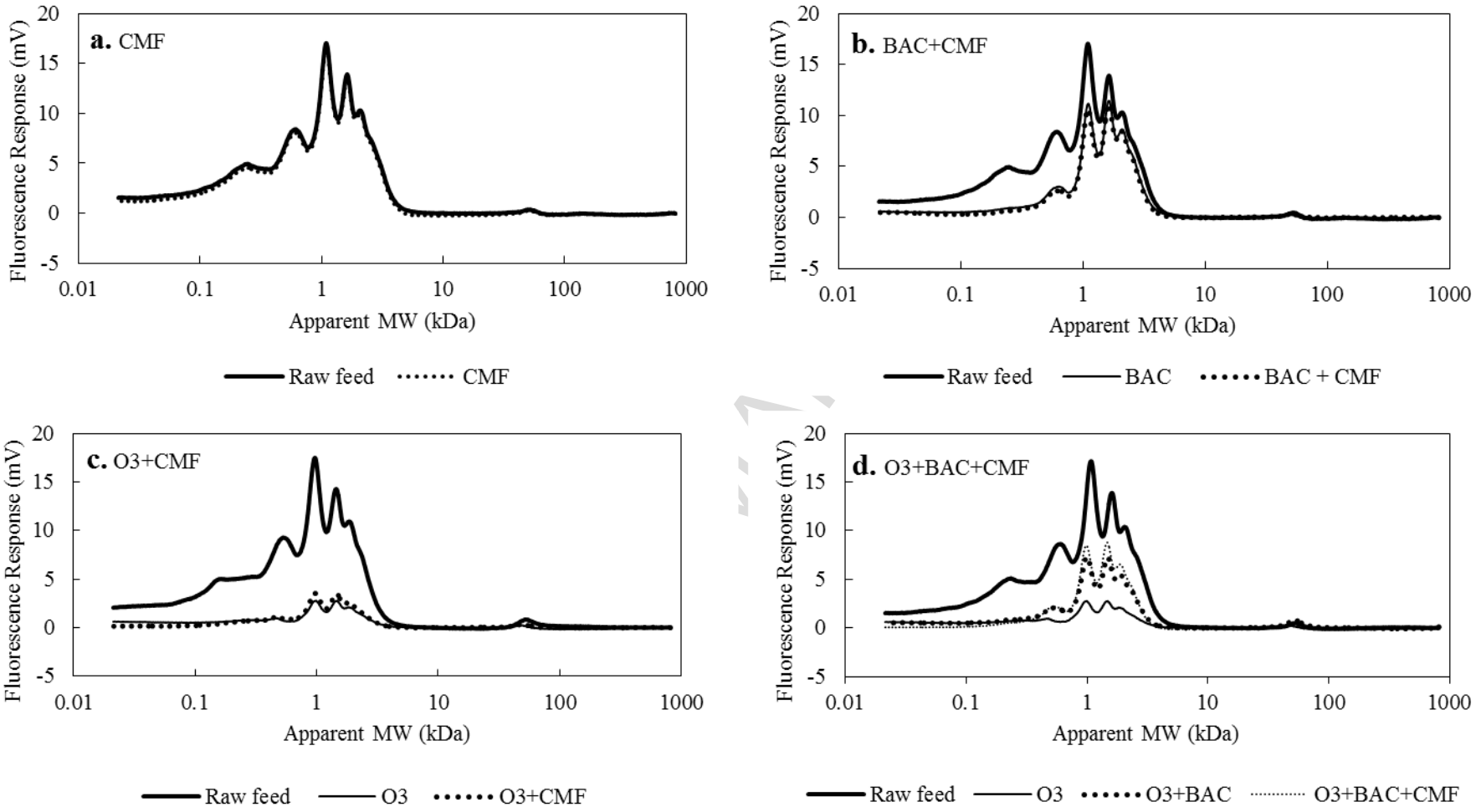


Figure 6: *Fluorescence spectrum at 330 nm/425 nm (Ex/Em) for treatment by* ***a.*** *CMF alone;* ***b.*** *BAC+CMF;* ***c.*** *ozone-CMF;* ***d.*** *ozone-BAC+CMF system.*

Table 3: Biopolymers and HS removal (%) relative to the feed water quality during different treatment steps of CMF (calculated by peak area from Figures 5 and 6).

Process	Post-stage Sample Point	Biopolymers Removal (%) (40 kDa-45 kDa) Ex/Em: 280/352 nm	Humic Substances Removal (%) (0.1 kDa-5.5kDa) Ex/Em : 330/425 nm
CMF	CMF	97	7
BAC+CMF	BAC	59	50
	CMF	99	55
O3+CMF	O_3	100	84
	CMF	86	84
O3+BAC+CMF	O_3	100	83
	BAC	75	66
	CMF	96	66

3.4 Effect of pre-treatment options on the permeability of CMF

The normalized permeability with time and total fouling index ($UMFI_T$) for the four different filtration options are shown in Figure 7. In Figure 7(a) it can be seen that the permeability decreases as the membrane becomes fouled by the wastewater constituents and this permeability is only partially restored during the DI water backwashes (every 30 minutes).

405 The membrane permeabilities with raw water, BAC treated water and the O3+BAC water
406 treated water were found to be similar. A large decrease in flux was found to occur in the
407 first filtration period. After 6 backwashes and 7 successive filtration cycles, the
408 normalized permeability was reduced from 1.0 to approximately 0.1 for these options.
409 The results for the ozone treated water, however, were much better. A much lower level
410 of fouling occurred in the first filtration period for the ozone treated water than for the
411 BAC treated water. The normalised permeability only decreased from 1.0 to 0.5 during
412 these 7 filtration cycles.

413 The low fouling nature of the ozone treated water can be seen from the total fouling index
414 data ($(UMFI_T)$, Figure 7(b)) and the reversible ($UMFI_R$) and irreversible ($UMFI_I$) fouling
415 index data (Figure 8). The $UMFI_T$ for the raw water was found to increase in a linear
416 fashion from 0.14 $m^2.L^{-1}$ to 0.73 $m^2.L^{-1}$. The BAC and ozone-BAC pre-treated feedwater
417 were found to exhibit a slower increase to 0.34 $m^2.L^{-1}$. The $UMFI_T$ of the ozone pre-
418 treated feedwater, however, exhibited a very low increase from 0.02 to 0.03 $m^2.L^{-1}$. This
419 can be attributed to the removal of biopolymers and HS (see Table 3). Ozone was found
420 to improve the permeability of ceramic membrane in other studies using ozone combined
421 with ceramic membranes to treat SE (Alpatova et al. 2013, Guo et al. 2014, Karnik et al.
422 2005, Kim et al. 2008).

423

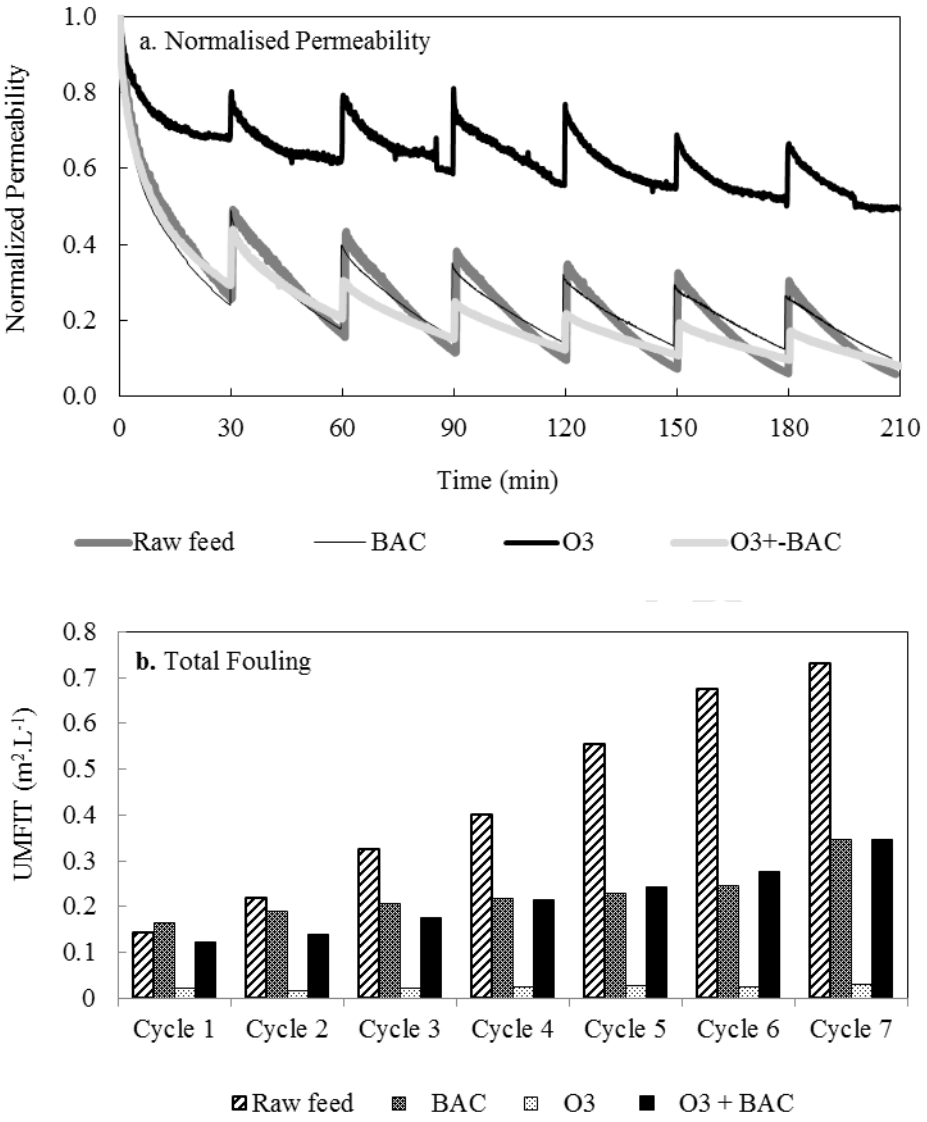


Figure 7: a. *Normalized permeability with time and* ***b.*** *total fouling index ($UMFI_T$) during multi-cycle treatment by CMF, BAC+CMF, Ozone-CMF and Ozone-BAC+CMF system.*

The reversible fouling index ($UMFI_R$) for the untreated feedwater was higher than the irreversible fouling index ($UMFI_I$) (Figure 8), indicating that the majority of raw water foulants were loosely attached to the membrane surface to form cake layers (Pramanik et al. 2015) and could be removed by the backwashing procedure. The role of biopolymers to form cake layers on the membrane surface was found in other studies (Gray et al. 2007, Pramanik et al. 2014) since the organics mostly rejected by the membrane are

434 biopolymers and would logically accumulate on the surface. Laine *et al.* showed that
435 high MW biopolymers are known to be the major component of the cake layer (Laine et
436 al. 1989). Pore fouling can also occur from materials that pass through the membrane
437 (Polyakov and Zydney 2013).

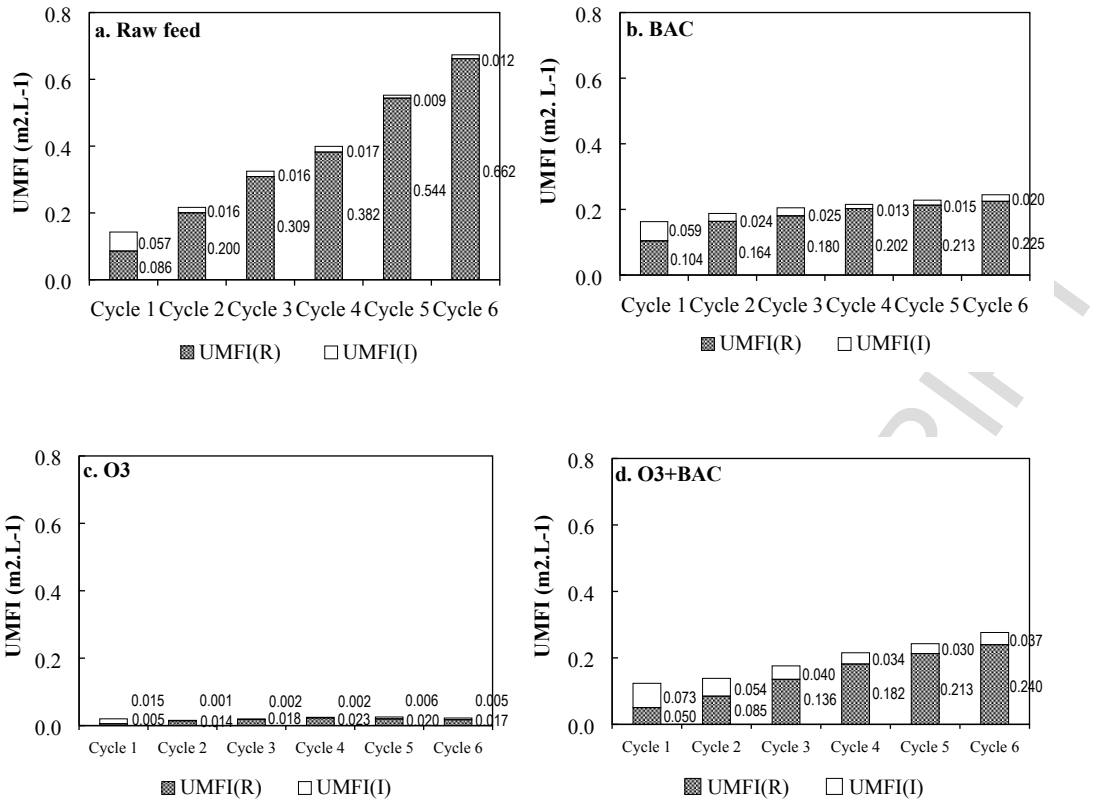
438 Comparison of Figure 8(a) and Figure 8(b) shows that the lower $UMFI_T$ of BAC treatment
439 than untreated water is largely due to the decrease in reversible fouling ($UMFI_R$), but the
440 irreversible fouling index was increased by the BAC pre-treatment. The overall
441 improvement can be attributed to the partial removal (59%) of biopolymers by the BAC
442 (see Table 3). The removal of low molecular weight HS (50%) seems to contribute to
443 increased irreversible fouling component. These results are consistent with the
444 biodegradation of HS components to more powerful foulants, allowing more to enter the
445 pores of the membrane and contribute to in-pore fouling (Polyakov and Zydney 2013).

446 Comparison of Figure 8(b) and Figure 8(d) shows that irreversible fouling is strongly
447 increased after O3+BAC pre-treatment. Nguyen et al. investigated the effect of ozonation
448 followed by BAC filtration on the characteristics and UF performance of activated sludge
449 effluent. Irreversible fouling in their study was reduced after ozonation while BAC
450 filtration did not cause any further decrease in this type of fouling (Nguyen and Roddick
451 2010). It was identified in a previous study that some microorganisms can be released due
452 to sloughing of the biomass and transport on granular activated carbon fines (Gottinger
453 et al. 2011). Moreover, when drinking water is treated by O3+BAC process, microbial
454 degradation can result in membrane clogging and reduce membrane flux (Jin et al. 2013).
455 It was also observed in another study that ozonation might lyse algae, releasing polymeric
456 substances from algal cell wall (Plummer and Edzwald 2001). In this study, it is therefore
457 possible that the broken pieces of biopolymers created by ozonation were captured at the
458 retention time of HS through porous channals of membrane, as the molecular mass of

biopolymers is about one order of magnitude higher than the molecular mass of HS (Siembida-Losch et al. 2015). This assumption can further be strenthened by another study of UF membrane where, the formation of irreversible fouling is attributed to the interaction between colloidal/particulate matter together with protein like substances and HS (Peiris et al. 2013).

The performance of the combined O3+BAC pre-treatment can further be improved by design optimization (*e.g.*, improved EBCT), which enables better control of membrane fouling in a cost effective and eco-friendly manner. Coagulation can be added as a complement of the combined pre-treatment process. The MF ceramic membrane can be coated with MnO_2 in order enhance the catalytic decomposition of ozone to hydroxyl radicals and increase hydrophobicity of the membrane surface (Yu et al. 2016a). The effect of ozone on the microorganisms of BAC column needs to be further investigated in detail.

477



478

479 ***Figure 8:*** *Reversible fouling ($UMFI_R$) and irreversible fouling ($UMFI_I$) with*

480 ***a.*** *Raw feedwater;* ***b.*** *BAC pre-treatment;* ***c.*** *O3 pre-treatment;* ***d.*** *O3+BAC pre-*

481 *treatment.*

482 ## 4 Conclusions

483 This study has shown that, individually, BAC pre-treatment and ozone pre-treatment lead
484 to better water quality and lower membrane fouling than without pre-treatment, but that
485 the combination of both pre-treatments with ozone followed by BAC leads to worse water
486 quality and more membrane fouling than the use of ozone pre-treatment alone.

487 BAC pre-treatment improved the overall permeability of the ceramic membranes and the
488 quality of the resulting permeate, primarily due to removal of a large proportion of
489 biopolymer component (~60%) which fouls the membrane by reversible cake layer
490 formation. BAC treatment also removed a large proportion of the humic substances

(~50%), but the net effect was associated an increase in irreversible fouling. The overall removal of colour and UVA_{254} of the BAC pre-treated water by ceramic filtration was 86% and 48% respectively, compared to 29% and 6% respectively for the untreated water. The BAC pre-treatment only increased DOC removal from 6% without pre-treatment to 13% with pre-treatment. This is consistent with poor adsorption of low molecular weight organic components onto the BAC column.

Ozone pre-treatment improved permeability and permeate quality to a greater extent than BAC pre-treatment. This was attributed to the excellent removal of biopolymers (100%) and high removal of HS components (84%). This pre-treatment was found to decrease both the reversible and irreversible fouling. The overall removal of colour and UVA_{254} for the ozone treated water by ceramic filtration was 97% and 63% respectively, compared to 29% and 6% respectively for the raw untreated water. Ozone pre-treatment, however, only increased DOC removal from 6% without pre-treatment to 7% with pre-treatment. This is consistent with a process that breaks down large organic constituents to smaller ones without removing them from solution.

The inclusion of a BAC stage between ozone treatment and ceramic filtration (O3+BAC+CMF option) was detrimental. The O3+BAC+CMF process was found to yield lower HS component removal (66%) than the O3+CMF process (84%), resulting in poorer permeability. This was tentatively attributed to the chemical oxidation effect of ozone on the BAC biofilm and adsorbed components, leading to the generation of foulants that are not generated in the O3+CMF process. This study provided new insights into the O3, BAC and O3+BAC pre-treatment processes prior to CMF of SE. Based on the results, it can be concluded that ozone pre-treatment could be an effective pre-treatment for reducing organic fouling and improving flux compared to O3+BAC pre-treatment.

Abbreviations

ATR-FTIR:	Attenuated total reflection-Fourier transform infrared
BAC:	Biological activated carbon
BDOC:	Biodegradable dissolved organic carbon
BET:	Brunauer–Emmett–Teller
BOD:	Biological oxygen demand
CMF:	Ceramic membrane filtration
COD:	Chemical oxygen demand
DBP:	Disinfection byproduct
DOC:	Dissolved organic carbon
DOM:	Dissolved organic matter
EBCT:	Empty bed contact time
EEM:	Excitation-emission matrix
Em:	Emission
Ex:	Excitation
HPLC-SEC:	High performance liquid chromatography – size exclusion chromatography
LC:	Liquid Chromatography
MF:	Microfiltration
MW:	Molecular weight
NOM:	Natural organic matter
PDA:	Photodiode array detector
PVDFl:	Polyvinylidenefluoride
RO:	Reverse osmosis
TDS:	Total dissolved solid

TMP: Trans-membrane pressure

TOC: Total organic carbon

UF: Ultrafiltration

UMFI: Unified membrane fouling index

$UMFI_I$: Hydraulically irreversible fouling potential

$UMFI_R$: Reversible fouling potential

$UMFI_T$: Total fouling index

UV: Ultra violate

Acknowledgement

The authors are grateful to the Collaborative Research Network (CRN), Australia, and Victoria University Central Research Grant Scheme (CRGS) for providing financial support of this project. The authors would also like to acknowledge the support from Melbourne Water, Australia for providing wastewater samples for this study. Further the authors would like to thank Dr Jianhua Zhang for preparing the BAC column for this study.

References

Alpatova, A.L., Davies, S.H. and Masten, S.J. (2013) Hybrid ozonation-ceramic membrane filtration of surface waters: The effect of water characteristics on permeate flux and the removal

562 of DBP precursors, dicloxacillin and ceftazidime. Separation and Purification Technology 107,
563 179-186.
564 Amy, G.L., Kuo, C.J. and Sierka, R.A. (1987) Ozonation of Humic Substances: Effects on Molecular
565 Weight Distributions of Organic Carbon and Trihalomethane Formation Potential. Ozone:
566 Science & Engineering 10(1), 39-54.
567 Bader, H. and Hoigné, J. (1981) Determination of ozone in water by the indigo method. Water
568 Research 15(4), 449-456.
569 Camel, V. and Bermond, A. (1998) The use of ozone and associated oxidation processes in
570 drinking water treatment. Water Research 32(11), 3208-3222.
571 Carroll, T., King, S., Gray, S.R., Bolto, B.A. and Booker, N.A. (1999) The fouling of microfiltration
572 by NOM after coagulation treatment. Water Sci. 34, 2861-2868.
573 Chen, W., Westerhoff, P., Leenheer, J.A. and Booksh, K. (2003) Fluorescence Excitation−Emission
574 Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter. Environmental
575 Science & Technology 37(24), 5701-5710.
576 Ciora Jr, R.J. and Liu, P.K.T. (2003) Ceramic membranes for environmental related applications.
577 Fluid - Particle Separation Journal 15(1), 51-60.
578 Cipparone, L.A., Diehl, A.C. and Speitel Jr, G.E. (1997) Ozonation and BDOC removal: Effect on
579 water quality - Batch experiments indicate biological treatment improves overall water quality
580 and reduces biological regrowth. Journal / American Water Works Association 89(2), 84-97.
581 Dow, N., Murphy, D., Clement, J. and Duke, M. (2013) Outcomes of the Australian
582 Ozone/Ceramic Membrane Trial on Secondary Effluent. Water (AWA) 40(6), 7.
583 EPA (2005) Membrane filtration guidance manual [electronic resource], U.S. Environmental
584 Protection Agency, Office of Water, [Washington, D.C.].
585 Fan, L., Nguyen, T., Roddick, F.A. and Harris, J.L. (2008) Low-pressure membrane filtration of
586 secondary effluent in water reuse: Pre-treatment for fouling reduction. Journal of Membrane
587 Science 320(1-2), 135-142.

588 Filloux, E., Gallard, H. and Croue, J.-P. (2012) Identification of effluent organic matter fractions
589 responsible for low-pressure membrane fouling. Water Research 46(17), 5531-5540.
590 Gaulinger, S. (2007) Coagulation Pre-Treatment for Microfiltration with Ceramic Membranes,
591 TECHNEAU.
592 Geismar, N., Bérubé, P.R. and Barbeau, B. (2012) Variability and limits of the unified membrane
593 fouling index: Application to the reduction of low-pressure membrane fouling by ozonation and
594 biofiltration. Desalination and Water Treatment 43(1-3), 91-101.
595 González, O., Justo, A., Bacardit, J., Ferrero, E., Malfeito, J.J. and Sans, C. (2013) Characterization
596 and fate of effluent organic matter treated with UV/H2O2 and ozonation. Chemical Engineering
597 Journal 226, 402-408.
598 Gottinger, A.M., McMartin, D.W., Price, D. and Hanson, B. (2011) The effectiveness of slow sand
599 filters to treat canadian rural prairie water. Canadian Journal of Civil Engineering 38(4), 455-463.
600 Gray, S.R., Ritchie, C.B., Tran, T. and Bolto, B.A. (2007) Effect of NOM characteristics and
601 membrane type on microfiltration performance. Water Research 41(17), 3833-3841.
602 Guo, J., Hu, J., Tao, Y., Zhu, J. and Zhang, X. (2014) Effect of ozone on the performance of a hybrid
603 ceramic membrane-biological activated carbon process. Journal of Environmental Sciences
604 (China) 26(4), 783-791.
605 Hendricks, D.W. (2006) Water Treatment Unit Processes: Physical and Chemical, Taylor &
606 Francis.
607 Her, N., Amy, G., McKnight, D., Sohn, J. and Yoon, Y. (2003) Characterization of DOM as a
608 function of MW by fluorescence EEM and HPLC-SEC using UVA, DOC, and fluorescence
609 detection. Water Research 37(17), 4295-4303.
610 Hiraide, M. (1992) Heavy metals complexes with humic substances in fresh water. Anal. Sci. 8,
611 47-54.

612 Huang, H., Young, T. and Jacangelo, J.G. (2009) Novel approach for the analysis of bench-scale,
613 low pressure membrane fouling in water treatment. Journal of Membrane Science 334(1-2), 1-
614 8.
615 Huck, P.M., Fedorak, P.M. and Anderson, W.B. (1992) Biodegradation of aquatic organic matter
616 with reference to drinking water treatment. Science of the Total Environment, The 117-118(C),
617 531-541.
618 Ishii, S.K.L. and Boyer, T.H. (2012) Behavior of reoccurring parafac components in fluorescent
619 dissolved organic matter in natural and engineered systems: A critical review. Environmental
620 Science and Technology 46(4), 2006-2017.
621 Ishizaki, K., Komarneni, S. and Nanko, M. (1998) Porous materials : process technology and
622 applications, Kluwer Academic Publishers, Dordrecht; Boston.
623 Jang, H.N., Lee, D.S., Park, M.K., Moon, S.Y., Cho, S.Y., Kim, C.H. and Kim, H.S. (2006) Effects of
624 the filtration flux and pre-treatments on the performance of a microfiltration drinking water
625 treatment system. Amy, G., Annachhatre, A., Arvin, E., Chen, J. and Cho, J. (eds), pp. 81-87.
626 Jin, P., Jin, X., Wang, X., Feng, Y. and Wang, X.C. (2013) Biomass Now - Cultivation and Utilization.
627 Matovic, M.D. (ed), p. Ch. 07, InTech, Rijeka.
628 Kalkan, Ç., Yapsakli, K., Mertoglu, B., Tufan, D. and Saatci, A. (2011) Evaluation of Biological
629 Activated Carbon (BAC) process in wastewater treatment secondary effluent for reclamation
630 purposes. Desalination 265(1–3), 266-273.
631 Karnik, B.S., Davies, S.H., Chen, K.C., Jaglowski, D.R., Baumann, M.J. and Masten, S.J. (2005)
632 Effects of ozonation on the permeate flux of nanocrystalline ceramic membranes. Water
633 Research 39(4), 728-734.
634 Kasprzyk-Hordern, B., Raczyk-Stanisławiak, U., Świetlik, J. and Nawrocki, J. (2006) Catalytic
635 ozonation of natural organic matter on alumina. Applied Catalysis B: Environmental 62(3–4),
636 345-358.

637 Kim, J., Davies, S.H.R., Baumann, M.J., Tarabara, V.V. and Masten, S.J. (2008) Effect of ozone
638 dosage and hydrodynamic conditions on the permeate flux in a hybrid ozonation–ceramic
639 ultrafiltration system treating natural waters. Journal of Membrane Science 311(1-2), 165-172.
640 Kim, J., Shi, W., Yuan, Y. and Benjamin, M.M. (2007) A serial filtration investigation of membrane
641 fouling by natural organic matter. Journal of Membrane Science 294(1–2), 115-126.
642 Kong, L.Y., Zhang, X.J. and Wang, Z.S. (2006) Pilot plant study on ozonation and biological
643 activated carbon process for drinking water treatment. Journal of Environmental Sciences 18(2),
644 232-235.
645 Lahoussine-Turcaud, V., Wiesner, M.R. and Bottero, J.Y. (1990) Fouling in tangential-flow
646 ultrafiltration: The effect of colloid size and coagulation pretreatment. Journal of Membrane
647 Science 52(2), 173-190.
648 Laine, J.M., Hagstrom, J.P., Clark, M.M. and Mallevialle, J. (1989) Effects of ultrafiltration
649 membrane composition. J. AWWA 81(11), 61-67.
650 Lehman, S.G. and Liu, L. (2009) Application of ceramic membranes with pre-ozonation for
651 treatment of secondary wastewater effluent. Water Research 43(7), 2020-2028.
652 Li, L., Zhang, P., Zhu, W., Han, W. and Zhang, Z. (2005) Comparison of O3-BAC, UV/O3-BAC and
653 TiO2/UV/O3-BAC processes for removing organic pollutants in secondary effluents. Journal of
654 Photochemistry and Photobiology A: Chemistry 171(2), 145-151.
655 Li, L., Zhu, W., Zhang, P., Zhang, Z., Wu, H. and Han, W. (2006) Comparison of AC/O3–BAC and
656 O3–BAC processes for removing organic pollutants in secondary effluent. Chemosphere 62(9),
657 1514-1522.
658 Lu, J., Fan, L. and Roddick, F.A. (2013) Potential of BAC combined with UVC/H2O2 for reducing
659 organic matter from highly saline reverse osmosis concentrate produced from municipal
660 wastewater reclamation. Chemosphere 93(4), 683-688.
661 Mallevialle, J., Odendaal, P.E., Foundation, A.R., Wiesner, M.R., eaux-Dumez, L.d. and
662 Commission, S.A.W.R. (1996) Water Treatment Membrane Processes, McGraw-Hill.

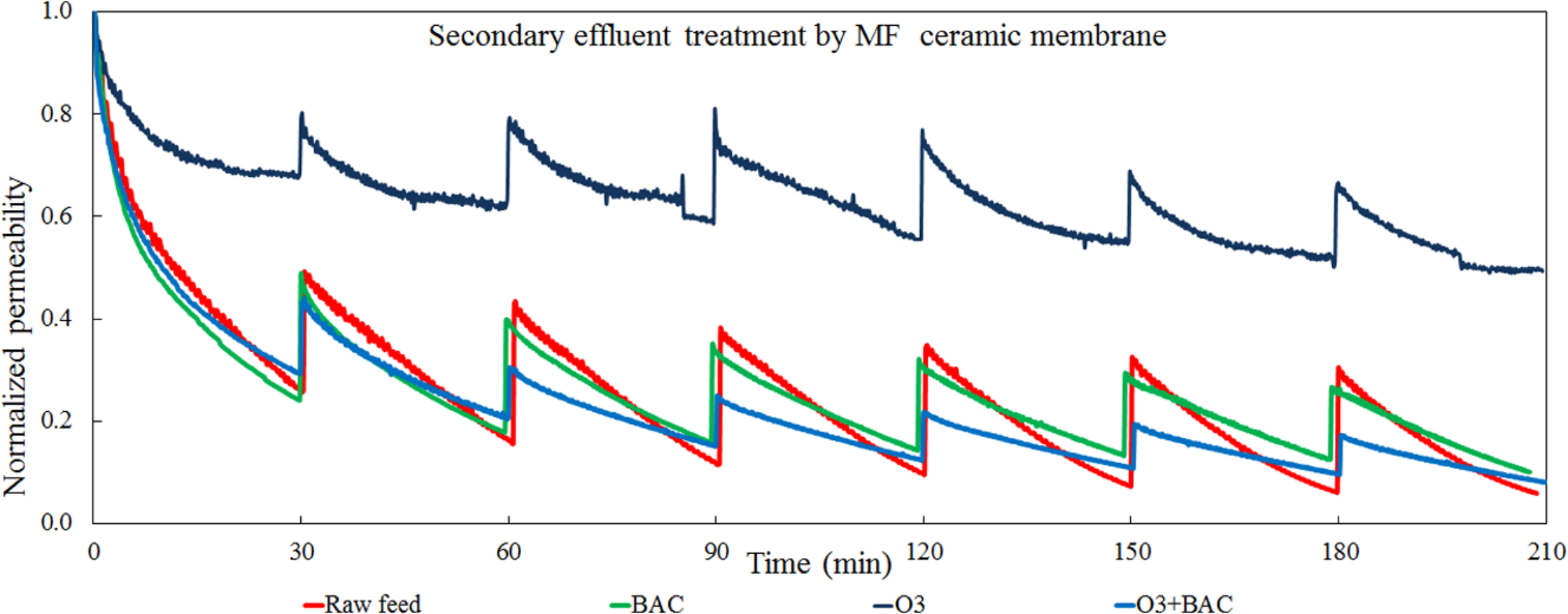
663 Miettinen, I.T., Vartiainen, T., Nissinen, T., Tuhkanen, T. and Martikainen, P.J. (1998) Microbial
664 growth in drinking waters treated with ozone, ozone/hydrogen peroxide or chlorine. Ozone:
665 Science and Engineering 20(4), 303-315.
666 Mo, L. and Huang, X. (2003) Fouling characteristics and cleaning strategies in a coagulation-
667 microfiltration combination process for water purification. Desalination 159(1), 1-9.
668 Murphy, K.R., Hambly, A., Singh, S., Henderson, R.K., Baker, A., Stuetz, R. and Khan, S.J. (2011)
669 Organic matter fluorescence in municipal water recycling schemes: Toward a unified PARAFAC
670 model. Environmental Science and Technology 45(7), 2909-2916.
671 Myat, D.T., Mergen, M., Zhao, O., Stewart, M.B., Orbell, J.D. and Gray, S. (2012) Characterisation
672 of organic matter in IX and PACl treated wastewater in relation to the fouling of a hydrophobic
673 polypropylene membrane. Water Res 46(16), 5151-5164.
674 Nguyen, S.T. (2012) Mitigation of membrane fouling in microfiltration & ultrafiltration of
675 activated sludge effluent for water reuse, RMIT University, Melbourne.
676 Nguyen, S.T. and Roddick, F.A. (2010) Effects of ozonation and biological activated carbon
677 filtration on membrane fouling in ultrafiltration of an activated sludge effluent. Journal of
678 Membrane Science 363(1-2), 271-277.
679 Pall (2006) Ceramic Membrane Filters SCHUMASIV™ & SCHUMASIV™ H Technical Information.
680 Corporation, P. (ed).
681 Park, H., Kim, Y., An, B. and Choi, H. (2012) Characterization of natural organic matter treated by
682 iron oxide nanoparticle incorporated ceramic membrane-ozonation process. Water Research.
683 Peiris, R.H., Jaklewicz, M., Budman, H., Legge, R.L. and Moresoli, C. (2013) Characterization of
684 hydraulically reversible and irreversible fouling species in ultrafiltration drinking water
685 treatment systems using fluorescence EEM and LC-OCD measurements, pp. 1220-1227.
686 Penru, Y., Simon, F.X., Guastalli, A.R., Esplugas, S., Llorens, J. and Baig, S. (2013) Characterization
687 of natural organic matter from Mediterranean coastal seawater. Journal of Water Supply:
688 Research and Technology - AQUA 62(1), 42-51.

689 Plummer, J.D. and Edzwald, J.K. (2001) Effect of ozone on algae as precursors for trihalomethane
690 and haloacetic acid production. Environmental Science and Technology 35(18), 3661-3668.
691 Polyakov, Y.S. and Zydney, A.L. (2013) Ultrafiltration membrane performance: Effects of pore
692 blockage/constriction. Journal of Membrane Science 434, 106-120.
693 Pramanik, B.K., Roddick, F.A. and Fan, L. (2014) Effect of biological activated carbon pre-
694 treatment to control organic fouling in the microfiltration of biologically treated secondary
695 effluent. Water Research 63, 147-157.
696 Pramanik, B.K., Roddick, F.A. and Fan, L. (2015) A comparative study of biological activated
697 carbon, granular activated carbon and coagulation feed pre-treatment for improving
698 microfiltration performance in wastewater reclamation. Journal of Membrane Science 475, 147-
699 155.
700 Pramanik, B.K., Roddick, F.A. and Fan, L. (2016) Long-term operation of biological activated
701 carbon pre-treatment for microfiltration of secondary effluent: Correlation between the organic
702 foulants and fouling potential. Water Res 90, 405-414.
703 Price, M.L. (1993) Evaluation of Ozone/Biological Treatment for Disinfection Byproducts Control
704 and Biologically Stable Water. Ozone: Science & Engineering 15(2), 95-130.
705 Rattier, M. (2012) Organic micropollutant removal by biological activated carbon filtration : a
706 review / Maxime Rattier, Julien Reungoat, Wolfgang Gernjak and Jurg Keller, Urban Water
707 Security Research Alliance, City East, Qld.
708 Reungoat, J., Escher, B.I., Macova, M., Argaud, F.X., Gernjak, W. and Keller, J. (2012) Ozonation
709 and biological activated carbon filtration of wastewater treatment plant effluents. Water
710 Research 46(3), 863-872.
711 Salanis, S.G., Croué, J.P., Kennedy, M., Schippers, J.C. and Amy, G. (2011) Innovative
712 characterization protocols for seawater natural organic matter (NOM): insight into membrane
713 fouling and control. Proceeding of the International Desalination Association World Congress.

714 Servais, P., Billen, G., Bouillot, P. and Benezet, M. (1992) A pilot study of biological GAC filtration
715 in drinking-water treatment. AQUA 41(3), 163-168.
716 Siddiqui, M.S., Amy, G.L. and Murphy, B.D. (1997) Ozone enhanced removal of natural organic
717 matter from drinking water sources. Water Research 31(12), 3098-3106.
718 Siembida-Losch, B., Anderson, W.B., Wang, Y.M., Bonsteel, J. and Huck, P.M. (2015) Effect of
719 ozone on biopolymers in biofiltration and ultrafiltration processes. Water Res 70, 224-234.
720 Stüber, J., Miehe, U., Stein, R., Köhler, M. and Lesjean, B. (2013) Combining Ozonation and
721 Ceramic Membrane Filtration for Tertiary Treatment. Chemie Ingenieur Technik 85(8), 1237-
722 1242.
723 Sutzkover-Gutman, I., Hasson, D. and Semiat, R. (2010) Humic substances fouling in
724 ultrafiltration processes. Desalination 261(3), 218-231.
725 Takahashi, N., Katoh, Y., Nakai, T. and Satoh, Y. (1995) Ozonolysis of Humic Acid and Its Effect
726 on Decoloration and Biodegradability. Ozone: Science & Engineering 17(5), 511-525.
727 Toor, R. and Mohseni, M. (2007) UV-H2O2 based AOP and its integration with biological
728 activated carbon treatment for DBP reduction in drinking water. Chemosphere 66(11), 2087-
729 2095.
730 Van Der Hoek, J.P., Hofman, J.A.M.H. and Graveland, A. (1999) The use of biological activated
731 carbon filtration for the removal of natural organic matter and organic micropollutants from
732 water, pp. 257-264, Trondheim, Norway.
733 van Der Kooij, D., Hijnen, W.A.M. and Kruithof, J.C. (1989) The Effects of Ozonation, Biological
734 Filtration and Distribution on the Concentration of Easily Assimilable Organic Carbon (AOC) in
735 Drinking Water. Ozone: Science & Engineering 11(3), 297-311.
736 Velten, S., Hammes, F., Boller, M. and Egli, T. (2007) Rapid and direct estimation of active
737 biomass on granular activated carbon through adenosine tri-phosphate (ATP) determination.
738 Water Research 41(9), 1973-1983.

739 Vickers, J.C., Thompson, M.A. and Kelkar, U.G. (1995) The use of membrane filtration in
740 conjunction with coagulation processes for improved NOM removal. Desalination 102(1-3), 57-
741 61.
742 Volk, C., Renner, C., Roche, P., Paillard, H. and Joret, J.C. (1993) Effects of Ozone on the
743 Production of Biodegradable Dissolved Organic Carbon (BDOC) During Water Treatment. Ozone:
744 Science & Engineering 15(5), 389-404.
745 Von Gunten, U. (2003) Ozonation of drinking water: Part I. Oxidation kinetics and product
746 formation. Water Research 37(7), 1443-1467.
747 Walker, G.M. and Weatherley, L.R. (1999) Biological activated carbon treatment of industrial
748 wastewater in stirred tank reactors. Chemical Engineering Journal 75(3), 201-206.
749 Wang, S., Ma, J., Liu, B., Jiang, Y. and Zhang, H. (2008) Degradation characteristics of secondary
750 effluent of domestic wastewater by combined process of ozonation and biofiltration. Journal of
751 Hazardous Materials 150(1), 109-114.
752 Wang, Z.P. and Zhang, T. (2010) Characterization of soluble microbial products (SMP) under
753 stressful conditions. Water Research 44(18), 5499-5509.
754 Xia, S., Nan, J., Liu, R. and Li, G. (2004) Study of drinking water treatment by ultrafiltration of
755 surfacewater and its application to China. Desalination 170(1), 41-47.
756 Xu, B., Gao, N.Y., Sun, X.F., Xia, S.J., Simonnot, M.O., Causserand, C., Rui, M. and Wu, H.H. (2007)
757 Characteristics of organic material in Huangpu River and treatability with the O3-BAC process.
758 Separation and Purification Technology 57(2), 348-355.
759 Yapsakli, K. and Çeçen, F. (2010) Effect of type of granular activated carbon on DOC
760 biodegradation in biological activated carbon filters. Process Biochemistry 45(3), 355-362.
761 Yu, W., Brown, M. and Graham, N.J.D. (2016a) Prevention of PVDF ultrafiltration membrane
762 fouling by coating MnO2 nanoparticles with ozonation. Scientific Reports 6.

763 Yu, W., Graham, N.J. and Fowler, G.D. (2016b) Coagulation and oxidation for controlling
764 ultrafiltration membrane fouling in drinking water treatment: Application of ozone at low dose
765 in submerged membrane tank. Water Research 95, 1-10.
766 Yu, W., Zhang, D. and Graham, N.J.D. (2017) Membrane fouling by extracellular polymeric
767 substances after ozone pre-treatment: Variation of nano-particles size. Water Research 120,
768 146-155.
769 Zhang, J., Northcott, K., Duke, M., Scales, P. and Gray, S.R. (2016) Influence of pre-treatment
770 combinations on RO membrane fouling. Desalination 393, 120-126.
771 Zheng, X., Ernst, M. and Jekel, M. (2010) Pilot-scale investigation on the removal of organic
772 foulants in secondary effluent by slow sand filtration prior to ultrafiltration. Water Research
773 44(10), 3203-3213.
774 Zhu, H., Wen, X. and Huang, X. (2012) Characterization of membrane fouling in a microfiltration
775 ceramic membrane system treating secondary effluent. Desalination 284, 324-331.
776 Zhu, H., Wen, X., Huang, X., Noguchi, M. and Gan, Y. (2009) Membrane fouling in the reclamation
777 of secondary effluent with an ozone-membrane hybrid system. Separation Science and
778 Technology 44(1), 121-130.


Secondary effluent treatment by MF ceramic membrane
Normalized permeability
1.0
0.8
0.6
0.4
0.2
0.0
0
30
60
90
120
150
180
210
Time (min)
Raw feed
BAC
O3
O3+BAC